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Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

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**REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
AND OPTIONS FOR REDUCING EMISSIONS**

SYNOPSIS

This report was prepared for Environment Canada in response to a project awarded in response to Request for Proposal K2A15-08-0015 entitled "Development of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions". The report is meant to provide an overview of existing emissions factors applied to the oil sands industry, the basis of these emissions factors, projections of emissions from the oil sands industry based on current and proposed facilities and available control technologies applicable to reduce emissions. The document specifically focuses on mine faces and tailings ponds although consideration has been given to emissions from other sources.

**PROJECT B2179 0000 - REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS
PONDS AND MINING FACES AND OPTIONS FOR REDUCING EMISSIONS**

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REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
AND OPTIONS FOR REDUCING EMISSIONS

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EXECUTIVE SUMMARY

The oil sands mining industry is anticipated to increase production by approximately 3.5 times over the next 15 years, increasing bitumen production from 3.1×10^8 barrels per year (bbl/yr) to 1.1×10^9 bbl/yr¹. This economic opportunity comes with challenges, such as the requirement to monitor and control emissions of pollutants of potential concern (PPCs) including air pollutants, greenhouse gases (GHG), volatile organic compounds (VOCs), benzene, methane (CH₄), total hydrocarbons (THC) and reduced sulphur compounds (RSC). The Government of Canada is considering regulation of these emissions from various sectors, including the oil and gas and oil sands sectors, respectively. In order to do so, the identification and quantification of emissions from oil sand mine faces and tailings ponds is required. EC is also interested in exploring potential mitigation measures that currently exist to reduce PPCs from mine faces and tailings ponds.

Oil sands are mined and processed to generate oil similar to that from conventional oil wells. However extracting oil from oil sands is more complex than conventional oil recovery. Oil sands recovery processes include extraction and separation systems to separate the bitumen from the clay, sand and water that make up the oil sands. Bitumen also requires additional upgrading before it can be refined. Because it is so viscous, non-upgraded bitumen also requires dilution with lighter hydrocarbons to make it transportable by pipelines.

Oil sands are mined through open pit mining operations when they are found at depths less than 75 m from the ground surface. The surfaces of the open pits are sources of fugitive VOCs and RSC emissions. The emissions depend on the age of the exposed surface, ambient temperature and wind speed.

The extraction process results in the production of tailings. Water used in extraction processes combines with sand, clay and residual bitumen to form tailings, which are stored on-site in settling basins and tailings ponds. Tailings composed of water, dissolved salts, organic compounds, minerals and bitumen are pumped from the separation vessels and froth treatment facilities to a series of tailings ponds. Generally, there are three oil sands tailings streams including coarse tailings from the primary bitumen separation step, the fine tailings from the secondary separation step and/or tertiary bitumen recovery step and the froth treatment tailings.

Oil sands operators do not release extraction wastes, but rather contain process-affected waters and fine tailings on site, primarily in large settling ponds. Settling basins known as tailings ponds receive effluent from the extraction plants that can contain total hydrocarbons (THC) and reduced sulphur compounds (RSC) from residual bitumen and/or diluent. Chemical and biological reactions in the pond can modify the THC and RSC speciation profile. The volatilization of THC and RSC compounds will

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depend on the nature of the received effluent, the temperature of the pond, ambient temperature, wind speed, area of open water surface and pond age. It has been shown that tailings ponds contain naphthenic acids (NA), asphaltenes, benzene, phenols and creosols, humic and fulvic acids, phthalates, polyaromatic hydrocarbons (PAH) and toluene. These constituents could be precursors to chemicals emitted to the atmosphere due to volatilization, biodegradation, photolysis and other chemical/physical reactions that can occur in the ponds.

Emissions from oil sands facilities are associated with several sources within the mines. Emissions of particular relevance to this report include fugitive emissions from mine faces and tailings ponds. These fugitive emissions include THC, VOC, CH₄ and RSC. Fugitive emissions from tailings ponds result from volatilization of residual amounts of diluent contained in the tailings discharged to tailings ponds. Fugitive emissions from mine faces result from volatilization of hydrocarbons from exposed oil sands deposits.

A number Environmental Impact Assessments (EIAs) completed for oil sands mining facilities were reviewed. Some of the reports provide a detailed estimate of individual species of VOCs, PAH and RSC for fugitive emissions (e.g. Mildred Lake Expansion Project (1998), Northern Lights Mining Project (2006) and Joslyn Mine (2006). VOC and PAH emissions were reported collectively as estimated emissions from the mine faces and tailings ponds. It should be noted that information contained in EIAs represent maximum expected emissions to allow for prediction of worst case environmental conditions due to the operation of the mining facility. Therefore these emission data likely do not represent emissions for normal operating conditions.

The National Pollutant Release Inventory (NPRI) for 2007 was also reviewed to obtain detailed emissions data for individual species of VOCs, PAH and RSC. Although the emissions are reported by individual chemical species and source category, the emissions from individual sources within a category are not specified. Instead, fugitive emissions, for example are reported as total fugitive emissions. Currently three oil sands mining operators have reported emissions to NPRI in 2007 as follows:

- Syncrude has two operating mines, Mildred Lake and Aurora North Mines, with a total bitumen production capacity of 452,700 barrels per day (bbl/d).
 - The total annual fugitive emissions from Mildred Lake Mine in 2007 were approximately 11,262 t. These fugitive emissions include 10,176 t of VOCs (90% of total fugitive emissions) and 54.3 t of benzene (0.4% of total fugitive emissions);
 - The total annual fugitive emissions from Aurora North Mine in 2007 were approximately 15,784 t. These fugitive emissions included 15,753 t of VOCs (99.8% of total fugitive emissions), 26 t of toluene (0.16% of total fugitive emissions) and 5 t of RSC (0.02% of total fugitive emissions);
- Suncor operates the Millennium Mine at a bitumen production capacity of 317,000 bbl/d. Total annual fugitive emissions in 2007 were approximately 24,290 t. These fugitive emissions include approximately 21,000 t of VOCs (86% of total fugitive emissions) and 9 t of benzene (0.04 % of total fugitive emissions); and

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- Shell operates the Muskeg River Mine producing bitumen at a capacity of approximately 155,000 bbl/d. Total annual fugitive emissions in 2007 were approximately 13.4 t. These fugitive emissions include approximately 8 t of VOC emissions (60% of total fugitive emissions) and 4 t of 1,2,4-trimethylbenzene emissions (30% of total fugitive emissions).

When predicting emissions of PAH, VOC, benzene, CH₄ and RSC from mine faces and tailings ponds, oil sands operators use emission factors (EFs) developed for Syncrude and Suncor oil sands facilities. The suitability of this method for prediction of emissions from proposed oil sands mining operations is questionable since the EFs are based on measurements from operational facilities and generally cannot be considered site-specific. EFs are generally based on the results of source sampling tests performed at one or more facilities within a specific industry. In the case of the EFs developed by Syncrude and Suncor, fluxes from various exposed surfaces of mine faces and tailings ponds were measured using enclosed flux chamber measurements at multiple locations in 1997 (Syncrude and Suncor) and 2007 (Suncor). The EFs can be used to predict emissions of future facilities and are widely used by oil sands operators to predict emissions from mine face and tailings ponds when applying for EIA approvals. EFs for mine faces were only available for data collected by Syncrude in 1997. EFs for tailings ponds were developed on the basis of data collected by Syncrude (1997) and Suncor (1997 and 2007) operating facilities. The largest fluxes are associated with tailings ponds which received tailings and fines matter from the extraction and cleaning process of bitumen.

The EFs were used to predict emissions from mine faces and tailings ponds for oil sands mining facilities between 2006 and 2022. It was calculated that by 2022 the total bitumen production will be approximately 3.5 times more than 2006 production capacity (from 3.1×10^8 bbl/yr to 1.1×10^9 bbl/yr). This agrees with the predictions made by NRCan. Hence the associated mine face surface areas will also increase. Surface areas of the mine faces were calculated to increase approximately 3 times, from 90 km² to nearly 260 km², resulting in an increase in emissions as follows:

- THC from approximately 1.1×10^5 to 3.1×10^5 t/yr;
- Benzene from approximately 5 to 7 t/yr;
- CH₄ from approximately 7.0×10^4 to 2.1×10^5 t/yr;
- RSC from approximately 1.19×10^4 to 1.20×10^4 t/yr;
- PAHs from approximately 35 to 110 t/yr; and
- VOC from approximately 3.5×10^4 to 1.0×10^5 t/yr.

Generally, predicting emissions from mine faces using EFs overestimate emissions relative to those emissions presented in EIAs. Exceptions include VOCs from CNRL Horizon and Suncor facilities and RSC from CNRL and Suncor North Steep Bank. Suncor does not use EF to predict emissions, but rather measured data collected from their facility. It is unclear why the discrepancy with CNRL, relative to other facilities, exists.



The general overestimation of emissions from mine faces using EFs could be due to EIAs considering more current emissions that were not provided by operators for evaluation. Additionally, in EIAs, more site-specific factors such as mine face orientation and location, bitumen quality and mine face age may have been factored into the prediction of emissions.

Similarly surface areas of the tailings pond were calculated to increase over this period approximately 1.6 times, from 80 km² to 140 km² with a total potential total surface disturbance² up to 1,400 km², resulting in an increase in emissions as follows:

- THC from approximately 7.4×10^4 to 2.2×10^5 t/yr;
- CH₄ from approximately 5.0×10^4 to 1.4×10^5 t/yr;
- Benzene from approximately 29 to 98 t/yr;
- RSC from approximately 344 to 805 t/yr;
- PAH from approximately 2.4×10^3 to 7.2×10^3 t/yr; and
- VOC from approximately 2.5×10^4 to 7.1×10^4 t/yr.

However, it is worth noting that the predicted emissions are based on historical information collected in 1997. Data on emissions of the same THC, VOCs and RSC need to be compiled for more recent monitoring programs and specifically for 2008 in order to examine the accuracy of the predicted emissions.

Generally predicting of emissions from tailings ponds using EF underestimate emissions relative to those emissions presented in EIAs. Exceptions include VOCs from Syncrude Mildred Lake, Suncor Millennium Mine and Synenco Northern Lights, Benzene from Syncrude Mildred Lake and methane from Syncrude Mildred Lake, CNRL Horizon and Total E&P Joslyn North Mine. These predictions may have used alternative methods to correct predicted emissions based on facility-specific factors.

The underestimation could be attributed to EIAs considering more current emissions data that were not provided by operators for evaluation. Additionally in EIAs, more site-specific factors such as ambient and water temperature, concentration of methanogens, improved bitumen extraction efficiency, type of diluent, agitation rate from outfalls and/or mixing, improved solvent recovery technologies or improved water treatment technologies in tailings ponds may have been factored into emissions in EIAs.

The review has identified an absence of technologies to directly mitigate emissions from mine faces. A potential method that could be explored includes covering or capping of mine faces using overburden when mining of a prepared pit is not taking place. This would be anticipated to reduce exposure of PPCs to the atmosphere, thus reducing volatilization and consequently emissions.

Currently solvent recovery and tailings ponds are in use. Operators use these technologies to reduce THC, VOC, benzene, RSC and methane emissions from oil sands mining operations that would occur in the absence of these technologies. The solvent recovery system currently operates at approximately 99% efficiency. However, the 1% of solvent discharge that occurs into tailings ponds still results in the emission of PPCs from tailings ponds associated with the diluent including THC, VOC and benzene.

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The absence of a solvent recovery system would be expected to yield substantially higher concentrations of THC, VOC and benzene emissions through diluent losses. Improvement in the efficiencies of the solvent recovery process would be expected to further reduce emissions. Tailings ponds are currently used to improve water quality and allow tailings to settle, thereby reducing quantities of THC, VOC, benzene and RSC emissions through management and remediation of contaminated water. However, the tailings ponds also result in the production of methane through the process of methanogenesis of organic compounds present in the tailings water as well as losses from diluent, other process related chemicals and unrecovered bitumen. Consolidation of tailings or decrease in tailings pond size could increase efficiencies in reduction of specific PPC emissions from tailings ponds.

Potential wastewater treatment technologies have been identified to reduce emissions by treating process waters and tailings. Potential water treatment technologies which could be used to treat produced water and hence reduce emissions included:

- activated carbon;
- polymer-modified bentonite adsorbent;
- activated sludge;
- microfiltration;
- hollow fibre ultrafiltration;
- nanofiltration; and
- ion exchange.

Currently the most effective technologies available include the solvent recovery system and tailings ponds. While these are currently in use, they are not anticipated to result in further emissions reductions unless these methods are improved through increasing removal efficiency of the solvent recovery system or through decreasing tailings pond surface area via consolidation of oil sands tailings. The 7 water treatment technologies were ranked according to operational costs, removal efficiency, CO₂ emissions and by-product handling and disposal. Capital costs were provided and therefore are not discussed further. Capital costs of these methods would require further evaluation, considering total volume of water treatment and application (either to existing facilities or to facilities under construction). The results of the ranking were as follows:

1. Microfiltration;
2. Activated sludge;
3. Polymer-modified bentonite adsorbent;
4. Activated Carbon
5. Ion exchange;



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-
6. Hollow fiber ultrafiltration; and
 7. Nanofiltration.

Notes:

1 Natural Resources Canada, 2006. Important Facts on Canada's Natural Resources, www.nrcan.gc.ca/statistics, Last Accessed January 2009.

2 New Paradigm Engineering Ltd., 2005. Strategic Needs for Energy Related Water Use Technologies Water and the EnergyINET, http://www.aeri.ab.ca/sec/new_res/docs/EnergyINET_and_water_Feb2005.pdf, Last Accessed March 2009.

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APPENDIX 1	TOXICITY PROFILES OF COPCS
APPENDIX 2	QUESTIONNAIRE
APPENDIX 3	AIR QUALITY GUIDELINES
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**REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
AND OPTIONS FOR REDUCING EMISSIONS**

List of Acronyms

AAAQG	Alberta Ambient Air Quality Guidelines
AEII	Alberta Employment, Immigration and Industry
AENV	Alberta Environment
AEUB	Alberta Energy and Utilities Board (for historical references)
AGS	Alberta Geological Survey
AOSTRA	Alberta Oil Sands Technology and Research Authority
API	American Petroleum Institute
ARC	Alberta Research Council
BA	BA Energy Inc.
BOD	Biochemical Oxygen Demand
bpd	Barrels per day
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
°C	Degrees Celsius
CAPP	Canadian Association of Petroleum Producers
Ca ²⁺	Calcium cation
CCME	Canadian Council of Ministers of the Environment
CDN	Canadian
CDPHE	Colorado Department of Public Health & Environment
CH ₄	Methane
C ₆ H ₆	Benzene
Chevron	Chevron Corporation
Cl ⁻	Chloride
Cl ₂	Chlorine
CMS	Carbon Molecular Sieve
CNOC	China National Offshore Corporation
CNRL	Canadian Natural Resources Limited
COD	Chemical Oxygen Demand
CHOPS	Cold Heavy Oil Production with Sand
CMS	Carbon Molecular Sieve



List of Acronyms

Conor	Conor Pacific Environmental Technologies Inc.
CPI	Corrugated Plate Interceptors
CSS	Cyclic Steam Stimulation
CT	Consolidated/Composite tailings
d	Day
Da	Dalton
DAF	Dissolved Air Flotation
DAP	Dissolved Air Precipitation
DOC	Dissolved Organic Carbon
DRU	Diluent Recovery Unit
EC	Environment Canada
EF	Emission Factor
EFIG	Emissions Factors and Inventory Group
Enbridge	Enbridge Inc.
EIA	Environmental Impact Assessment
EIS	Environment Impact Statement
EnCana	EnCana Corporation
EPA	United States Environmental Protection Agency
ERCB	Energy Resources and Conservation Board
EU	European Union
ExxonMobil	Exxon Mobil Canada
FAC	Fibrous Activated Carbon
FBR	Fluidized Bed Reactor
FGD	Flue Gas Desulphurizer
GAC	Granular Activated Carbon
GDP	Gross Domestic Product
GHG	Green House Gases
H ⁺	Hydrogen Ion
H ₂ O ₂	Hydrogen Peroxide
H ₂ S	Hydrogen Sulphide
HPAM	Hydrolyzed Polyacrylamide

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List of Acronyms

Husky	Husky Energy
IEA	International Energy Agency
IGF	Induced Gas Flotation
Imperial	Imperial Oil Limited
JACOS	Japan Canada Oil Sands Ltd.
kg/s	Kilogram/s
km ²	Square Kilometre
LCA	Life Cycle Assessment
mbd	Million barrels per day
MEG	MEG Energy Corporation
MFT	Mature Fine Tailings
MLSB	Mildred Lake Settling Basin
MnO ₄ ⁻	Permanganate
NRU	Naphtha Recovery Unit
NA	Naphthenic Acids
NaOH	Sodium Hydroxide
n.d.	Non-detected
NEB	National Energy Board
NH ₃	Ammonia
NO _x	Nitrogen Oxides
NPRI	National Pollutant Release Inventory
NRCan	Natural Resources Canada
O ₃	Ozone
OH ⁻	Hydroxide Ion
OG	Oil and Grease
OSA	Oil Sands Area
PAC	Powdered Activated Carbon
PAH	Polycyclic Aromatic Hydrocarbons
PCE	Tetrachloroethylene
PET	Polyethylene Terephthalate
PetroChina	PetroChina International Company



List of Acronyms

PM	Particulate Matter
PPC	Pollutants of Potential Concern
ppm	Parts Per Million
PVF	Polyvinyl Fluoride
QA	Quality Assurance
QC	Quality Control
RSC	Reduced Sulphur Compounds
S	Sulphur
SAGD	Steam Assisted Gravity Drainage
SCO	Synthetic Crude Oil
SFR	Sand-to-Fine Ratio
Shell	Shell EP Americas
SO ₂	Sulphur Dioxide
SRU	Solvent Recovery Unit
SWSS	Southwest Sand Storage
Suncor	Suncor Energy
Synenco	Synenco Energy
TCE	Trichloroethylene
TEM	Transient Electromagnetic Survey
TDS	Total Dissolved Solids
THC	Total Hydrocarbons
THAI	Toe to Heel Air Injection
TiO ₂	Titanium Dioxide
TOC	Total Organic Carbon
TPW	Tailing Pond Water
TRS	Total Reduced Sulphur
TSRU	Tailings Solvent Recovery Unit
TV/BIP	Total Volume to Bitumen In Place Ratio
tCO ₂	Tonnes of Carbon Dioxide
t/s	Tonnes/Second
t/y	Tonnes/year

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REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
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List of Acronyms

UKNAQA	United Kingdom National Air Quality Archive
USD	United States Dollar
UTS	UTS Energy Corporation
UV	Ultra Violet Light
VAPEX	Vapour Extraction Method
VOC	Volatile Organic Compounds
VRU	Vapour Recovery Unit
WCSB	Western Canada Sedimentary Basin
wt%	Percent weight basis

1. INTRODUCTION

1.1 Background

Canada has experienced significant economic growth, driven in part by the natural resources sectors. Natural resources include three categories: energy, mineral and timber resources. Canada's wealth associated with the natural resources sector grew an average of 10% per year over the last decade, and accounted for between 12% and 19% of Canada's total wealth in 2007 (Islam, 2007). Natural Resources Canada (NRCan) (2006) reported that the natural resources sector comprises 13% of Canada's Gross Domestic Product (GDP). Energy resources contributed 7.2% to the GDP in 2006, worth an estimated \$85.5 billion (NRCan, 2006). Prior to the economic downturn, the Canadian Energy Research Institute estimated that investments in the oil sands may reach \$472 billion Canadian dollars (CDN) between now and 2030, becoming larger than any other sector in Canada's economy during that same time (Bentein and Jaremko, 2009). While current economic conditions have slowed production (Oils Sands Review, 2008) and may impact expansions and new projects, it is still anticipated that this industry will experience substantial growth. Between 1996 and 2006, the oil sands industry spent an estimated \$47 billion on new projects. Based on survey results from early 2007, the Alberta oil sands industry was forecast to spend \$110 billion on new oil sands projects between 2007 and 2011 (Alberta Employment, Immigration, and Industry [AEII], 2007). However, project capital expenditures peaked in 2008 and are anticipated to enter several years of decline. Fossil fuels, such as oil, natural gas and coal make Canada one of the world's most attractive energy centres for continuing investment and development. However, this economic opportunity comes with challenges, such as the requirement to monitor and control emissions of pollutants of potential concern (PPCs), including air pollutants, greenhouse gases (GHG), volatile organic compounds (VOCs), benzene, methane (CH₄), total hydrocarbons (THC) and reduced sulphur compounds (RSC). The Government of Canada is considering regulation of these emissions from the various sectors, including the oil and gas and oil sands sectors, respectively.

Environment Canada (EC) is evaluating the merits of regulating emissions of toxic substances and air pollutants from various industrial sectors including the oil sands sector. This task requires the identification of emissions sources such as mine faces and tailing ponds, quantification of these emissions and identification of the factors that influence these emissions. In addition, EC is interested in exploring potential mitigation measures that currently exist or are in the process of development for reducing and/or preventing emissions of THC, VOCs, benzene and CH₄ from tailings ponds and possibly mine faces. As there is very little publicly available information related to emissions of these compounds from tailings ponds and mine faces, EC requires additional investigations to clarify emissions/flux rates, what factors influence these emissions and how the emissions associated with tailings ponds and mine faces originate.



1.1.1 Alberta's Regulatory Framework for Oil Sands Facilities

Currently oil sands mining facilities are regulated primarily by the Alberta Provincial Government. The Oil Sands Conservation Regulation (AENV, 2000a) was made under the Oil Sands Conservation Act (AENV, 2000a). This Act establishes a regulatory regime and scheme of approvals administered by the Alberta Energy Resources and Conservation Board (ERCB; previously the Energy and Utilities Board [EUB]) for the development of oil sands resources and related facilities in Alberta.

Regulations and legislation specific to oil sands mining, operations and royalty regulation in Alberta include the Oil Sands Tenure Regulation (Alberta Environment [AENV], 2000b), the Mines and Minerals Administration Regulation (AENV, 1997a), the Oil Sands Royalty Regulation (AENV, 1997b), the Environmental Protection and Enhancement Act (requires environmental impact assessments for approvals to operators) and the Petroleum Royalty Regulation (1990), enabled under the Mining and Minerals Act (AENV, 2000c). The Mining and Minerals Act governs the management and disposition of rights in Crown owned mines and minerals, including the levying and collection of bonuses, rental and royalties.

Oil sands operators are required by AENV and ERCB to predict emissions from their facilities in Environmental Impact Assessment reports (EIAs). Currently, emissions factors (EFs) are one of the key quantification techniques used in EIAs to estimate emissions from oil sands facilities prior to facility construction. The definition of EFs from EC National Pollutant Release Inventory (NPRI) is as follows (2007):

EFs are mean numerical values that relate the quantity of substances emitted from a source to a common activity associated with those emissions and can be categorized as either published or site-specific EFs. These are defined as follows:

- published emission factors: EFs that have been published by the Government of Canada or another government or an industry association for application to an emission source that falls under the jurisdiction of the Government of Canada or another government or to emission sources of a specific industry sector; or
- site-specific emission factors: EFs that have been developed by an individual facility using their own specific emission-testing data and source-activity information.

1.1.2 Scope of Contract

EC has awarded WorleyParsons a contract to:

- Review mine face and tailings pond air emissions;
- Compile current EFs for mine faces and tailings ponds;
- Determine the factors affecting mine face and tailings ponds emissions; and

- Report recommended control options for reducing or preventing VOCs, benzene, methane (CH₄) and THC.

1.2 Introduction to Oil Sands

Oil sands are found in about 70 countries around the world, including Canada, Venezuela, United States, Russia, Cuba, Indonesia, Brazil, Trinidad and Tobago, Jordan, Madagascar, Colombia, Albania, Romania, Spain, Portugal, Nigeria and Argentina. The world's two largest oil sands deposits are found in Canada and Venezuela respectively. Today, the largest single oil sand deposit in the world is the Athabasca oil sands located in northeastern Alberta. This deposit comprises at least 85% of the total immobile bitumen in place in the world (American Association of Petroleum Geologists, 2004; Dusseault, 2001; Zhou et al., 2008).

The three main regions where the oils sands are located in Alberta include the Athabasca, Cold Lake and Peace River oil sands areas (OSA) (Figure A). The Athabasca and Cold Lake oil sands areas extend into northwestern Saskatchewan across from the Firebag area in Alberta and into the Pasquia Hills region of east-central Saskatchewan (National Energy Board [NEB], 2006). These main OSAs cover a combined area of approximately 140,800 km² (ERCB, 2008; Alberta Geological Survey [AGS], 2008). There is also a small localized oil sand deposit found on Melville Island in the Arctic (Northwest Territories/Nunavut) (Gingras and Rokosh, 2004). The three main deposits in Alberta were originally recorded as early as 1719, with the first commercial production occurring in 1967 (Alberta ERCB, 2006). Since then, the oil sands have become an important economic factor in Alberta and Canada and as of the end of 2007 accounted for 64% of the value of all major projects in the province (AEII, 2007).

Figure A: Location of Oil Sands Deposits within Alberta



(Source: Alberta Somby, 2008)



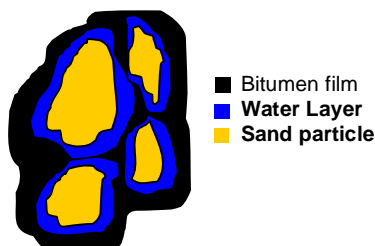
Contained within the OSA are 15 oil sands deposits, which designate the specific geological zone containing the oil sands. The established reserve of crude bitumen for the OSA was 27.45 billion m³ in 2008 (Alberta ERCB). The Athabasca OSA contains the largest deposits of bitumen including the Wabiskaw-McMurray deposit which is the most significant area of bitumen reserves. The other two OSA also contain significant bitumen reserves including the Cold Lake Clearwater and Peace River Bluesky-Gething deposits. Bitumen is also found within other formations, including the Grosmont Formation; however, this bitumen has not been commercially produced.

1.2.1 Bitumen

Natural bitumen (also referred to as tar sands or oil sands) and heavy oil differ from light oils by their high viscosity (resistance to flow) at reservoir temperatures, high density (low American Petroleum Institute [API] gravity) and significant content of nitrogen, oxygen and sulphur compounds, and heavy metals. The liquid hydrocarbons that comprise bitumen include a range of low to high molecular weight compounds. Low molecular weight compounds contain low numbers of carbon atoms bound to hydrogen, oxygen, nitrogen, sulphur and/or other elements. Higher molecular weight compounds consist of longer chains of carbon atoms, with the same covalently bound elements.

In Alberta, crude bitumen occurs in sand (clastic) and carbonate formations within the OSA. The oil sands primarily comprise quartz sand surrounded by a thin film of water, fines and bitumen and exclude associated gases (i.e., natural gases) (Figure B). The composition of particulates from the oil sands is approximately 5% water, 11% bitumen, 12% fines and 72% sand. The thin layer of water prevents irreversible binding of the bitumen film to the sand particles, allowing for separation of the bitumen from the sand in situ or during the extraction of mined ore (Alberta ERCB, 2008; AGS, 2008; Caughill et al., 1993; Industry Canada, 2008; Meyer and Attanasi, 2003).

Figure B: Oil Sands Composition



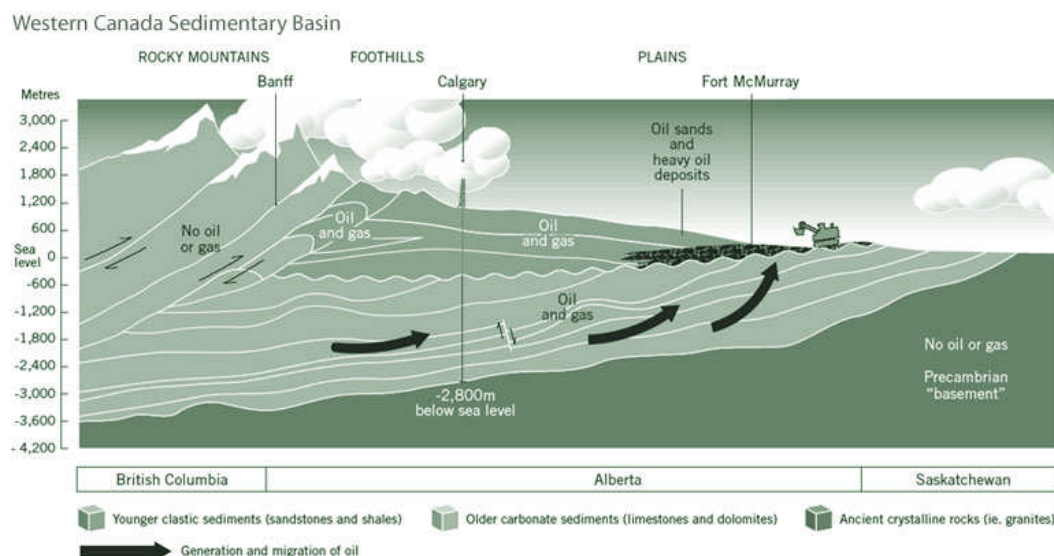
(Source: Suncor, 2008)

Bitumen in the oil sands was formed when sediments containing organic material, including plants, algae and plankton, were buried at the bottom of an inland sea. As the depth of burial increased, heat and pressure resulted in the transformation of carbohydrates in the organic matter into hydrocarbon compounds and hence oil. This process typically occurs in source rocks and most commonly in fine-

grained black shales. Once oil formation occurs, continued pressure from overlying rock strata forces oil migration through permeable rock layers until it becomes trapped in a reservoir of porous sedimentary rock such as sandstone or limestone, or until it escapes at the surface. It is the latter of these processes that results in deposits such as the oil sands.

Over time, the oil-bearing sediments became covered by more than a kilometre of sedimentary rock. Then, over 50 million years ago, vast amounts of the liquid hydrocarbons migrated more than 100 kilometres eastward and upward until they reached and saturated large areas of sandstone at, and just below, the surface of what is now northern Alberta (Figure C). Micro-organisms present in the sandstone slowly consumed the hydrocarbons, beginning with the lightest. The heavy oil and bitumen are the remnants of that migration and biological degradation.

Figure C: Oil Sands Formation within the Western Canada Sedimentary Basin



(Canadian Centre for Energy Information, 2004)

1.2.2 Oil Sands Reserves

As described previously, the majority of the oil sands resources in Canada are located in Alberta, though they extend eastwards into northwestern Saskatchewan across from the Firebag area in Alberta and into the Pasquia Hills region of east-central Saskatchewan, with a localized deposit located in the Arctic (Humphries, 2008). The Cold Lake region contains the largest reserve; however the Athabasca region contains the largest volume of economically mineable bitumen, since the deposits lie under an overburden layer of less than 75 m, making mining a suitable method of extraction. The oil resources in OSA areas are summarized in Table A for the end of 2007. For 2007, of the total 27.45 billion m³ (173 billion barrels) remaining established reserves, approximately 22.49 billion m³ (82%) is considered recoverable by in situ



methods and 4.96 billion m³ by surface mining methods. Of the in situ mineable totals, 3.5 billion m³ are within active development areas. Only 3.3% of the initial established crude bitumen reserves have been produced since commercial production started in 1967 (ERCB, 2008).

In 2007, Alberta produced 45.5 million m³ (286 million barrels) from the mineable area and 31.1 million m³ (196 million barrels) from the in situ area, totalling 76.6 million m³ (482 million barrels). This is equivalent to 209.9 thousand m³ (1.32 million barrels) per day. Bitumen produced from mining was upgraded, yielding 40.0 million m³ (251 million barrels) of synthetic crude oil (SCO). In situ production was mainly marketed as non-upgraded crude bitumen (ERCB, 2008). In 2008, Alberta produced a total of 1.71 million barrels per day (Mbpd) and a total of 2.2 Mbpd of SCO (Dunbar, 2009).

Table A In situ Crude Bitumen Reserves in Areas under Active Development as of December 31, 2007 (ERCB, 2008)

Development	Initial Volume in place (10 ⁶ m ³)	Initial Established Reserves (10 ⁶ m ³)	Cumulative Production (10 ⁶ m ³)	Remaining Established Reserves (10 ⁶ m ³)
Peace River Oil Sands Area	176.4	28.4	13.7	14.6
Athabasca Oil Sands Area	1,339.9	237.1	54.2	182.9
Cold Lake Oil Sands Area	7,504.1	633.0	241.3	391.7
Experimental schemes (all areas)	95.5	10.3	6.9	3.5

ERCB estimates that about 140 billion barrels and 2.4 trillion barrels of surface-mineable and in situ crude bitumen reserves, respectively, will be discovered (ERCB, 2004). The NEB (2008) predicts that oil sand production will reach approximately 2.0 Mbpd by 2010 and will almost triple to approximately 472 000 m³ (3.0 million barrels) per day by 2015 compared to production of 175 000 m³ (1.1 million barrels) per day in 2005. According to the International Energy Agency (IEA, 2003), Canada's oil sands production could exceed 5.0 Mbpd by 2033.

1.2.3 Description of Oil Sands Mining Projects

The significant oil sands reserves have resulted in ongoing construction and development of mines across the Athabasca region. Although the first oil sands operation owned by Great Canadian Oil Sands (now Suncor), began in 1967 little development of the oil sands occurred prior to 2002. Since this increased interest in mining of the oil sands, a significant number of projects have been proposed. The following

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table (Table B) briefly summarizes the mining projects within the OSA that are operating, under active construction, or approved. Please refer to Dunbar (2009) for a complete list of projects.

Table B Summary of Mining within the OSA as of end of 2008

Organization	Project	Status	Announced Startup	Capacity (barrels per day [bbl/d])
Suncor	Steepbank and Millennium Mines	Operating	1967	294,000
	Millennium Mine	Operating	2007	4,000
	Steepbank Debottleneck Phase 3	Operating	2008	23,000
	Millennium Debottlenecking	Approved	2010	-
	North Steep Bank Extension			
	Voyageur South Project Phase 1	Application	2011	120,000
Syncrude	Mildred Lake and Aurora Stages 1 and 2	Operating	1978	290,700
	Stage 3 Expansion	Operating	2006	116,300
	Stage 3 Debottleneck	Announced	2011	46,500
	Stage 4 Expansion	Announced	2015	139,500
Athabasca Oil Sands Project	Muskeg River (Shell)			
	Existing Facilities	Operating	2002	155,000
	Expansion and Debottlenecking	Approved	2009/2010	115,000
Chevron	Jackpine			
Marathon Oil	Phase 1A	Construction	2010	100,000
	Phase 1B	Approved	2012	100,000
Albian Sands	Phase 2	Application	2014	100,000
	Pierre River Phase 1	Application	2018	100,000
	Phase 2	Application	2021	1000,00
Petro-Canada	Fort Hills			
UTS	Phase 1	Approved	2011	165,000
Teck Cominco	Debottleneck	Approved	To be determined	25,000



Organization	Project	Status	Announced Startup	Capacity (barrels per day [bbl/d])
CNRL	Horizon			
	Phase 1	Operating	2008	135,000
	Phase 2 and 3	Approved	2010/2013	135,000
	Phase 4	Announced	2013	145,000
	Phase 5	Announced	2017	162,000
Synenco Energy	Northern Lights			
	Phase1	Application	2010	57,250
	Phase 2	Application	2010	57,250
Imperial oil	Kearl Mine			
	Phase 1	Approved	2010	100,000
	Phase 2	Approved	2012	100,000
	Phase 3	Approved	2018	100,000
Total E&P Canada Ltd.	Joslyn Mine			
	Phase 1	Approved	2015	50,000
	Phase 2	Approved	2018	50,000
	Phase 3	Application	2021	50,000
	Phase 4	Application	2022	50,000
UTS Energy Corp.	Equinox	Disclosure	2014	50,000
	Frontier 1	Disclosure	2015	100,000
	Frontier 2	Disclosure	2017	60,000

1.3 Oil Sands Emissions

The operations at oils sands facilities, including mining and extraction processes, result in the production and release of controlled and fugitive emissions which include gases and particulate matter (PM), to the atmosphere. The emissions from oil sands sources can include combustion emissions that result from burning fossil fuels, fugitive emissions that result from venting, tank leaks, valve connections, mine faces and tailings ponds and other emissions. Emissions from these sources include a wide variety of organic and inorganic compounds. Emissions can be measured or estimated. For existing facilities, measurements can be collected through use of discrete sampling techniques. For proposed facilities, predictive modelling is required to estimate emissions for reporting in environmental impact assessments (EIAs). Predictions can be made using emission factors (EFs) based on emissions from existing mine facilities. For the purpose of this report, EFs from mine face and tailings ponds of oil sands facilities are discussed.

1.3.1 Sources of Emissions

Oil sands mining fugitive emissions are mainly from mine faces and tailings ponds and include the following:

- Exposed mine face emissions mainly comprising VOCs including THC and benzene and reduced sulphur compounds (RSC); and
- Tailings ponds emissions comprising VOCs, including THC, benzene and other organic compounds, CH₄ and RSC. In general VOCs, including THCs, benzene and other organic compounds, contribute to over half of these fugitive emissions from tailings ponds due to the volatilization of residual amounts of solvents used in the bitumen cleaning process, which will be described in Sections 2.3-2.5. The emission magnitude depends on the windspeed, temperature of the pond surface, the nature and age of the tailings and the exposed area of the surface (Golder and Conor, 1998). The emissions from tailings ponds are also due to the presence of residual hydrocarbon not extracted from the oil sands. Quantities of residual hydrocarbon inflows can not be determined at the time of the study due to lack of information available on inflow rates.

1.4 Measurement of Emissions for EF Determination

Emissions from oil sands mine faces and tailings ponds are currently measured using the flux chamber technique. This technique is for measurement of air emissions rates from liquid and solid surfaces such as mine faces and tailings ponds. Data collected using flux chamber measurements can subsequently be used to develop EF for mine faces and tailings ponds.

1.4.1 Flux Chamber Measurements

Flux measurements are performed using the United States Environmental Protection Agency (EPA) (Kienbusch, 1986) isolation flux chamber design. This method involves purging the chamber with a known flow rate of purified air until a peak or steady-state pollutant concentration is achieved in the exhaust stream and then collecting a sample of the chamber exhaust for detailed analysis. A simple mass balance is performed to determine the flux rate using the following equation:

$$E_i = C_i Q / A \quad (\text{Equation 1})$$

Where,

E_i = emission flux rate of the target species;

C_i = concentration of the target species;

Q = purified air sweep rate; and

A = surface area enclosed.



The parameters recorded for each flux measurement include: water temperature, ambient air temperature, barometric pressure, time and date, temperature inside the chamber, purified air sweep rate or exhaust gas flow rate (depending on the type of measurement) and THC concentrations in the chamber exhaust. The THC concentrations are monitored using a TVA 1000 organic vapour analyser calibrated to CH₄ and equipped with both a flame ionization detector and a photo-ionization detector.

Several key assumptions inherent to the use of the flux chamber technique are as follows:

- good mixing occurs in the chamber;
- a representative gas sample is collected for analysis;
- no physical or chemical reactions occur between the inside surfaces of the chamber and the emissions (e.g., condensation); and
- the natural emission process is not disrupted or significantly altered by the presence of the chamber.

The first three assumptions are addressed through appropriate design and quality assurance (QA)/quality control (QC) measures (i.e., a standard chamber design is used, a method blank is run, the selected protocol as well as previous unpublished data showed good recovery efficiencies for the target pollutants). The validity of the last assumption is dependent on the nature of the emission process. Flux chambers do not attempt to replicate natural wind effects at the measurement surface, may cause some change in surface temperatures and, in the case of liquids, may alter small scale surface currents (Gholson et al., 1989). Accordingly, disruptions caused by the flux chamber may only be insignificant in situations where resistances at the air-surface interface are small compared to those below the surface, or where the emission rate is kinetically controlled and not mass-transfer controlled. Moreover, pollutant concentrations in the chamber must not be allowed to build up to greater than 10 percent of the equilibrium vapour-phase concentration as this would be expected to suppress the emission rate from the surface. This is why careful real-time monitoring of conditions in the chamber is required. The sensitivity of the method depends on the detection limit of the associated sample collection (and therefore analytical) technique. The results are generally within 50 to 124 percent of the true emission rate (Kienbusch, 1986). Thus, the results of isolation flux chamber measurements would be expected to underestimate actual emissions although the potential also exists to overestimate emissions.

1.4.2 Sample Collection Techniques

Canisters

Canisters provide the most common means of collecting samples from flux chamber measurements. Generally, the samples are collected into canisters that have been placed under vacuum. The canisters are typically silico-coated steel canisters. The silico coating is necessary to prevent degradation of the electro-polished stainless steel by RSC such as H₂S and methyl mercaptan. Additionally, the silico coating limits the potential for permanent absorption of other polar compounds such as alcohols, aldehydes and other oxygenated compounds.

To sample into canisters, a valve is opened that allows air (the sample) to fill the evacuated canister. The fill rate of the canister is dependent on whether the sample is collected as a grab versus flow restricted sample. Flow restricted samples can be collected at variable flow rates or over variable times, including time-weighted average samples.

Other

Other sample collection techniques include tubes filled with charcoal, Tenax/Carbon Molecular Sieve (CMS) or other sorbents, Tedlar bags or impingers. While these sample collection techniques are not commonly applied with flux chamber measurements, they have specific applications that may require intermittent use.

Sampling into tubes is based on drawing a known volume of air through tube with a sorbent that will adsorb the analyte(s) of interest. Adsorbed compounds can subsequently be extracted by a laboratory and the mass estimated. This can subsequently be used to derive a concentration, based on the known flow rate of air passed through the tube.

Tedlar bags are bags manufactured from polyvinyl fluoride (Tedlar) film. They are generally considered inert and can be used to collect samples containing hydrocarbons, chlorinated solvents and other classes of compounds. Tedlar bag sampling allows collection of a representative grab sample of a gaseous media for analysis. However, losses from adsorption, reaction and leakage can occur within a relatively short (48 to 72 hours) period of time after sample collection. Hence, this technique is not typically applied. Tedlar bags do provide the advantage that for samples with high concentrations of adsorbent materials, such as sulphur compounds, screening can be done to protect the integrity of the more expensive, non-disposable Summa canisters.

Impingers represent a specialized sampling technique that is required for sampling of highly reactive species. Impingers are typically glass vessels that contain a known volume of some chemical which will react with the target compound. Impingers are only used when a chemical reaction is required to derivatize the target compound to afford sufficient stability for laboratory analysis.



2. MINING AND PROCESSING METHODS

Oil sands are mined and processed to generate oil similar to oil pumped from conventional oil wells, but extracting oil from oil sands is more complex than conventional oil recovery. Oil sands recovery processes include extraction and separation systems to separate the bitumen from the clay, sand and water that make up the oil sands. After extraction and cleanup, bitumen is diluted with lighter hydrocarbons to make it transportable by pipelines to upgrading plants.

Oil sands deposits near the surface can be recovered by open pit mining techniques. These systems use large hydraulic and electrically powered shovels to dig up oil sands and load them into enormous trucks that can carry up to 320 tonnes of oil sands per load.

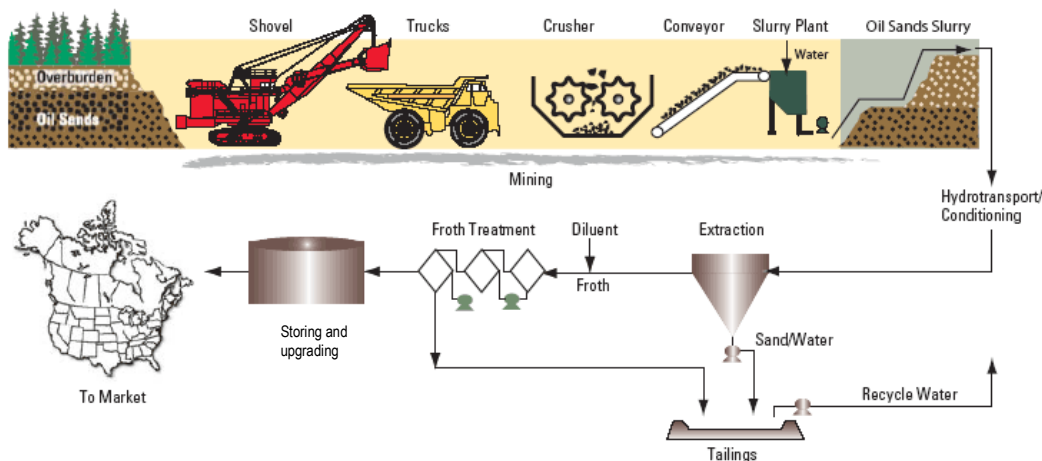
After mining, the oil sands are transported to an extraction plant, where a hot water process separates the bitumen from sand, water and minerals. The separation takes place in separation cells. Hot water is added to the sand and the resulting slurry is piped to the extraction plant where it is agitated. The combination of hot water and agitation releases bitumen from the oil sand and causes tiny air bubbles to attach to the bitumen droplets, that float to the top of the separation vessel, where the bitumen can be skimmed off. Further processing removes residual water and solids. The bitumen is then transported and eventually upgraded into synthetic crude oil.

In situ production methods are used on bitumen deposits buried too deep for mining to be economically recovered. These techniques include steam injection, solvent injection and firefloods in which oxygen is injected and part of the resource burned to provide heat. So far steam injection has been the favoured method. Some of these extraction methods require large amounts of both water and energy (for heating and pumping).

2.1 Bitumen Recovery from the Oil Sands

Bitumen recovery can occur through mining or in situ methods. Since in the scope of this work is restricted to air emissions from mine faces and tailings ponds, this report will focus primarily on mining operations for bitumen extraction and the associated processes for production of oil. The primary processes of interest associated with mining of bitumen from the oil sands include crushing, extraction and upgrading (Figure D). Upgrading is not directly associated with the mining process and does not necessarily take place within the mining facility. These processes will be discussed in further detail in sections 2.3 through 2.5.

Figure D: Oil Sands Process Description



In order to mine oil sands deposits, the following five key steps are required to initiate mining activities:

1. A resource evaluation program is conducted using geological data, to develop an understanding of the geology and resource extent.
2. A variety of geological data are used to develop and understand the local geology and delineate the resource. The types of data include: core hole data; auger hole data; and geophysical data. Core hole drilling programs are used in the development of the resource estimate in the area of the mine. Core holes are described, logged, sampled and analyzed for bitumen content.
3. A test mining program is completed. The test mining program involves the advancement of boreholes at different locations across the resource area. The boreholes provide geophysical data allowing for the ratio of total volume of the area to volume of bitumen in place (TV/BIP). This allows for oil sand density and bitumen density in the formation to be established.
4. If the oil sands deposit is economically viable and of suitable quality, the landscape overlying the proposed mine site must be drained. Typically the oil sands are beneath the muskeg, including water saturated peat moss. To allow for recovery, drainage is required, which can take one year or more.
5. The overburden, including till, gravel and/or sand is removed and stockpiled. This includes removal of trees and vegetation from the muskeg layer followed by draining of residual water in the muskeg. Muskeg is then removed using large electric cable shovels and is used directly, or after stockpiling, for reclamation.



2.1.1 Mining

Mining of oil sands deposits is typically applied to deposits with less than 75 m of overburden. The overburden consists of water-laden muskeg (peat bog) overtop of clay and barren sand. The mines have surface areas which are approximately 1.5-8.5 km², with pit volumes of approximately 43×10⁶-500×10⁶ m³ (Golder and Conor, 1998) and with average stripping ratios 0.5 and 0.6. Strip ratio is the ratio of the amount of waste to the amount of ore. In general, the lower the strip ratio, the more likely an oil sands ore body is to be mined.

In many large open pit operations, such as coal mines, the extent of overburden is substantial and often mining activities must be put on hold to reveal the seam in the subsurface. Conversely in oil sands operations, the extent of overburden may be limited to muskeg, since most near-surface soils contain bitumen. This requires that the extraction plant must be designed to accept large and continuous volumes of oil sand ore daily. For example, at Syncrude, oil sand delivery and extraction processing rates average 4 tonnes/second (t/s) (Hyndman and Luhnig, 1991).

Mining technology used in the oil sands mining industry has undergone changes over the last few decades in order to achieve operational and economic goals, without sacrificing flexibility and reliability. Numerous mining schemes and equipment types are adopted from construction methods. The current technology predominantly used in the oil sands region is comprised of large haul trucks and shovels. This technology has the benefit of providing:

- flexibility in the mine operation (to respond to variances in production demand and ore body characteristics); and
- a proven history of low-cost, reliable production rates.

Large electric cable shovels (up to 37 m³) load the oil sands ore onto large (85-400 t) trucks (Figure E) that will haul ore to the crusher unit (described in Section 2.2). The ore may occasionally be drilled and blasted either before winter to alleviate freezing or during winter to ease mining of frozen ore. In the crusher, the ore is mixed with water and caustic soda (NaOH) and is piped (hydrotransported) to an extraction facility where the bitumen is extracted (described in Section 2.3) (Humphries, 2008). This results in slurry consisting of bitumen, water, sand and caustic soda.

Figure E: Oil Sands Mining



(Source: Syncrude, 2008)

Mining is currently used in Muskeg River mine (Shell), Millennium Mine (Suncor), Mildred Lake and Aurora Mine (Syncrude) and the Horizon Mine (Canadian Natural Resources Limited), all located in the Athabasca region, where oil sands deposits are located under less than 75 m overburden. The average operating cost for this technique is CDN\$ 9-12/barrel (Syncrude, 2008), which is considered advantageous due to the rising cost of energy and costs less than the in situ bitumen recovery methods.

2.1.2 In situ bitumen recovery

For deeper oil sands (i.e., with > 75 m of overburden located above the deposits), bitumen is extracted via in situ methods from the sand while the oil deposit is still in place underground.

Typically in situ oil sands recovery uses one of three primary extractions techniques:

- primary or “cold” production, which is employed in reservoirs where the oil sands flow to the surface of wells without the introduction of heat. The oil is simply pumped out of the sands using wells, equipped with sand filters, often using progressive cavity pumps. This only works well in areas where the oil is fluid enough. The Cold Heavy Oil Production with Sand (CHOPS) is a second alternative, where the sand filters are removed (Dusseault, 2002);
- cyclic steam stimulation (CSS) where the well is put through cycles of steam injection, soak and oil production; and



- steam assisted gravity drainage (SAGD) where two horizontal wells are drilled in the oil sands, one at the bottom of the formation and another about 5 metres above it. Steam is injected into the upper well, the heat melts the bitumen, which allows it to flow into the lower well, where it is pumped to the surface.

2.2 Crushing

Oil sand recovered through the mining process is typically in the form of large sized masses. These masses are reduced to smaller sizes using a crushing process to sizes smaller than 2 inches, since it increases the efficiency of bitumen extraction as it increases the surface area.

2.3 Extraction Process

As illustrated in Figure F, once crushing of recovered oil sands is complete, crushed material is suspended into a slurry and “hydrotransported” to the extraction plant. To extract the bitumen from the oil sands, the cohesive forces that bind the bitumen to the sands have to be weakened. The current technology to accomplish this uses the Clark caustic hot water process where the oil sands ore from the crusher is mixed in drums with steam and caustic hot water at 80°C. Caustic hot water is a hot solution of sodium hydroxide (NaOH), forming a strong alkaline solution. The mixture swells the clay particles in the water film surrounding sand particles, and disintegrates the ore structure (Chalaturnyk et al., 2002). Using caustic hot water solubilizes the asphaltic acids in bitumen. These asphaltic acids act as surfactants (wetting agents that lower the surface tension of the water) allowing easier dispersion of the bitumen and lowering the interfacial tension between the water and bitumen. Reduction of surface and interfacial tensions by increasing pH of the suspension results in the disintegration of the oil sands ore structure and recovery of the bitumen. The resulting slurry of bitumen and caustic water is referred to as “pulp” by operators.

The pulp is transferred to a conical bottom primary separation tank. In the primary separation tank, coalescence of bitumen micelles followed by flotation takes place. Air trapped in the oil sands forms froth promoting the flotation of bitumen (Figure G). The bitumen-rich froth is skimmed by rakes to a peripheral launder and pumped to a solvent extraction plant. The middling stream, containing primarily bitumen, clay and water, is withdrawn from the primary separation tank and pumped both to feed for recycling and to the secondary separation cells. The coarse mineral matter settles to the cone bottom of the separation tank. This bottom fraction is combined with that from the secondary tank and pumped to the tailings pond. The settled coarse minerals contain unrecovered bitumen, containing PPCs which are emitted to the atmosphere over time as they are stored in the tailings ponds.

The secondary separation tank is a large air flotation unit. The bitumen froth, which contains significant quantities of water and mineral matter, is pumped to froth settlers. The froth recovered at the froth settlers is combined with that from the primary and secondary separation tanks and further treated to obtain a product free of sand and water. This is accomplished by using either naphtha- or paraffin-based solvent process. The naphtha- or paraffin- based solvent is also known as a diluent. The solvent decreases the viscosity of the bitumen and reduces the emulsion of the water-in-bitumen. The water-in-bitumen emulsion

occurs because of compounds within the bitumen mixture that are of relatively high polarity. The use of non-emulsifying solvents allows partitioning of less polar components from the bitumen into the non-polar solvent. This allows bitumen separation to occur.

Figure F: Extraction Process

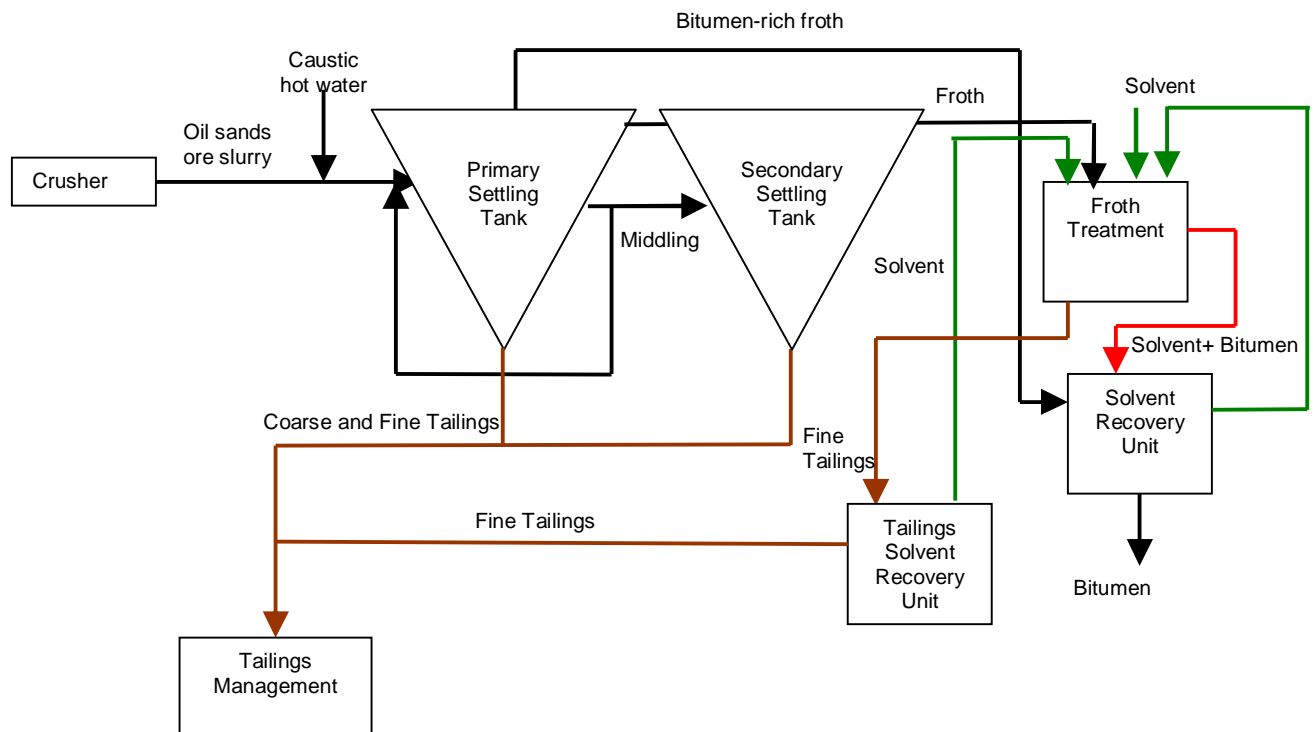


Figure G : Bitumen Separation Tank



(Source: Suncor, 2008)



Tailings from the froth treatment process are directed to a tailings solvent recovery unit (TSRU) to extract and recycle the solvent for use in the froth treatment process. A detailed description of the TSRU is found in Section 5.2, as part of the discussion on emissions reductions methods. The remaining tailings from the TSRU are pumped to the tailings ponds, where residual VOCs from the solvent are emitted to the atmosphere via volatilization.

The solvent treated froth that is not disposed as tailings is passed through primary and secondary centrifuges to remove coarse sands, clay and the remaining water on its way to the solvent recovery unit. The bitumen is separated from the solvent in a diluent/solvent recovery unit and stored in heated tanks for the upgrading process. The diluent is recycled for further use. The water, clay, coarse sands and non-recovered bitumen are pumped from the centrifuges to tailing ponds for disposal. Similarly to the mixture that comes from the TSRU, the mixture from the diluent/solvent recovery system will also contain solvent residue, which is an additional source of some of the VOCs emitted to the atmosphere from the tailings ponds.

2.4 Upgrading

Upgrading is a process used to convert heavy tar-like bitumen recovered from oil sands into a synthetic crude oil feedstock for conventional petroleum refineries. Upgrading removes several undesirable compounds from the bitumen, increases the hydrogen to carbon ratio thereby decreasing the viscosity and density and further improves product quality to make the oil transportable in the conventional crude oil pipelines. The synthetic crude oil feedstock has properties which more closely resemble light conventional crude oils, which have supplied the majority of feedstock of central and western Canadian facilities (Hyndman and Luhning, 1991). Upgrading of bitumen achieves the following:

- modifying the boiling point range and reduce the residue from the synthetic crude oil;
- reducing sulphur content;
- reducing nitrogen content; and
- producing a saturated or hydrogenated product.

Upgrading is a separate process that is not necessarily part of the oil sands mining facility and does not generally contribute to waste streams deposited in the tailings ponds.

2.5 Oil Sands Tailings

Water and solvent used in the extraction process combines with sand, clay and residual bitumen to form tailings. Tailings composed of water, dissolved salts, organic compounds, minerals and bitumen are pumped from the separation vessels and froth treatment facilities to a series of on-site tailings ponds. Tailings produced from the extraction process of bitumen include three streams as follows:

- coarse tailings;
- fine tailings; and

- thickened tailings.

Generally, tailings, regardless of whether they are coarse or fine tailings, contain approximately: 70 to 80 percent weight basis (wt%) water, 20 to 30 wt% solids (sands, silt and clays) and 1 to 3 wt% bitumen (Allen, 2008a). The composition of tailings is dependent on ore quality, source, extraction processes and age (Allen, 2008a)

One stream of tailings from the primary and secondary bitumen separation step is coarse tailings. Coarse tailings refer to coarse-grained materials recovered during the separation process and may comprise sands, gravels, minerals, unrecovered bitumen and water. These tailings generally segregate in the tailings ponds upon discharge, forming a beach. The segregation process relates in part to the use of the Clark hot water extraction process, but also relates to the more rapid settlement of coarser (and therefore heavier) materials.

A second stream of tailings from the primary and secondary bitumen separation step, as well as the tertiary bitumen recovery step and the froth treatment step, is fine tailings. Fine tailings refer to fine-grained materials recovered during the separation process and may comprise silts, clays, minerals, solvent, unrecovered bitumen and water. Similarly to coarse tailings, fine tailings will also segregate. Approximately 20 wt% of solids in fine tailings will settle quickly; an additional 10 wt% of solids will settle over a period of several years (Chalaturnyk et al., 2002; Allen, 2008a).

The fine tailings undergo consolidation (volume reduction due to the stress applied during particulate settling) once placed in the tailings ponds. This consolidation process results in a specific category of fine tailings referred to as mature fine tailings (MFT). The MFT remain in a fluid state for decades after deposition in the tailings ponds because of slow consolidation rates associated with fine tailings (Chalaturnyk et al., 2002). It is estimated that MFT accumulation in the tailings ponds is between 0.1 to 0.2 m³ per ton of oil sands processed (Quagraine et al., 2005). Removal and/or treatment of MFT may be completed to promote further consolidation and dewatering.

Factors affecting the amount of fine tailings generated include:

- amount of mineral materials in the oil sands ore and their degree of dispersion in the tailings;
- temperature of the conditioning process (high temperatures create more fines);
- chemical environment during oil sands processing (higher alkalinity operations increase the creation of fine tailings);
- the proportion of the fine minerals that become captured in sand dykes and beaches;
- size of tailings ponds and the age of MFT they contain; and
- the activation of natural microbes that biodegrade a portion of the hydrocarbons thereby releasing CH₄ and increasing the rate of settling of MFT.

Fine tailings can be thickened before depositing into tailings ponds using a thickener and with the addition of flocculants. These tailings are referred to as thickened tailings. Thickened tailings are produced by



feeding tailings streams from the primary and secondary bitumen separation step, as well as the tertiary bitumen recovery step and the froth treatment step into a thickener. The thickener is a large tank or vessel that centrifuges tailings with the thickener and/or flocculant to improve consolidation, thereby increasing the solid content of the mixture. Thickened tailings are subsequently disposed into on-site tailings ponds.

Consolidated tailings (CT), also known as non-segregating tailings, are tailings which did not segregate when deposited in tailings ponds and have subsequently been forced to consolidate through chemical or mechanical methods in situ and/or ex situ. Chemical methods include the addition of coagulants, such as gypsum or other flocculating agents, to produce CT from the tailings. Mechanical methods include the separation of tailings into coarse and fine streams using cyclones. Similarly to other tailings streams, the fine tailings stream arising from CT is directed through a thickener where it is dewatered and then recombined with the coarse stream before deposition in the tailings ponds.

2.6 Management of Oil Sands Tailing

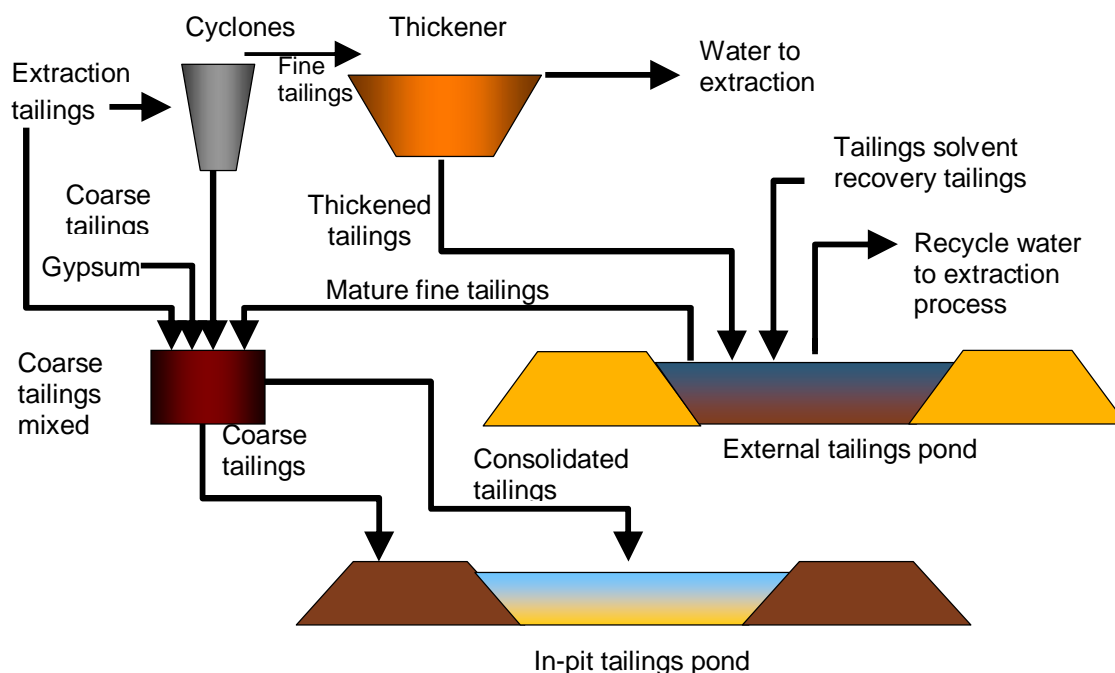
The oil sands companies do not release extraction wastes; rather they contain all process-affected waters and fine tailings on site, primarily in large tailings or settling ponds (Holowenko et al., 2000). Figure H provides an illustration of a typical tailings management system.

Presently, oil sands facilities initially store their tailings from the mining process in temporary external tailings ponds until enough in-pit storage becomes available. The external tailings ponds dykes are constructed using overburden until sufficient in-pit storage and coarse tailings becomes available. When sufficient in-pit storage is available, on-site tailings ponds are constructed. Typically on-site tailings ponds are constructed using sand, although in some situations (particularly for initial tailings ponds), overburden is also used for dyke construction. If sand is used, this is typically extracted from CT. Typically, CT have a sand-to-fine ratio (SFR) ranging from 3.5 – 5. This renders CT unsuitable for dyke construction. Upon extraction of the sand from the CT, the SFR of the CT will decrease since sand has been removed. This can result in delayed long term settling of CT.

Historically, oil sands facilities constructed off-site tailings ponds for tailings management similar to the current processes for tailings pond construction. However, rather than using CT when sufficient in-pit storage space became available, they used sand removed from the tailings or alternatively, sand augmented with MFT. This approach historically resulted in large volumes of tailings that required management. This method has since been superseded by the CT method described above.

Coarse tailings can also be deposited separately. While this will reduce initial tailings disposal volumes and consequently increase the quantity of sand available for use in dyke construction, this also results in fewer fine tailings becoming encapsulated in dyke cells and beaches than those dykes constructed using whole tailings. This may result in a larger final volume of tailings for disposal, depending on the solids content of the thickened tailings deposits.

Figure H: Tailings Management System



2.7 Tailings Ponds Design

Tailings ponds vary in size with surface areas ranging between 0.5 and 25 km² and depths ranging between an average of 20 and 30 m. Figure I provides a schematic representation of a tailings pond. As is shown in Figure I, tailings ponds typically consist of perimeter dykes constructed from overburden which will act to contain the tailings in the impoundment. As tailings volume increases, expansion of the overburden dyke is completed using coarse sand derived from coarse tailings. This results in the formation of the beach as a result of coarse tailings deposition near the perimeters of the pond. Fine tailings also settle and form a layer of MFT which is overlain by process water. This process water can subsequently be withdrawn for reuse.

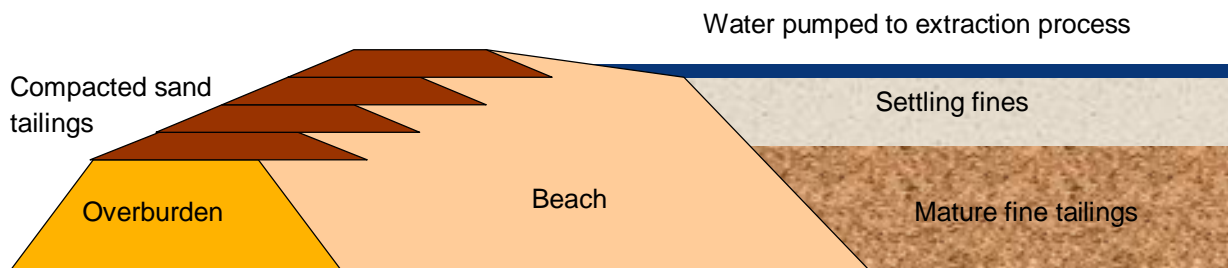
Tailings ponds, either external or in-pit, are surface impoundment structures designed to store tailings and process water. The purpose of storage is to reclaim process water for re-use in the extraction process, as required. There are two main designs of tailings ponds (Vick 1990). The first design involves a water retention type dam, which is constructed to its full height prior to any discharge to the pond (EPA 1994). This is typically constructed of natural soils (Vick 1990). This type of tailings pond design is not commonly used in the oil sands.

The second design involves a raised embankment type dam, which is constructed gradually as tailings are deposited. A review of the tailings management plans from EIAs for oil sands facilities indicate that the



majority of proposed tailings ponds will be constructed with the raised embankment dam design. This is likely a result of the dynamic nature that embankment dam design affords. Specifically, the embankment can be raised at specific time intervals to increase the available volume for the storage of tailings and water. Since construction of the dyke occurs gradually, this provides options for construction material since smaller quantities are required at any one time including a combination of natural soil, tailings and waste rock in any combination (Vick 1990). Raised embankment dam design will be constructed using one of three designs: the upstream design, downstream design or centreline design. The difference between these designs relates to the direction in which the embankment crest moves in relation to the starter dyke at the base of the embankment wall (Vick 1990).

Figure I: Typical Tailings Pond



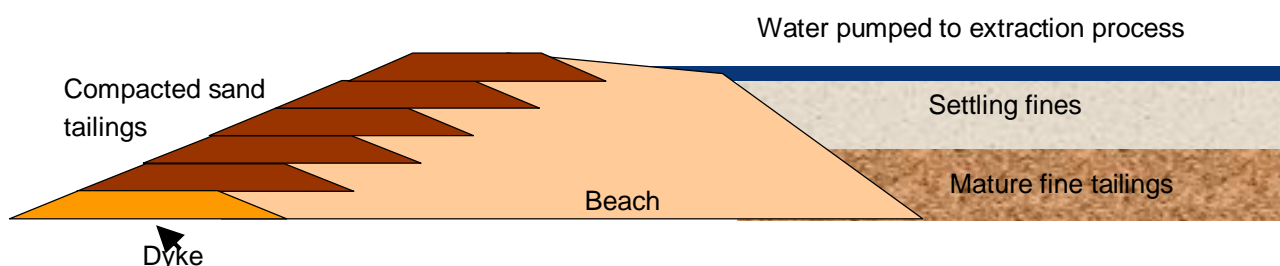
Note: Adapted from McRoberts (2008)

2.7.1 Upstream Design

The construction of an upstream designed embankment begins with a starter dyke foundation constructed using overburden (Figure J). The tailings are usually discharged from the top of the dam crest creating a beach that becomes the foundation for future embankment raises (Vick 1990). Coarse material settles closest to the discharge point of the tailings in the tailings pond; fines settle further away. Cyclones can be used to accelerate particle segregation for certain types of tailings. This allows the slurry portion of the tailings to be sent to the centre of the pond with the sand fraction settling at the beach behind the crest. The conventional method of upstream design relies on no compaction of the beach that forms the embankment shell (Martin 1999). Generally the settled coarse fraction from the discharge point is used as the raise material for the embankments. For multiple spigot discharges, a series of shallow pits are dug in front of the discharge points once the tailings have dried and consolidated. Tailings are subsequently placed on the embankment crest and compressed, and tailings lines are lifted and reassembled.

The upstream method is the most popular design for a raised tailings embankment design. The upstream method requires the lowest initial investment. This is primarily related to the minimal quantity of fill material required for initial construction and subsequent raising. The raising is primarily completed using the coarse fraction of the tailings.

Figure J: Upstream Design Embankment

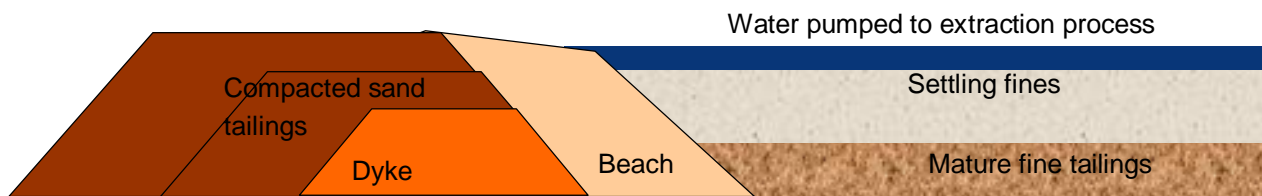


2.7.2 Downstream Design

Similarly to the upstream design, a downstream designed embankment begins with a started dyke foundation constructed using overburden (Figure K). The tailings are initially deposited behind the dyke and as the embankment is raised, the extension of the dyke wall is constructed and supported on top of the downstream slope of the previous section. This shifts the centreline of the top of the dam downstream as the embankment stages are progressively raised (Vick 1990). The downstream design is very versatile for a range of site specific design parameters and behaves similarly to water retention dams. The downstream design was developed specifically to reduce the risks associated with upstream design subjected to dynamic loading (e.g., as the result of an earthquake).

The main advantage of downstream design is that the dykes can have unrestricted heights due to each raise being structurally independent of the tailings. Additionally, raised sections can be designed to have variable porosity to address any problems that might be associated with the phreatic surface of the embankment. This can be particularly useful where a processing plant has made changes to increase efficiency and as a result has altered the tailings characteristics such as higher water content or variable drainage characteristics. The main disadvantage of downstream design is the cost of raising the embankment, as large volumes of fill are generally required which increases exponentially as embankment height increases. Subsequently a large area around the dam itself is required as the toe of the dam moves out and additional raises are added.

Figure K: Downstream Design Embankment



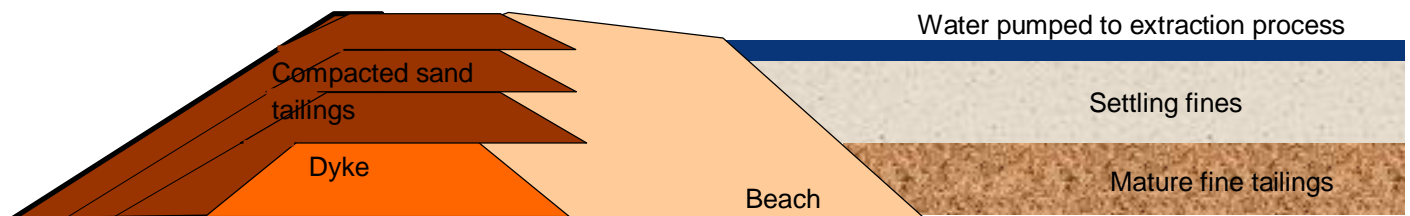


2.7.3 Centreline Design

The construction of a centreline design, like upstream and downstream designed embankments begins with a starter dyke foundation constructed from overburden (Figure L). Like the upstream method, in the centreline design, tailings are generally discharged by spigots from the embankment crest to form a beach behind the dam wall. When subsequent raising is required, material is placed on both the tailings and the existing embankment. Through this deposition, the embankment crest is raised vertically and does not move horizontally in relation to the upstream and downstream directions of subsequent raises. This allows for internal drainage zones to be incorporated into the design that are similar to those found in downstream design. Free water can subsequently encroach upon the dam crest without increasing the phreatic surface, limiting the risk of potential failure.

The advantage to the centreline method is that it is generally a compromise between the upstream and downstream designs (Benckert and Eurenus 2001). Hence, it affords the stability of the upstream method while not requiring the extent of construction material required for the downstream design. The disadvantage of centreline design is that it cannot be used as a large water retention facility solely due to the subsequent raises in the structure being partially constructed on CT. To overcome this problem, a suitable decant system is required to prevent free water from submerging the beach around the dam crest.

Figure L: Centerline Design Embankment



3. MINE FACE AND TAILING POND AIR EMISSIONS

The operation of oil sands mining, extraction and upgrading facilities results in controlled and fugitive gaseous and particulate matter (PM) emissions to the atmosphere. The emissions from oil sands sources are mainly from:

- Extraction, upgrading and energy services plant operations which include combustion methods resulting in emissions of NO_x, CO, THC, RSC and PM.
- Mining operations streams which include diesel fuelled truck and shovel operations and their associated internal combustion engines. Products of combustion include NO_x, CO, THC, VOCs, PM and PAH. The truck and shovel mining operations typically run continuously (i.e. 24 hours per day, 7 days a week). Fugitive mine emission of THC and RSC are associated with exposed mine surfaces and are expected to be greatest during warm summer periods. PM emissions also result from tire/haul road surface abrasion and the resulting entrainment of dust into the atmosphere (which has not been estimated in this assessment).
- Fugitive emissions from tailings and ponds and consolidated tailings surfaces. THC, VOC and RSC emissions result from the volatilization of residual amounts of diluent and bitumen contained in the tailings discharged to tailings ponds. The emission magnitude depends on the age of the pond, temperature of the pond surface, the nature of the VOC and the exposed area of the surface (Golder and Conor, 1998). Fugitive emissions from tailings ponds can also arise from exposed CT, including those used in dyke construction and the overlying capping water layer above CT. Residual VOC and RSC can subsequently volatilize from the water surface and/or exposed CT surfaces.

The Canadian Association of Petroleum Producers (CAPP) (1998) defines fugitive emissions as evaporation losses and unintentional leaks. Evaporation losses can occur from tailings storage areas, sewage lagoons and mine surfaces. The main sources of fugitive emissions are the tailing ponds.

VOCs are light hydrocarbon compounds, which are of concern since there are possible associations with human health effects. VOCs are a large group of chemicals that participate in atmospheric photochemical reactions. Individual VOCs may be toxic to humans and may combine with NO_x in the presence of sunlight to form ground level ozone (RWDI, 2005).

3.1 Identification and Quantification of Pollutants of Potential Concern

Oil sands projects are major emitters of several PPCs. Air emissions of particular importance from oil sands operations include VOCs, CH₄, PAHs and RSC. These emitted PPCs have potential human health and environmental impacts. This section reports the results of a review completed by WorleyParsons on emission levels of VOCs, PAHs, CH₄ and RSC as presented in EIAs, industry responses to a questionnaire prepared by WorleyParsons and data found in NPRI. The review determined that six RSC



compounds, twenty-four VOCs and four PAHs in addition to CH₄ have been measured in association with oil sands operations. These compounds are listed in Table C.

Table C Species and Compounds Reported in Environmental Impact Assessments and NPRI

Species	Compound/Group
RSC	Hydrogen sulphide (H ₂ S), carbonyl sulphide (COS), carbon disulphide (CS ₂), mercaptans and thiophenes
VOCs	Xylenes, toluene, n-hexane, butanes, cyclohexane, nonane, octane, decane, propanes, ethylene, ethylene glycol, propylene, benzene, 1,2,4-trimethylbenzene, 1,3-butadiene, C ₂ -C ₈ aliphatic, C ₉ -C ₁₆ aliphatic C ₁₆ + aliphatic, C ₆ -C ₈ aromatic (excluding benzene), C ₉ -C ₁₆ aromatic, aldehydes, ketones, acrolein and formaldehyde
PAHs	Acenaphthene, acenaphthylene, benzo(a)phenanthrene and cumene
Other	Methane

Where data on the toxicity and environmental fate of these PPCs was available, it has been compiled in Appendix 1 for reference. CH₄ is also included in Appendix 1 since it is emitted from the tailings ponds as described in Section 3.2.2.

3.1.1 Emissions Reported in EIAs

The EIAs from the applications listed in Table D were reviewed. These include EIAs for oil sands mines that have been proposed, are in application, are approved, are under construction and are operational. The EIA document for Syncrude's original facility was not available and hence has not been included. In most EIAs, VOC and PAH emissions were reported collectively as estimated emissions from the mine faces and tailings ponds. In the EIAs, VOC and PAH emissions were either reported as individual species or as a groups of compounds. These emissions were reported to allow ambient air quality to be predicted using results of air dispersion modelling. Methane emissions were generally reported individually in the context of GHG emissions. Emissions reported in EIAs from mine faces and tailings ponds are presented in Table 1, found after the main body of the report.

It should be noted that when applying for project approval, operators are expected to show that emissions from oil mining facilities will not cause ambient air quality levels to exceed Alberta Ambient Air Quality Guidelines (AAAQG), even during upset conditions and extreme operating conditions. The consultants completing the EIAs therefore use a methodology that is supposed to predict the maximum expected emissions for the project. Based on this reasoning, the emission data presented in EIAs likely do not represent emissions for actual/normal operating conditions.

ENVIRONMENT CANADA

**REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
AND OPTIONS FOR REDUCING EMISSIONS**

Table D List of Reviewed Environmental Impact Assessment Reports

Company	EIA Application (ERCB [EUB] Application Number)	Date of Application
Canadian Natural Resources Limited	Horizon oil Sands Project-Application for Approval (1273113)	June 2002
Deer Creek Energy Limited/ Total E&P Canada	Joslyn North mine Project-Alberta Utilities Board Alberta Environment Integrated Application (1445535)	February 2006
Esso Imperial Oil	Kearl Oil Sands Project Mine Development (1408771)	July 2005
Albian Oil Sands/ Shell Canada	Application for Approval for the Muskeg River Mine (970588)	December 1997
Shell Canada Energy	Application for Approval for the Muskeg River Mine Expansion (1398411)	April 2005
Shell Canada Energy	Application for Approval of the Jack Pine Mine –Phase 1 (1271285)	May 2002
Shell Canada Energy	Application for Approval of the Jack Pine Mine Expansion and Pierre river Mine (1554388)	December 2007
Suncor Energy	Project Millennium Application (Not Available)	April 1998
Suncor Energy	Application for Steepbank Extension Project (1554396)	March 2005
Syncrude	Mildred Lake Upgrader Expansion Application and Environmental Impact Assessment (980381)	July 1998
Synenco Energy	Application for Approval of the Northern Lights Mining and Extraction project (1468146)	June/November 2006

In order to predict emissions from oil sands facilities in EIAs, oil sands operators and their consultants are required to make assumptions about mine faces and tailings ponds. The review of EIAs identified several similarities in the methods used by oil sands operators to predict emissions for proposed facilities. The five intrinsic assumptions associated with these methods are described below.

Assumption 1: VOCs emitted from the tailings ponds are assumed to be equal to the diluent loss to the pond from the extraction process.

Discussion: Diluent (either naphtha or paraffin solvents) is added to bitumen to decrease the viscosity and density. The diluent is subsequently recovered using TSRU (see Section 5.3) prior to disposal of tailings in the tailings pond. Failure to recover the diluent prior to disposal of the tailings



in the tailings ponds is expected to result in the emission of VOCs. The quantities of VOC emissions are predicted to equal the unrecovered amount of diluent. Currently operators design solvent recovery systems to operate at an efficiency exceeding 99%.

Implications: VOC emissions from tailings ponds are not strictly related to diluent concentration. Additional factors that may influence VOC emissions include pond surface area, pond age, ambient temperature and pressure, wind speed and concentration gradient (between the surficial waters and ambient air). VOC emissions from tailings ponds are unlikely to account for 100% of the mass of diluent. It is more likely that a large portion of the diluent would be transformed to methane and emitted. Therefore, the VOC emitted is not equal to the diluent, but rather the total carbon in the diluent is equivalent to carbon emitted as methane plus carbon emitted as VOCs. Hence, it is expected that this assumption would generally overestimate VOC emissions from tailings ponds.

Assumption 2: Diluent loss from the tailings pond varies linearly with mean monthly temperatures of Fort McMurray, Alberta.

Discussion: This emission scheme is based on a percent loss according to the difference in temperature between a reference temperature (typically 0 °C) and the average temperature of the month. According to this method, nearly 100% of residual diluent in the ponds is emitted during the warmest month. Conversely, it is assumed that nearly 0% (no losses) occur during the coldest month. The monthly variable emission scheme is presented in Table E.

Table E Monthly Variable Tailings Pond Emissions of Solvents

Month	Ft. McMurray Average Monthly Temperatures (°C days)	% solvent Loss Emitted from Tailings Pond
January	1.6	2.7
February	5.1	3.4
March	23.1	6.9
April	139.3	29.6
May	322	65.3
June	439.9	88.3
July	519.2	100
August	474.2	95
September	282.4	57.5
October	119.9	25.8
November	7.4	3.8
December	1.4	2.6

It is assumed that this emissions scheme infers that the emission rate in July significantly exceeds rate of solvent discharge to the pond to account for solvent accumulation during colder months such that 100% of the diluent lost to the pond is emitted over the year. EIAs reviewed generally reference this scheme to Suncor, CNRL and Imperial Oil.

Implications: Emissions from tailings ponds are not strictly related to ambient air temperature above the tailings ponds. Emissions are also influenced by pond surface area, pond age, ambient pressure, wind speed and concentration gradient (between the surficial waters and ambient air). Freezing of the pond surface would also be expected to limit emissions to low or negligible rates. Additionally, diluent losses can occur not only through volatilization, but also through methanogenic processes in the pond, resulting in a decrease in VOC emissions, but increased CH₄ emissions. It is assumed that VOC emissions would be overestimated using this assumption. However, as a result of this assumption, it is expected that CH₄ emissions would be underestimated.

Assumption 3: Emissions rates from tailings ponds are based on the assumption that approximately 4 barrels of diluent are lost per 1,000 barrels of bitumen produced.

Discussion: Diluent recovery systems generally operate at efficiencies of 99% or greater. The solvent loss may be variable and hence the emissions rate from a pond may not be accurately reflected by an emissions rate that assumes solvent loss to the pond of approximately 4 bbl/1000 bbl of bitumen.

Implications: Emissions rates from tailings ponds will vary dependent on the diluent recovery system in place and production rate. Additionally, emissions rates will vary between facilities based on the type of diluent, bitumen and extraction process. This assumption is expected to generally overestimate emissions for oil sands mining facilities.

Assumption 4: RSC and H₂S fugitive emissions from tailings ponds, similar to VOC, PAH, methane and THC emissions, can be scaled from measured emissions associated with tailings ponds at Syncrude's Mildred Lake Mine (Syncrude 1998) if a correction for diluent volume released to tailings ponds is applied.

Discussion: The emissions from tailings ponds across oil sands mines are typically estimated using EF based on measured data from the Syncrude Mildred Lake Mine. This assumes that the tailings pond footprint, tailings management systems and diluent are equivalent to conditions at the Mildred Lake Mine.

Implications: Since diluent composition and use is variable, and since tailings pond design can vary substantially between facilities, this assumption may not be valid for all oil sands facilities. Critical evaluation of the agreement between proposed design and Syncrude's Mildred Lake Mine design should be completed prior to applying the EF; additional correction of EF may be required to account for additional confounding factors relating to variability in mine design. Without this critical evaluation, it is difficult to assess whether the EF would underestimate or overestimate actual emissions. It is expected that underestimation versus overestimation would primarily depend on diluent release and composition, although other factors may also influence the emissions rate.

Assumption 5: Emissions from mine faces can be scaled from measured emissions associated with mine faces at Syncrude's Mildred Lake Mine (Syncrude 1998) if a correction for exposed surface area is applied.



Discussion: The emissions from mine faces across oil sands mines are typically estimated using EF based on measured data from the Syncrude Mildred Lake Mine. This assumes that the bitumen composition in the oil sands deposit, ore composition and physical properties, elevation, exposed surface area and direction of the exposed face (e.g., windward versus sheltered) and mining process are analogous to those employed at Syncrude's Mildred Lake Mine.

Implications: Since bitumen composition and mine design will vary depending on localized conditions including geography, geology, topography and drainage, this assumption may not be valid for all oil sands facilities. Similarly to EF for tailings ponds, a critical evaluation of agreement between conditions at the proposed facility versus Syncrude's Mildred Lake Mine should be completed; additional correction of EF may be required to account for additional confounding factors relating to variability in mine design. Without this critical evaluation, it is difficult to assess whether the EF would underestimate or overestimate actual emissions. It is expected that underestimation versus overestimation would depend on the design of the mining pits, the direction of exposed faces and localized geographic and geological conditions that may shelter or promote air movement (e.g., wind) across the surface.

3.1.2 Reported Emissions from Questionnaire

Information on emissions from tailings ponds and mine faces were also obtained using a questionnaire prepared by WorleyParsons and distributed among various oil sand mining operators. The questionnaire inquired about operating facilities, the size and surface area of mine faces and tailings ponds, as well as emissions from tailings ponds and mine faces. Completed questionnaires are provided in Appendix 2.

Syncrude provided emissions data for mine faces and tailings ponds at their operational facilities including the Mildred Lake Mine and Aurora North Mine. Suncor provided CH₄ emissions estimated using the surface areas of the pond and mine faces multiplied by the average CH₄ emission factors of tailings ponds and mine areas. Emissions were calculated on the basis of a flux survey completed in the fourth quarter of 2001. Suncor also provided emissions data, reported as emissions flux, for tailings ponds at their facility. However, EF were not available to quantify actual emissions from mine faces. Ambient air concentrations measured within the facility boundaries were also provided.

Table F summarizes 2006 emissions reported from the active mine faces and tailings ponds in Mildred Lake and Aurora North Mines. Additionally, it summarizes CH₄ emissions, provided by Suncor in their response to the questionnaire, for tailings ponds and mine faces at Suncor's Millennium Mine (2007 data).

ENVIRONMENT CANADA

REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
AND OPTIONS FOR REDUCING EMISSIONS

Table F Reported 2006 Emissions from the Active Mine Faces and Tailings Ponds of Mildred Lake and Aurora North Mines (Syncrude) and 2007 Emissions from the Active Mine Faces and Tailings Ponds of Millennium Mine (Suncor)

	VOC (t/y)	Benzene (t/y)	CH ₄ ⁽¹⁾ (t/y)	RSC (t/y)
Mildred Lake Mine – Mine Faces	3,004	0.7	-	21
Mildred Lake Mine – Tailings Ponds	5,994	39	-	62
Total Emissions – Mildred Lake Mine	8,998	39.7	-	83
Aurora North Mine – Mine Faces	15,291	.03		63
Aurora North Mines – Tailings Ponds	461	0.16		9
Total Emissions – Aurora North Mine	15,752	0.19	-	72
Millennium Mine - Tailings ponds	-	-	14,087	-
Millennium Mine - Mine faces	-	-	531	-
Total Emissions – Millennium Mine	-	-	14,618	-

⁽¹⁾ Mildred Lake Mine and Aurora North Mine CH₄ production were reported as the total production for both mines from mine face (23,975 t) and tailings ponds (1,852 t) in 2007.

Table G provides calculated emissions for CH₄, VOCs and RSC. The calculations were completed using data provided by Suncor in their response to the questionnaire. Emissions were calculated by considering the average of three zonal emissions flux measurements (collected from the outfall, 1/3 of the pond distance from the outfall and 2/3 of the pond distance from the outfall) and the surface area of the associated pond.



Table G Calculated Emissions – Suncor Millennium Mine Tailings Ponds

PPC	Calculated Emissions (t/y)
Benzene	9
Toluene	142
Ethylbenzene	49
Xylenes	298
THC	10,236
Total VOCs	10,734
H ₂ S	228
RSC	1,798
Methane	7,313

3.1.3 Reported Emissions from NPRI

Overview

The NPRI was also reviewed to obtain detailed emissions data for individual species of VOCs, PAHs and RSC. The data reviewed was for the 2007 reporting year. As of the date of this report, 2008 data were not yet available. Although the emissions are reported by individual chemical species, these values are not categorized by emission source in the mining facility. Instead, the emissions are reported as total fugitive emissions (Table 2 found after the main body of the report). Hence, VOCs and RSC reported for each of the mines includes evaporative losses from tailings, storage areas, sewage lagoons, processes, tank fugitive emissions and mine surfaces. Figures M through P summarize the NPRI emissions data from Mildred Lake Mine – Syncrude, Aurora Mine – Syncrude, Muskeg River Mine – Shell and Millennium Mine – Suncor, respectively.

Currently the three operators that have operational mines produce a combined total of approximately 924,000 bbl/d of bitumen as follows:

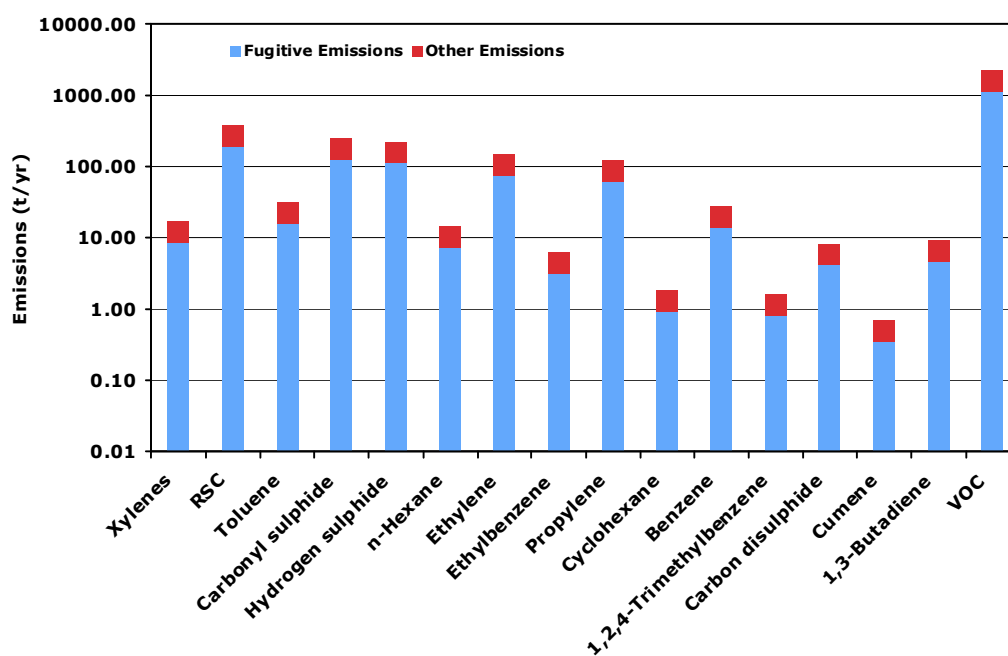
- Syncrude has two operating mines, which are Mildred Lake and Aurora North mines, with a total bitumen production capacity of 452,700 bbl/d;
- Suncor operates the Millennium mine at a bitumen production capacity of 317,000 bbl/d; and
- Shell operates the Muskeg River mine producing bitumen at a capacity of approximately 155,000 bbl/d.

Mildred Lake Mine-Syncrude

Figure M presents fugitive and other emissions compiled from NPRI (2007 reporting year) for Syncrude's Mildred Lake Mine. Where possible, individual chemical species have been isolated and presented separately. Total VOCs have also been presented. The key points associated with Figure M are as follows:

- the total annual fugitive emissions from Mildred Lake Mine in 2007 were approximately 11,262 t;
- these fugitive emissions include 10,176 t of VOCs (90% of total fugitive emissions) and 54.3 t of benzene (0.4% of total fugitive emissions); and
- the total fugitive emissions of VOCs were approximately 60% of total VOC emissions from the mine.

Figure M: Mildred Lake Mine-Syncrude NPRI Emissions Data



Aurora North Mine-Syncrude

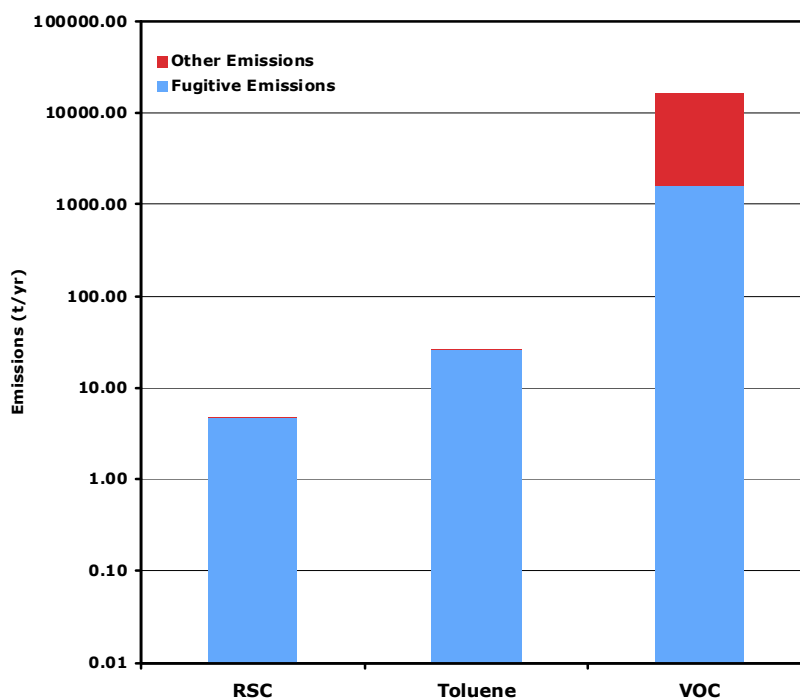
Figure N presents fugitive and other emissions compiled from NPRI (2007 reporting year) for Syncrude's Aurora North Mine. Generally details on individual chemical species were not available, as only toluene was reported separately from other VOCs. The key points associated with Figure N are as follows:

- the total annual fugitive emissions from Aurora North Mine in 2007 were approximately 15,784 t;



- these fugitive emissions include 15,753 t of VOCs (99.8% of total fugitive emissions), 26 t of toluene (0.1% of total fugitive emissions) and 4.7 t of RSC (0.03% of total fugitive emissions); and,
- the total fugitive emissions of VOCs were approximately 96% of total VOC emissions from the mine.

Figure N: Aurora Mine-Syncrude NPRI Emissions Data



Muskeg River Mine-Shell

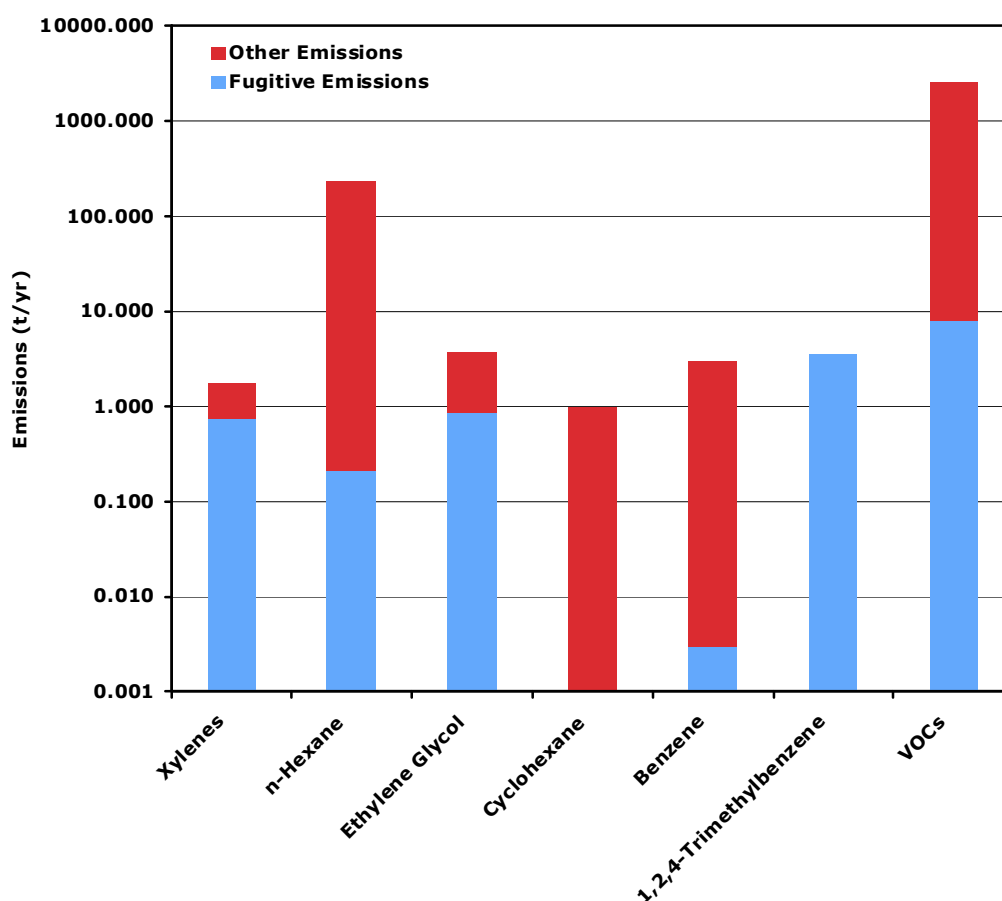
Figure O presents fugitive and other emissions compiled from NPRI (2007 reporting year) for Shell's Muskeg River Mine. Where possible, individual chemical species have been isolated and presented separately. Total VOCs have also been presented. The key points associated with Figure O are as follows:

- the total annual fugitive emissions from Muskeg River Mine in 2007 were approximately 13.4 t; and,
- the total annual fugitive emissions include approximately 8 t of VOC emissions (60% of total fugitive emissions) and 4 t of 1,2,4-trimethylbenzene emissions (30% of total fugitive emissions).

It should be noted that Shell's Muskeg River Mine reported substantially lower fugitive emissions than other oil sands mining operations in 2007. Additionally, they reported fugitive emissions as a lower percentage of total mine emissions than other facilities. This has historically been true for the Shell Muskeg River Mine. The reason for this discrepancy is unclear. However, a substantial quantity of VOCs

was reported as spills (461 t) and other non-point emissions to air (2,032 t) in 2007. This is consistent with NPRI data from previous years, although reported emissions for 2007 were generally lower than previous years.

Figure O: Muskeg River Mine-Shell NPRI Emissions Data



Millennium Mine-Suncor

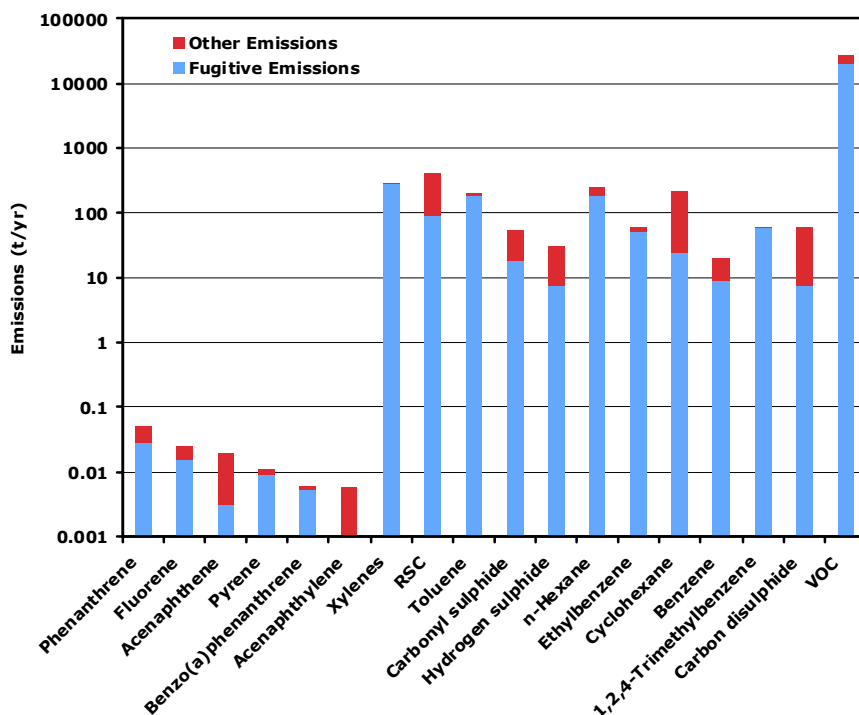
Figure P presents fugitive and other emissions compiled from NPRI (2007 reporting year) for Suncor's Millennium Mine. Where possible, individual chemical species have been isolated and presented separately. Total VOCs have also been presented. The key points associated with Figure P are as follows:

- the total annual fugitive emissions from Millennium Mine in 2007 were approximately 24,290 t;
- these fugitive emissions include approximately 21,000 t of VOCs (86% of total fugitive emissions) and 9 t of benzene (0.04% of total fugitive emissions);



- the total fugitive emissions of VOCs were approximately 76% of total VOC emissions from this mine; and,
- the total fugitive emissions of VOCs were approximately 50% of the total emissions from the mine.

Figure P: Millennium Mine-Suncor NPRI Emissions Data



3.2 Potential Sources and Mechanisms of Oil Sands Emissions

3.2.1 Overview

Potential sources and mechanisms of oil sands emissions are dependent on facility design and footprint, chemical and mechanical processes completed within the mine, including mining, extraction and tailings management. Additional factors such as geological and geographical conditions, hydrogeological and hydrological conditions, topography, climatology and drainage can also influence the rate, quantity and quality of emissions. Combined, these factors can influence oil sands emissions subtly or significantly, depending on the interrelation between these factors.

3.2.2 Potential Sources of Oil Sands Emissions

The primary sources of oil sands fugitive emissions include mine faces and tailings ponds. For mine faces, factors such as the exposed mine face surface area, age of the mine faces, composition of the bitumen in the formation, composition of the deposit, ambient conditions, including temperature, pressure and wind speed, and geographical setting can influence the quantity and quality of emissions. For tailings ponds, diluent quantity and type, tailings pond age, surface area and design, tailings management system, tailings quality, quantity of residual bitumen, tailings pond water temperature, ambient air temperature, pressure and wind speed and geographical setting can influence the quantity and quality of emissions.

Mine Faces

Mine faces form one of the primary sources of fugitive emissions in the oil sands industry. Studies on emissions from mine faces are limited. However, it is anticipated that the primary source of emissions from mine faces would relate to the quantity and quality of bitumen in the oil sands formation. Specifically, removal of overburden to facilitate mining of the bitumen results in the exposure of hydrocarbons to the elements. Prior to exposing the bitumen, overburden acts as a capping feature to limit the losses of light hydrocarbon compounds to the atmosphere. Exposure of these surfaces eliminates the ability of overburden materials to capture volatile components of the mixture, thereby facilitating emissions.

Tailings Ponds

Tailings ponds form another of the primary sources of fugitive emissions in the oil sands industry. Studies on tailings ponds have related primarily to water quality, although more recently consideration has been given to ambient air emissions. The primary sources of emissions from tailings ponds relate to quantity of residual bitumen, quantity of residual diluent and tailings pond water quality. Additional sources of emissions may include secondary biological and/or chemical reactions such as methanogenesis.

Oil sands tailing ponds hold water, dissolved salts, organics, minerals and bitumen. A study on the water quality of the tailings ponds revealed that the water is typically of moderate hardness (15-25 mg/L Ca^{2+} , 5-10 mg/L Mg^{2+}) and alkalinity (pH of 8.0-8.4), and contains NA, asphaltenes, benzene, phenols and creosols, humic and fulvic acids, phthalates, PAHs, and toluene (Allen, 2008a). An overview of oil sands tailings pond water quality is presented in Table H



Table H Mean Values of Inorganic and Organic Water Chemistry of Oil Sands Tailings Ponds

Parameter (mg/L)	Syncrude MLSB ⁽¹⁾	Suncor TPW ⁽²⁾	Suncor CT ⁽³⁾ release Water	Suncor CT Pond Seepage	Suncor Tailings
pH	8.2	8.4	8.1	7.7	-
TDS ⁽⁴⁾	2221	1887	1551	1164	-
Sodium	659	520	363	254	-
Calcium	17	25	72	36	-
Magnesium	8	12	15	15	-
Chloride	540	80	52	18	-
Bicarbonate	775	950	470	780	-
Sulphate	218	290	564	50	-
Ammonia	14	14	0.35	3.4	-
DOC ⁽⁵⁾	58	-	-	-	62-67
BOD ⁽⁶⁾	25	-	-	-	<10-70
COD ⁽⁷⁾	350	-	-	-	86-525
OG ⁽⁸⁾	25	-	-	-	9-31
NA	49	-	-	-	68
Cyanide	0.5	-	-	-	0.01
PAHs	0.01	-	-	-	-
Toluene	-	-	-	-	1-3
Benzene	-	-	-	-	<0.6-6
BTEX ⁽⁹⁾	<0.01	-	-	-	-

Source: Allen, 2008a and sources within

⁽¹⁾ Mildred Lake Settling Basin

⁽²⁾ Tailings pond water

⁽³⁾ Consolidated/composite tailings

⁽⁴⁾ Total dissolved solids

⁽⁵⁾ Dissolved organic carbon

⁽⁶⁾ Biochemical oxygen demand

⁽⁷⁾ Chemical oxygen demand

⁽⁸⁾ Oil and grease

⁽⁹⁾ Benzene, toluene, ethylbenzene, xylene.

Tailings pond water quality may represent an important source of oil sands emissions. Particularly, the organic constituents of oil sands tailings are precursors to chemical emissions through a variety of mechanisms including volatilization, biodegradation, photolysis and other chemical/physical reactions that can occur in the ponds.

3.2.3 Potential Mechanisms of Oil Sands Emissions

Volatilization

Volatilization is the process of phase transition by a chemical substance from the liquid to gaseous or vapour phase. The rate and ability of a substance to volatilize depends on the physical-chemical properties of the substance and the surrounding environment including the vapour pressure and Henry's Law constant of the substance, the quantity of the substance in vapour phase relative to the dissolved phase, temperature and pressure.

The volatilization of substances from a liquid or dissolved to vapour or gaseous phase is governed by two relationships including Raoult's Law and Henry's Law. Raoult's Law describes the relationship between the vapour pressure of an ideal solution and the dependence on the vapour pressure of each chemical component and mole fraction within the solution. Hence, the presence of multiple substances in a mixture will generally be anticipated to decrease volatilization of all substances within the mixture accordingly.

Henry's Law describes the equilibrium between the dissolved concentration and overlying gaseous phase concentration such that at a constant temperature, the amount of a substance dissolved in any type and volume of liquid is directly proportional to the partial pressure of the gaseous phase overlying that liquid. Hence, the presence of volatile dissolved phase substances in a tailings pond would act as an ongoing source of emissions if gaseous phase concentrations of substances are cleared from the area overlying the liquid through naturally occurring or anthropogenic physical and mechanical conditions.

Photolysis

Photolysis is the chemical process by which molecules are degraded into smaller molecular components through the absorption of light. The photolysis of chemical substances is governed by the molecular structure, degree of molecular conjugation and the number of photons available for reaction. The rate of photolysis (Thomman and Mueller 1987) depends on:

- The adsorption spectrum of the chemical which is dependent on the structure of the chemical. Chemicals will absorb or emit light at different wavelengths. Since wavelength is inversely proportional to energy, the wavelength absorbed influences the quantity of energy absorbed, and can result in modification of a chemical's molecular structure;
- Incoming solar radiation, which depends on the meteorological and geographical conditions such as cloud cover, elevation, latitude/longitude and season; and



- The subsequent penetration and attenuation of the incoming solar radiation to various depths; a function of the suspended solids (only in aqueous environments) and dissolved organic carbon (only in aqueous environments), smog, latitude/longitude and season.

Hydrolysis

Hydrolysis is the degradation of reaction of a chemical compound as a result of interaction with water. The interaction with water can induce cleavage of a chemical bond through acidification or basification of the substance. The resulting chemical by-products are typically alcohols or saturated hydrocarbon compounds. Hydrolysis is dependent on the chemical structure of the chemical compound, the pH of the solution, the presence and quantity of water and the degree of saturation of the chemical compound.

Biological Processes

Naturally occurring bacteria and fungi can facilitate the degradation and/or transformation of chemical species. This occurs through metabolism of the chemical substances by organisms that have adapted to utilize the substance as an energy source. The ability of bacteria and/or fungi to degrade or transform chemical species is dependent on microbial species, the recalcitrance of chemical substances, the toxicity to the organisms, the pH, temperature and carbon availability of the environment as well as the presence/absence of electron donors and/or acceptors and the density of microbes within the area.

Methane Production

Methane production from tailings ponds is of concern to regulators and the public as it can potentially affect human health and the environment. Methane is an important GHG and plays an important role in atmospheric chemistry by influencing the ability of the atmosphere to oxidize other chemical pollutants (Holowenko et al, 2000). It is estimated that in 1999 the Mildred Lake tailings pond (known as Mildred Lake Settling Basin (MLSB)) produced approximately 40 million litres of CH₄ per day by biodegradation (Holowenko et al., 2000). Sidique et al (2000) indicated that MFT contains unrecovered bitumen (including insoluble and complex asphaltenes at approximately 2-5 wt%) from the extraction process and is likely relatively resistant to rapid biodegradation. Some of the lower molecular weight aliphatic and monoaromatic hydrocarbons in the MFT are derived from the diluent which comprises a complex mixture of n-alkanes (e.g., heptane, octane, nonane), BTEX (benzene, toluene, ethylbenzene, and xylenes), and other low molecular weight iso-paraffins and naphtha. Most of the diluent used in the extraction process is recovered, but a fraction that escapes with the tailings is likely a better substrate than bitumen for methanogenesis in MFT. Methanogenesis mainly occurs in the anaerobic regions of the tailings ponds.

Some naphtha components, specifically short chain n-alkanes (C₆-C₁₀) and some BTEX compounds (toluene and xylenes), more readily support CH₄ biogenesis. BTEX compounds degradation rates were reported in the following sequence: toluene > o-xylene > m-/p-xylene > ethylbenzene > benzene (Sidique et al, 2007). It has also been reported that as much as 15-23% of whole naphtha is metabolized in the tailings ponds (Sidique et al., 2007).

An approximation method was developed to predict CH₄ production and the scale of methanogenic activities in the MLSB (Sidique et al, 2008). The method employed included:

- a modelling study, completed using Equation 2; and
- use of microcosms containing oil sands tailings pond water (MLSB) to field verify the model.

The model comprised a lag phase, rate of hydrocarbon metabolism and stoichiometric conversion to CH₄. The lag period is the time required for the microorganisms in the ponds to get acclimated to the surrounding conditions. To predict CH₄ generation from oil sands tailings, the rate of hydrocarbon metabolism was translated to CH₄ production from all hydrocarbons in a pond at any time (t). To predict this, Sidique et al. (2008) developed the following equation:

$$[CH_4] = \sum \int_0^t \left(\delta_i \frac{dC_i}{dt} SF_i \eta_i \right) dt \quad (\text{Equation 2})$$

Where:

CH₄ = methane;

[CH₄] = methane production;

δ_i = a step function that takes a value of zero during the lag periods for the ith individual hydrocarbon and a value of 1 after the lag period;

SF_i = a stoichiometric factor, which is the maximum theoretical yield calculated using stoichiometric equations;

η_i = conversion efficiency; and

C_i = concentration of the ith individual hydrocarbon (mmol/L).

The model predictions exceeded CH₄ production measured in the microcosm experiments by a factor ranging from 3 to 10 times (Sidique et al., 2008). This was attributed to the heterogeneity and density of tailings, presence of nutrients in the microcosms, and/or overestimation of the readily biodegradable fraction of the naphtha in MLSB.

3.3 Factors Affecting Mine Face and Tailing Ponds Emissions

3.3.1 Overview

Mine faces and tailings ponds are heterogeneous, and vary in their physical properties, chemical composition and age. As described previously, volatilization, photolysis, hydrolysis and biological processes (Thomman and Mueller 1987) can influence quantity and rate of emissions of VOCs, PAH, CH₄ and RSC from mine faces and tailings ponds.



3.3.2 Mine Faces

Mine surfaces include a combination of freshly exposed and aged mine faces. These surfaces are sources of fugitive VOC, CH₄ and RSC emissions. Mine face emissions can occur as a result of volatilization from near surface deposits, photolysis of exposed surfaces by sunlight, hydrolysis of exposed surfaces as a result of contact and reaction with rainwater and surficial drainage and through microbial processes including methanogens that consume hydrocarbons present in the mine surface for energy. Hence, the age of the exposed surface, ambient temperature, moisture content and wind speed can all influence the quantity and rate of emissions from mine faces (Golder and Conner, 1998).

3.3.3 Tailings Ponds

Similarly to mine faces, tailings ponds vary in chemical composition, physical properties and age. Tailings ponds are sources of VOC, CH₄ and RSC emissions. Tailings ponds emissions, similarly to mine faces, can occur as a result of volatilization, photolysis, hydrolysis and microbial processes. Factors that affect fugitive emissions rates and quantities from tailings ponds include water quality, pond design, temperature of the tailings pond, ambient temperature, wind speed and open water surface area.

The rate and quantity of chemical compounds volatilized will increase with higher concentrations of volatile chemical substances in tailings pond water, with increased ambient and water temperature, with increased wind speed and with increased open water surface area. Additionally, mechanical processes, such as outfalls or discharge points, can increase volatilization in localized areas across the pond surface. The nature of the effluent in the tailings pond can also influence volatilization rates.

Hydrolysis of chemical substances can occur throughout the pond since it is an aqueous environment. The rate of hydrolysis will depend on the pH of the pond as well as ambient and pond temperature. Hydrolysis reactions will only occur for chemical species that have molecular structures that are conducive to hydrolysis reactions.

Photolysis of chemical substances can occur throughout the pond, although it is generally confined to the surface of the pond where sunlight can penetrate. This is particularly important since water within the 10 m of Syncrude and Suncor tailings ponds generally contain more species of chemicals, and in higher concentrations, than deeper zones of the pond (Quagrine et al., 2005).

Biological reactions can occur throughout the pond, although it is expected that in areas of high agitation or mechanical mixing, that microbial populations would be decreased. The success of microbial degradation and transformation reactions depends on pond water temperature, pH and chemical composition. The presence of oxygen, carbon dioxide and other dissolved gases are important considerations since toxicity may be associated with exposure for some organisms. Other toxic agents can also prevent biodegradation from occurring.

3.4 Air Quality Criteria

As mentioned previously, the oil sands mining operator of a proposed project must provide an air quality assessment study as part of the EIA. The objective of the air quality assessment is to identify and analyze

potential air quality effects associated with emissions of the proposed project. The majority of the proposed projects are located in an airshed which contains other sources of air emissions. The air quality assessment completed by an operator for a proposed project has to consider cumulative effects of their project by evaluating the impacts of facilities that are planned, approved or existing in the region. The assessment focuses on determining changes to the quality of air within the airshed. The operator of the proposed oil sands project produces estimates of emissions associated with different processes in the mining facility, including mine faces and tailings ponds, in order to establish potential impacts to air quality within the region. This is done through use of air dispersion modelling or other techniques.

3.4.1 Ambient Guidelines and Objectives

The effects of air emissions introduced into the atmosphere by industrial activities can be broad. The emissions can have direct and indirect effects on humans, animals, vegetation, soil and water. For these reasons, environmental regulatory agencies have established maximum ambient air concentration limits.

Appendix 3 presents the Alberta Provincial Guidelines (AAAQG), Federal Government Ambient Air Quality Objectives and Canada-Wide Standards for criteria air pollutants. The list provided is meant to be comprehensive and hence includes PM, NO_x and other substances that are not included in the scope of work for this document. In addition, the Federal Government has established three levels of objectives as follows:

- The desirable level defines the long-term-term goal for air quality and provides a basis for an anti-degradation policy for the unpolluted parts of the region and for the continuing development of control technology;
- The acceptable level is intended to provide adequate protection against adverse effects on soil, water, vegetation, materials, animals and visibility; and
- The tolerable level, which is usually the threshold where no adverse effects are expected. An exceedance of the tolerable level denotes a concentration of an air contaminant that requires abatement to avoid further deterioration to air quality since it can endanger the prevailing Canadian lifestyle or ultimately poses substantial risk to public health.

Modelling can be used to predict short-term and/or long-term levels of PPCs associated with a project. Additionally, modelling can be used to predict PPC concentrations in the airshed if the project was not completed. These predicted concentrations can subsequently be compared to established guidelines, objectives and/or standards to establish whether an exceedance of permissible levels will occur as a result of the project. If an exceedance is noted, then mitigation is required to reduce emissions to permissible levels. Upon facility construction, the operator is required to manage air quality impacts by minimizing emissions to the atmosphere. In order to achieve this objective, regulators typically require monitoring programs, including through continuous monitoring or point monitoring of emission on- and off-site, as well as through implementation of emissions reduction strategies and identification of mitigation options.



3.4.2 Canada-Wide Standards

The Canadian Council of Ministers of the Environment (CCME) reached an agreement in 1998 on the harmonization of environmental regulations across Canada. As part of the process, CCME has established a sub-agreement for creation of Canada-Wide Standards with respect to the environment, including air quality. The Canada-Wide Standards take into consideration social implications and technical feasibility of achieving the standards; however, they do not have legal standing. Each provincial jurisdiction participating in the harmonization accord implements the standards under existing provincial legislation or by drafting new legislation that meets at least equivalent levels of protection.

The compounds for which Canada-Wide Standards have been adopted include fine PM, ground-level ozone (O₃) and mercury. The CCME has not yet established acceptable ambient air quality standards for benzene, but has set targets for reducing benzene emissions. The targets for benzene emissions reductions were set using a phased approach. Currently two phases have been defined including Phase 1 (endorsed by CCME in June 2000) and Phase 2 (endorsed by CCME in October 2001). Phase 1 targeted a 30% reduction, nationally, in total benzene emissions levels by the end of 2000 relative to 1995 emissions inventory levels (CCME 2000). Phase 2 included a conditional target such that facilities addressed under Phase 1 would be required to achieve a further 6 kt reduction in benzene emissions by the end of 2010, based on 1995 emissions levels (CCME 2001). Additionally, for new and expanding facilities, minimization of benzene emissions through application of best available pollution prevention and control technologies as recognized in sector specific best management practices, jurisdictional regulations or developed through other air issue programs is required (CCME 2001).

3.4.3 Trace Air Compounds

Industrial and residential activities in the domain where the air quality assessment is performed can result in the release of numerous trace air compounds. The assessment can provide a screening level evaluation for the compounds that have formal air quality criteria.

The trace air compounds evaluated in the air quality assessment are mainly divided into four categories: RSC, VOCs, PAHs and metals. Air quality criteria of RSC, VOCs, and PAHs are summarized in Appendix 3.

4. CURRENT EF FOR MINE FACES AND TAILINGS PONDS

EFs are representative values that attempt to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant (NPRI, 2008; EPA, 2009). EFs are generally based on the results of source sampling tests performed at one or more facilities within a specific industry. When predicting emissions of PAH, VOCs, CH₄ and RSC from mine faces and tailings ponds, oil sands operators use EFs developed for Syncrude and Suncor oil sands facilities. A technical reference document was prepared by Golder Associates and Conor Pacific Environmental Technologies Inc. (Conor) (1998), which provides a detailed technical reference for the oil sands region air quality assessments. The document includes sections on meteorological conditions, air emission sources and the ambient air quality of the Athabasca Oil Sands Region. The document is designed to provide some of the technical background information for air quality assessments completed for Suncor and Syncrude in support of EIAs. The document integrates three documents previously issued in support of oil sands EIAs including:

- Sources of Atmospheric Emissions in the Athabasca Oil Sands Region (Report 1). Prepared for Suncor Inc., Oil Sands Group and Syncrude Canada Ltd. Prepared by BOVAR Environmental. June 1996;
- Ambient Air Quality Observations in the Athabasca Oil Sands Region. Prepared for Suncor Inc. Prepared by Golder Associates and BOVAR Environmental. May 1996; and
- Meteorology Observations in the Athabasca Oil Sands Region. Prepared for Suncor Inc. Prepared by Golder Associates and BOVAR Environmental. May 1996.

EFs used by most oil sands mine operators to estimate emissions from mine faces were obtained from 1997 fugitive emissions survey conducted at Syncrude (Golder and Conor 1998). EFs used by most oil sands mine operators to estimate emissions from tailings ponds were obtained from 1997 fugitive emissions surveys conducted at Syncrude and Suncor (Golder and Conor 1998). Both sets of EFs are based on measurements that were collected during the last half of July and early August of 1997. Fluxes from various exposed surfaces were measured using enclosed flux chamber measurements at multiple sampling locations. In addition to EFs developed by Golder and Conor (1998), Suncor provided EFs that were developed for their tailings ponds based on 2007 data in their response to the questionnaire prepared by WorleyParsons (Appendix 2).

4.1 EF for Mine Faces

Fugitive emissions of PAH, VOCs, CH₄ and RSC from oil sands mines faces are associated with exposed mine surfaces and are expected to be greatest during warm summer periods. A review of Golder and Conor's (1998) technical reference document, indicates that EFs were developed based on mine face emissions data collected only from Syncrude's Mildred Lake Base Mine. The period when the measurements were taken in 1997 was characterized by sunny and extremely warm conditions, with temperatures exceeding 30°C on some days (Table I; Golder and Conor, 1998).



In order to account for the variations due to temperature and wind speed during other months of the year a mass transfer model assessed monthly variability of the PAH, VOCs and RSC emissions using average wind speed and ambient temperature. Using the mass transfer model, the monthly emissions were estimated relative to the data collected on July emissions (Table I). The emissions were expressed as a percentage of July emissions (Table I). Temperatures and wind speeds are two factors that can affect the emissions rates of chemical compounds. Higher temperatures and wind speeds increase the rate of volatilization and therefore emissions rate and vice versa. The emissions were found to vary from -35% to 60% of emissions values measured during this period using the mass transfer model. However, the mass transfer model also indicated that the measurements collected during this period were generally within 5% of annual average emissions (Golder and Conor, 1998).

Table I Seasonal Variation of Fugitive Emissions Based on Monthly Average Temperatures and Wind Speeds (Golder and Conor, 1998)

Month	Average Monthly Temperature (°C)	Average Monthly Wind Speed (m/s)	Variation of Measured Emission Rate (Percentage of July ⁽¹⁾ emission rate)
January	-15	3.2	65
February	-15	3.5	76
March	-1.4	3.6	98
April	4.9	3.8	120
May	11.5	1.0	158
June	16.9	3.0	123
July	18.3	2.9	100
August	17.9	3.1	113
September	10.5	4.0	158
October	3.7	3.4	99
November	-5.2	3.2	77
December	-13.2	3.0	63
Average	2.8	3.4	105

⁽¹⁾Percent variation of emissions from the month of July taking in consideration average monthly temperatures and wind speeds.

4.1.1 Syncrude Emissions Factors

Syncrude EF were developed through direct measurement of emissions in 1996 and 1997. Data were collected from existing mine faces at the Mildred Lake Base Mine. The Mildred Lake Base Mine is subdivided into three areas including the East, West and North Base Mine.

Table J presents the emissions factors for the North, West and East Base mine faces. The EFs have been grouped according to human and photochemical (ozone precursor) considerations. The reason for differences in emissions factors between the mines appears to be related to variable age, surface area and production rates for the mines (Golder and Conon 1998). Older mine faces would be expected to have decreased flux and therefore lower emission rates. However, differences may also relate to variable bitumen composition and/or differences in meteorological conditions during the time of sample collection. The bitumen composition and ore quality may be more or less conducive to microbial degradation, photolysis, hydrolysis and/or volatilization. Ambient conditions, such as slope of the mine face and localized geographical conditions, including formations that could shelter mine faces from wind or produce shaded areas, would also be expected to influence emissions.

Table J Fugitive Emission Factors (kg/km²/d) for Syncrude Base Mine (Golder and Conon, 1998)

Grouping	North Mine	West Base Mine	East Base Mine	Composite ⁽¹⁾
General, [kg/km²/d]				
Total hydrocarbon (C ₁₊)	3,749	4,420	1,755	3,308
Methane (C ₁)	2,759	2,641	1,421	2,274
C ₂₊	990	1,779	334	1,034
Human Health [kg/km²/d]				
C ₂ to C ₄ alkanes and alkenes	10	36	60	35.1
C ₅ to C ₈ Alkanes and alkenes	12	27	20	19.8
C ₉ to C ₁₂ alkanes and alkenes ⁽²⁾	956	1,698	248	967
Cyclohexane	0	2	1	0.78
Benzene	0.076	-	0.013	0.030
C ₆ to C ₈ non-benzene aromatics	0.97	0.72	0.64	0.78
Total aldehydes	0	0	0	0
Total ketones	0	0	0	0
RSC	4.47	6.34	8.98	6.60



Grouping	North Mine	West Base Mine	East Base Mine	Composite ⁽¹⁾
Photochemical, [kg/km²/d]				
Methane (C ₁)	2,759	2,641	1,421	2274
Ethane (C ₂)	7	31	42	26.5
C ₃ to C ₄ alkanes	3	4	14	7.1
C ₅ to C ₈ alkanes ⁽³⁾	907	1,621	237	922
C ₉ to C ₁₂ alkanes	36.6	63.7	19.9	40.1
C ₁₃₊ alkanes	8.80	13.01	3.46	8.42
Ethylene (C ₂)	0	0	0	0
C ₃ to C ₄ alkenes	0.61	0.91	2.98	1.50
C ₅ to C ₈ alkenes	5.40	9.11	2.21	5.57
C ₉ to C ₁₂ alkenes	18.7	31.3	9.79	19.9
C ₁₃₊ alkenes	2.28	3.23	1.16	2.23
Benzene (C ₆)	0.08	0.00	0.01	0.030
C ₆ to C ₈ non-benzene aromatics	0.97	0.72	0.64	0.78
C ₉ to C ₁₂ aromatics	0.50	0.59	0.09	0.39

⁽¹⁾ Composite is equivalent to the arithmetic mean of emissions factors of the North, West Base and East Base Mines.

⁽²⁾ Unknown is placed in C₉ to C₁₂ category for health assessment.

⁽³⁾ Unknown is placed in C₅ to C₈ category for photochemical assessment.

4.1.2 Suncor Emissions Factors

A review of emissions reports and available EIAs and answers provided from the questionnaire indicate that EFs were not developed for Suncor's mine faces. The EFs that Suncor used in their EIAs were the composite EF for the three mine faces (East, West and North) of Syncrude's Mildred Lake Mine (Golder and Conon, 1998)

4.2 EF for Tailings Ponds

4.2.1 Syncrude Emission Factors

Syncrude completed a fugitive emissions study in 1997 on tailings ponds of the Mildred Lake Base Mine (Golder and Conon, 1998). Since 1978 Syncrude has stored tailings in the MLSB, a 25 km² tailings pond that currently holds over 400 million m³ of tailings. As of 1992, the MLSB was divided into three discrete zones including a 5 m deep surface water layer (comprising less than 1 wt% solids), a transition zone from 5-15 m (comprising approximately 15-35 wt% solids), and a sludge zone from 15-50 m (comprising approximately 40 wt% solids) (Allen, 2006).

Fresh tailings from Syncrude's Mildred Lake Mine operation are pumped to the South West Sand Settling (SWSS) basin to allow for sand to settle out prior to disposal of water and fine tailings in MLSB. Seepage water from sand dykes is collected in storage ponds and returned to MLSB. In 1995, when sand dykes

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approached 350 m from ground surface, Syncrude began removing large volumes of MFT from MLSB for burial in the West In-Pit (WIP) tailings pond (Allen, 2006). Release water from the WIP tailings pond is recycled for extraction purposes. In 2000 Syncrude began to operate a CT plant using mined-out areas (Southeast and Northeast mine pits) for storage.

The study in 1997 determined surface emission fluxes from water and wetted soil surfaces using the enclosed flux chambers. An overall flux estimate for a given type of surface was estimated from multiple samples at several locations. However, actual emission may differ from those derived from the flux chamber measurements due to variability in wind speed and ambient temperature. On the basis of measured data, a mass transfer model was configured using average wind speeds and ambient temperatures to assess the monthly variability of VOC and RSC emissions (Table I).

Table K summarizes the emission fluxes from the water surface areas. The largest fluxes are associated with the MLSB (CH₄ and VOCs) and Southwest sand storage area (RSC; water portion; different from the Southwest sand settling basin).

Table K Fugitive Emission Factors (kg/km²/d) for Selected Syncrude Mildred Lake Tailings Surfaces (Water Surfaces) (Golder and Conor, 1998)

Surface	Mildred Lake Settling Basin	Southwest Sand Storage Area	West & East In-Pit Pond
General, [kg/km²/d]			
Total hydrocarbon (C ₁₊)	6051	365	1774
Methane (C ₁)	4957	46	1705
C ₂₊	1094	320	69
Human Health, [kg/km²/d]			
C ₂ to C ₄ alkanes and alkenes	0	0	0
C ₅ to C ₈ alkanes and alkenes	73	1	5
C ₉ to C ₁₂ alkanes and alkenes ⁽¹⁾	957	290	60
Cyclohexane	2	0	0
Benzene	4	0	0
C ₆ to C ₈ non-benzene aromatics	38	2	3
Total aldehydes	0	0	0
Total ketones	0	0	0
RSC	5	7	4
Photochemical, [kg/km²/d]			
Methane (C ₁)	4,956.8	45.6	1,704.6
Ethane (C ₂)	0	0	0
C ₃ to C ₄ alkanes	0	0	0
C ₅ to C ₈ alkanes ⁽²⁾	977.06	276.76	64.13
C ₉ to C ₁₂ alkanes	39.19	14.51	0.83
C ₁₃₊ alkanes	3.01	2.54	0.18
Ethylene (C ₂)	0	0	0
C ₃ to C ₄ alkenes	0	0.01	0
C ₅ to C ₈ alkenes	11.46	0	0.10
C ₉ to C ₁₂ alkenes	2.21	0.03	0.03



Surface	Mildred Lake Settling Basin	Southwest Sand Storage Area	West & East In-Pit Pond
C ₁₃₊ alkenes	0.18	0	0
Benzene (C ₆)	3.97	0.16	0.24
C ₆ to C ₈ non-benzene aromatics	38.21	1.80	2.63
C ₉ to C ₁₂ aromatics	18.68	23.97	1.32

⁽¹⁾ Unknown is placed in C₉ to C₁₂ category for the health assessment.

⁽²⁾ Unknown is placed in C₅ to C₈ category for the photochemical assessment.

Table L summarizes emission fluxes for the dry land surfaces. The largest fluxes were associated with the Southwest Sand Storage area (land component). The overall fluxes of THC for the dry land surfaces are considerably less than those for the water surfaces. This could be due to having decreased concentrations of PPCs in sand since the sand was stored in the tailings ponds prior to its collection and storage in the Southwest sand storage area.

Table L Fugitive Emission Factors (kg/km²/d) for Selected Syncrude Mildred Lake Tailings Surfaces (Dry Land Surfaces) (Golder and Conon, 1998)

Surface	Mildred Lake Settling Basin	Southwest Sand Storage Area
General, [kg/km²/d]		
Total hydrocarbon (C ₁₊)	24.1	333.1
Methane (C ₁)	8.1	6.9
C ₂₊	16.0	326.2
Human Health, [kg/km²/d]		
C ₂ to C ₄ alkanes and alkenes	0	0
C ₅ to C ₈ alkanes and alkenes	0	0
C ₉ to C ₁₂ alkanes and alkenes ⁽¹⁾	14.7	324.6
Cyclohexane	0	0
Benzene	0.026	-
C ₆ to C ₈ non-benzene aromatics	0.34	1.48
Total aldehydes	0	0
Total ketones	0	0
RSC	3.32	8.81
Photochemical, [kg/km²/d]		
Methane (C ₁)	8.1	6.9
Ethane (C ₂)	0	0
C ₃ to C ₄ alkanes	0	0
C ₅ to C ₈ alkanes ⁽²⁾	14.1	321
C ₉ to C ₁₂ alkanes	0.53	3.95
C ₁₃₊ alkanes	0.21	-
Ethylene (C ₂)	0	0
C ₃ to C ₄ alkenes	0	0
C ₅ to C ₈ alkenes	0	0
C ₉ to C ₁₂ alkenes	0.06	0
C ₁₃₊ alkenes	0	0
Benzene (C ₆)	0.03	0

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Surface	Mildred Lake Settling Basin	Southwest Sand Storage Area
C ₆ to C ₈ non-benzene aromatics	0.34	1.48
C ₉ to C ₁₂ aromatics	0.79	0.12

⁽¹⁾ Unknown is placed in C₉ to C₁₂ category for the health assessment.

⁽²⁾ Unknown is placed in C₅ to C₈ category for the photochemical assessment.

4.2.2 Suncor Emissions Factors

As of 2005 Suncor's oil sands operations included a total of 9 ponds covering an area of 22.8 km² (Allen, 2006). At their primary mining and extraction site a series of 6 tailings ponds have historically been used to manage tailings and release water. In 1992 Ponds 1 and 2/3 contained 88 million m³ of sludge and covered an area of 7 km². The maximum depths of the ponds ranged from 35-60 m with a surface water zone ranging from 2 to 5 m depth (Allen, 2006). Pond 1 is in the process of undergoing decommissioning and no longer accepts fresh tailings. Hence, fresh tailings are currently discharged into Pond 2/3. However, surface water from Pond 2/3 is pumped to Pond 1 for recycling in the plant facility. Ponds 5 and 6 are currently used for consolidated tailings processing. Ponds 7, 8, and 9 are situated across the Athabasca River at the Steepbank and Millennium Mines.

In 1997, ponds, 1, 2/3 and 4 were operational. Table M provides a summary of the emission fluxes from these surfaces. No VOC and limited RSC emissions were detected in measurements collected from tailings ponds other than Pond 1. This may relate to differences in pond age, surface area, configuration, tailings quality, conditions during sample collection or pond location.

Table M Fugitive Emission Factors (kg/km²/d) for Selected Suncor Tailings Surfaces (Water Surfaces) (Golder and Conon, 1998)

Surface	Pond 1 ⁽³⁾	Pond 1A ⁽⁴⁾	Pond 2/3	Pond 4 ⁽⁵⁾
General, [kg/km²/d]				
Total hydrocarbon (C ₁₊)	72,700	597.5	24.5	146.5
Methane (C ₁)	10,708	597.5	24.5	146.5
C ₂₊	61,992	0.0	0.0	0.0
Human Health, [kg/km²/d]				
C ₂ to C ₄ alkanes and alkenes	16.5	0.0	0.0	0.0
C ₅ to C ₈ alkanes and alkenes	35,494	0.0	0.0	0.0
C ₉ to C ₁₂ alkanes and alkenes ⁽¹⁾	12,899	0.0	0.0	0.0
Cyclohexane	8,724	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0
C ₆ to C ₈ non-benzene aromatics	4,134	0.0	0.0	0.0
Total aldehydes	0.0	0.0	0.0	0.0
Total ketones	0.0	0.0	0.0	0.0
RSC	725	12.0	0.0	0.8



Surface	Pond1 ⁽³⁾	Pond 1A ⁽⁴⁾	Pond 2/3	Pond 4 ⁽⁵⁾
Photochemical, [kg/km²/d]				
Methane (C ₁)	10,709	597.5	24.5	146.5
Ethane (C ₂)	0.0	0.0	0.0	0.0
C ₃ to C ₄ alkanes	16.5	0.0	0.0	0.0
C ₅ to C ₈ alkanes ⁽²⁾	32,442	0.0	0.0	0.0
C ₉ to C ₁₂ alkanes	8,533	0.0	0.0	0.0
C ₁₃₊ alkanes	1,433	0.0	0.0	0.0
Ethylene (C ₂)	0.0	0.0	0.0	0.0
C ₃ to C ₄ alkenes	0.0	0.0	0.0	0.0
C ₅ to C ₈ alkenes	10,848	0.0	0.0	0.0
C ₉ to C ₁₂ alkenes	3,861	0.0	0.0	0.0
C ₁₃₊ alkenes	0.0	0.0	0.0	0.0
Benzene (C ₆)	133	0.0	0.0	0.0
C ₆ to C ₈ non-benzene aromatics	6,151	0.0	0.0	0.0
C ₉ to C ₁₂ aromatics	1,456	0.0	0.0	0.0

⁽¹⁾ Unknown is placed in C₉ to C₁₂ category for the health assessment.

⁽²⁾ Unknown is placed in C₅ to C₈ category for the photochemical assessment.

⁽³⁾ Emission factor used for Suncor Secondary Extraction ponds.

⁽⁴⁾ Emission factor used for Suncor Recycle Water ponds.

⁽⁵⁾ Emission factor used for Suncor CT, MFT and flue gas desulphurizer FGD ponds.

In addition, Suncor has also provided EFs for tailings ponds generated from isolation flux testing done in 2007 (Table N). The EFs provided are for specific compounds which include CH₄, benzene, toluene, ethylbenzene, xylenes, THC, H₂S and RSC.

Table N Fugitive Emission Factors (kg/km²/d) for Selected Suncor Tailings Ponds from 2007 Isolation Flux Testing Program

	Methane	Benzene	Toluene	Ethylbenzene	Xylene	THC	RSC
Pond 1	2,679	1	3	1	26	3,085	77
Pond 1A	532	6	115	24	121	1,834	852
Pond 2/3	3,081	5	105	29	175	4,782	942
Pond 5	95	2	4	6	18	338	94
Pond 6	2,106	0	3	6	21	2,472	104

Comparing EFs of THC, CH₄, benzene and RSC reported in 1998 and 2007, the following is observed:

- THC EFs reported in 1998 for Pond 1 are almost 25 times greater than those reported in 2007;
- THC EFs reported in 1998 for Pond 1A are almost 0.5 times the EFs reported in 2007;
- THC EFs reported in 1998 for Pond 2/3 are approximately three orders of magnitude less than EFs reported in 2007;
- CH₄ EFs reported in 1998 from Pond 1 are approximately 5 times greater than their corresponding EFs in 2007;
- CH₄ EFs reported in 1998 from Pond 1A is almost equal to the 2007 reported EFs;

- CH₄ EFs reported in 1998 from Pond 2/3 almost two orders of magnitude less than EFs reported in 2007;
- Benzene EFs were reported from all ponds in 2007, while EFs were negligible in 1997;
- RSC EFs for Pond 1 reported in 1998 were approximately 10 times greater than EFs reported in 2007;
- RSC EFs for Pond 1A reported in 1998 were almost two orders of magnitude less than EFs reported in 2007; and
- RSC EFs for Pond 2/3 reported in 1998 were negligible.

4.2.3 Summary and Interpretation

EFs from the late 1990s show that emissions were greater in Suncor's Pond 1 and Syncrude's MLSB, which received tailings including process water and fine material, than other tailings ponds which received only sand or fine tailings. It is likely that because Pond 1 and MLSB were the initial points of entry into the pond system, there was a greater concentration of substrate (diluent and bitumen) available for decomposition. As the substrate decomposes, the PPCs are released to the atmosphere, hence lowering the concentration of the substrates in the tailings transferred to subsequent ponds in the system. Therefore as the tailings travel through the pond system, the rate of emissions of the PPCs decreases along with the decrease in the concentration of the substrate. This demonstrates that EFs vary according to the type of tailings being stored in the tailings pond.

EFs for Suncor's Pond 1A and 2/3 have increased between 1997 and 2008. This could be due to the fact that Pond 1 has been decommissioned and the tailings have been diverted to other ponds, thus increasing the amount of PPCs in the other tailings ponds. This illustrates that EFs can vary with time for each tailings pond.

4.3 Emissions Factors Rating

The reliability or robustness of the EFs need to be evaluated in order to obtain an understanding of the accuracy of using EFs in predicting emissions from mine faces and tailings ponds. In this section the EFs are rated in accordance to EPA's AP-42 rating determination. AP-42 is a series of methods by which the Emissions Factor and Inventory Group (EFIG) in the EPA develop and maintain emission estimating tools for specific industries. Up to this date, AP-42 does not include methods to determine emissions from oil sands mine faces and tailings ponds. However, AP-42 methodologies will be used to rate the EFs developed for Syncrude and Suncor and their use to predict emissions for other oil sands mining facilities.

The rating is based on the estimated reliability of the tests used to develop the factors and on both the amount and the representative characteristics of those data. In general, factors based on many observations, or on more widely accepted test procedures, are assigned higher rankings. Conversely, a factor based on a single observation of questionable quality, or one extrapolated from another factor for a



similar process, would probably be rated much lower. AP-42 factor ratings do not imply statistical error bounds or confidence intervals for each EF. The rating should be considered an indicator of accuracy and precision of a given factor being used to estimate emissions from a large number of sources.

Two steps are involved in factor rating determination. The first step is an appraisal of data quality, the reliability of the basic emission data that will be used to develop the factor. The second step is an appraisal of the ability of the factor to stand as a national annual emission factor for that source.

Test data quality is rated A through D, and the ratings are assigned:

- A= Tests are performed by a sound methodology and are reported in enough detail for adequate validation;
- B = Tests are performed by a generally sound methodology, but lacking enough detail for adequate validation;
- C = Tests are based on an unproven or new methodology, or are lacking a significant amount of background information; or
- D = Tests are based on a generally unacceptable method, but the method may provide an order-of-magnitude value for the source.

The AP-42 emission factor rating is an overall assessment of how good a factor is, based on both the quality of the test(s) or information that is the source of the factor and on how well the factor represents the emission source. Higher ratings are for factors based on many unbiased observations, or on widely accepted test procedures.

AP-42 emission factor quality is rated A through E, and the ratings are assigned:

- A= Excellent. Factor is developed from A- and B-rated source test data taken from many randomly chosen facilities in the industry population. The source category population is sufficiently specific to minimize variability;
- B= Above average. Factor is developed from A- or B-rated test data from a "reasonable number" of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with an A rating, the source category population is sufficiently specific to minimize variability;
- C= Average. Factor is developed from A-, B-, and/or C-rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability;
- D= Below average. Factor is developed from A-, B- and/or C-rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source population; or

- E= Poor. Factor is developed from C- and D-rated test data, and there may be reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population.

The test quality rating for the EFs can be considered as B, since the sample collection and analysis are performed by a generally sound methodology. For both tailings ponds and mine faces EFs, the lack details on validation based on the limited number of facilities, and consideration of variable factors that affect emissions from mine faces and tailings ponds have limited the in-field validation. The quality rating of the EFs used for predicting emissions from mine faces and tailings ponds is D, which is below average. Similarly to test quality, since the test data are from only two facilities, these EFs do not represent a random sampling of industry but rather data from two operational facilities.

4.4 Predicted Future Emissions

EFs can be used to predict emissions of THC, CH₄, VOCs, RSC and benzene associated with existing and future oil sands mining facilities. It is important to understand the effect of the increase of the number of mining facilities on the emissions levels in the Athabasca Oil Sands region since it is anticipated that the oil sands mining facilities will increase from 4 to approximately 10 mining facilities with the next 15 years.

As described in Section 4.1 EFs applied in EIAs for the prediction of air emissions from mine faces were developed only from Syncrude's Mildred Lake Mining Facility, while EF for tailings ponds were developed based on monitoring data from Syncrude's Mildred Lake Mine and Suncor's Millennium Mine. These EFs will be applied to predict emissions up to the year 2022 when according to the Oil Sands Review (2008), the latest proposed and planned oil sand mining facilities will be operational.

The Oil Sands Review (December 2008) has indicated that Shell Muskeg River Mine, Suncor Millennium Mine and Syncrude Mildred Lake and Aurora mines are currently in operation. Other mining facilities are planned and/or proposed for operation by the year 2022 by companies such as Shell, Syncrude, Suncor, CNRL, Imperial Oil, Petro-Canada, Synenco, Total E&P and UTS.

EIAs from different oil sands operators were used to compile information on operating mines, facilities that have applied for approvals and for future planned and proposed mining facilities. The data used from EIAs include:

- mine face surface area;
- tailings pond surface area; and
- the bitumen production capacity.

The EF provided by Syncrude and Suncor (presented in Tables K, L, M and N), presented as flux rates (kg/m²/d) for tailings ponds or mine faces, were used to estimate emissions on the basis of these data compiled from the EIAs. These flux rates were multiplied by the surface area of the tailings ponds or mine faces from planned, proposed or approved facilities, based on descriptions provided in the EIAs to estimate emissions between 2006 and 2022 as follows:



-
- data for existing, approved and planned mining facilities were compiled from EIAs and the Oil Sands Review Report (2008);
 - bitumen production capacity was assumed to be the maximum specified capacity in the Oil Sands Review Report (2008) for approved and disclosed mining operations;
 - the year when all phases of the mine are expected to be in operation was assumed to be the year when maximum capacity is reached;
 - for mine faces:
 - the surface areas of the mine faces were compiled (Table 3);
 - Syncrude's composite EFs for mine face emissions were used to estimate the VOC, THC, CH₄, RSC and benzene emissions for each facility by multiplying the EFs by the surface areas of the mine faces (Table 4);
 - the emissions from mine faces of the same year were summed, to estimate annual total emissions from mine faces (Appendix 4; Table 4-I); and
 - cumulative emissions of VOC, THC, CH₄, RSC and benzene from mine faces were estimated annually from 2006 through 2022 (Appendix 4; Table 4-II);
 - for tailings ponds:
 - surface areas of tailings ponds were compiled (Table 5);
 - Syncrude or Suncor EFs for tailings ponds emissions were used to estimate the VOC, THC, CH₄, RSC and benzene emissions for each facility;
 - the EFs were selected according to the similarity of the proposed extraction process and tailings ponds of each facility to either Suncor or Syncrude;
 - tailings ponds surface areas were multiplied by the selected EFs (Table 6);
 - the emissions from tailings ponds of the same year were summed, to estimate annual total emissions from tailings ponds (Appendix 4; Table 4-III); and
 - cumulative emissions of VOC, THC, CH₄, RSC and benzene from tailings were estimated annually from 2006 through 2022 (Appendix 4; Table 4-IV);
 - cumulative emissions of VOC, THC, CH₄, RSC and benzene were estimated annually from 2006 to 2022 considering estimated emissions from mine faces and tailings ponds;
 - in the absence of additional information, cumulative emissions, surface areas, and total production capacities for any given year were assumed equivalent to the values for the previous years if no new mining operations were planned for start-up.
 - The exception to this was CNRL's Horizon Mine, where details on mine start up were limited. Phase 1 of CNRL's Horizon Mine started production in 2009, at a capacity of approximately

4×10^7 bbl/yr. Hence, 2009 was taken as the base year. CNRL's targeted production for the Horizon Mine is 577,000 bbl/d (2.11×10^8 bbl/yr) by 2017. To achieve this production target, start up of Phases 2 through 4 is required. CNRL did not provide details on their proposed timeline for start-up of these phases. Hence, assumptions were required to estimate emissions from this facility over this period. Herein, a linear increase in annual production and therefore mine face surface area, tailings ponds surface area, mine face emissions and tailings ponds emissions, was assumed between 2009 and 2017. It was assumed that the increase in mine face and tailings pond surface area was directly proportional to the increase in production and therefore, the increase in emissions from mine faces and tailings ponds.

4.4.1 Emissions from Mine Faces

Table 3 (located after body of report) summarizes the EFs used to predict emissions from mine faces. EFs were based on Syncrude's program for monitoring emissions from mine faces of the Mildred Lake Mine (Golder and Conner, 1998). Calculated annual emissions for planned, proposed, approved and operating facilities between 2006 and 2022 are presented in Table 4 (located after body of report), with detailed calculations presented in Tables 4-I and 4-II in Appendix 4. It is estimated that by 2022 the total bitumen production from oil sands mining will be approximately 3.5 times more than 2006 production capacity (from 3.1×10^8 bbl/yr to 1.1×10^9 bbl/yr). Hence the associated mine face surface areas will also increase accordingly. Surface areas of the mine faces are expected to approximately triple, from 90 km² to nearly 260 km² (Figure Q). Figure R summarizes the predicted increases in THC, CH₄, benzene, RSC, PAHs and VOC emissions between 2006 and 2022.

The estimated increase in production from oil sands mining operations has been based on predictions detailed in the Oil Sands Review (2008). CAPP and NEB forecasts were reviewed (CAPP, 2008; NEB, 2007) and consistently indicate the following:

- that production from the oil sands is estimated to increase to 3 million bbl/d. However, this includes both in situ and mining operations;
- that only 20% of all oil sands deposits represent mineable resources; and
- that production from oil sands deposits in Saskatchewan is anticipated to start in 2017.

These factors were not incorporated into the predicted production capacity since additional details were not available. However, it is anticipated that production from oil sands deposits in Saskatchewan may contribute additional emissions than those predicted herein. Specifically, it is unclear whether the oil sands deposits in Saskatchewan contain mineable reserves and if mineable reserves are present, what the proposed production capacity of these mines may represent.



Figure Q: Predicted Increase in Exposed Surface Areas of Mine Faces and Bitumen Production Capacity (2006-2022)

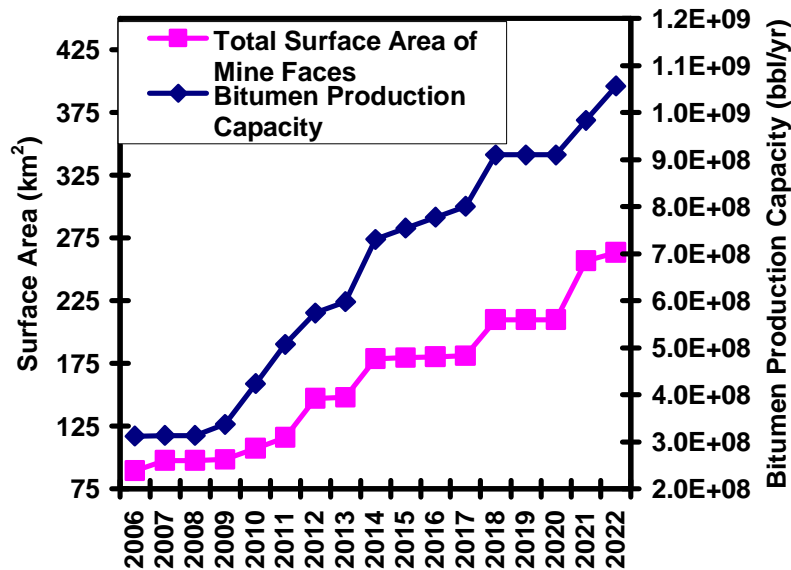
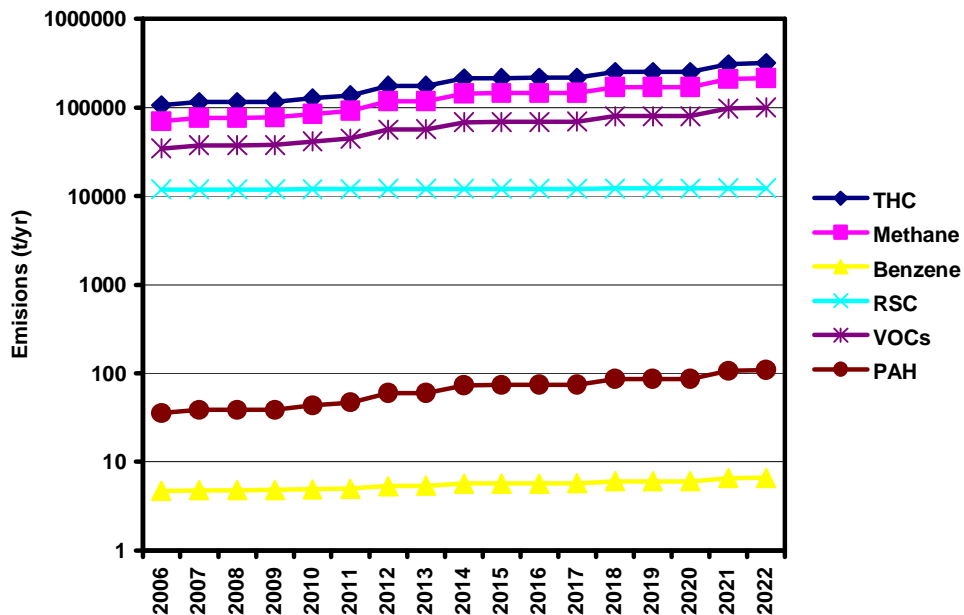


Figure R: Predicted Increase in Emissions from Exposed Mine Faces (2006-2022)



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It is estimated that:

- THC will increase from approximately 1.1×10^5 to 3.1×10^5 t/yr;
- Benzene emissions will increase from approximately 5 to 7 t/yr;
- CH₄ emissions will increase from approximately 7.0×10^4 to 2.1×10^5 t/yr;
- RSC will increase from approximately 1.19×10^4 to 1.20×10^4 t/yr;
- PAHs emissions will increase from approximately 35 to 110 t/yr; and
- VOC emissions will increase from approximately 3.5×10^4 to 1.0×10^5 t/yr.

RSC are generally produced in relatively low quantities although initial production of RSC from Suncor's facility (e.g., 1960s through 1970s) were significant ($\sim 10^4$ t). RSC emissions are dependent on the location of mine face exposure and hence, chemical composition of the bitumen. Recent monitoring data suggests that average production of RSC per facility is generally less than 100 t/yr. Hence, increases in RSC emissions predicted from 2006 through 2022 are nominal.

The mine face emissions predicted herein were validated by comparing estimated emissions to emissions reported in EIAs using a ratio. If the ratio exceeded 1, this was considered to indicate that calculated mine face emissions overestimated emissions relative to those presented in EIAs. Conversely, a ratio less than 1 was considered to indicate that calculated mine face emissions underestimated emissions relative to those presented in EIAs. This comparison is presented in Table O.

Table O Ratio of Mine Face Emissions Estimated Using EF to Mine Face Emissions Reported in EIAs

Mines	VOC	RSC	Benzene	CH₄
Shell Jack Pine Mine	3.37	3.34	-	14.67
Shell Pierre River Mine	7.84	6.22	-	
Shell Muskeg River Mine	1.50	1.49	-	
CNRL Horizon Mine	0.89	0.96	-	0.89
Suncor Millennium Mine	0.41	13.48	-	
Suncor North Steep Bank Mine	0.81	0.88	-	
Total E&P Joslyn North Mine	-	-	2.28	0.81
Imperial Oil-Kearl Mine	7.42	7.22	-	15.07
Synenco Northern Lights	1.24	1.25	1.24	



Generally, the ratio of predicted emissions compared to emissions presented in EIAs was greater than 1 for mine faces, suggesting that predictions using EF typically overestimate emissions relative to those emissions presented in EIAs. Exceptions include VOCs from CNRL Horizon and Suncor facilities and RSC from CNRL and Suncor North Steep Bank. Suncor does not use EF to predict emissions, but rather measured data collected from their facility. It is unclear why the discrepancy with CNRL, relative to other facilities, exists.

It should be noted that the EF used to estimate mine face emissions herein were based on data from 1997 and considered mine face surface area reported in EIAs. In EIAs, it is anticipated that more current emissions data may have been considered, that were not provided by operators for evaluation. Additionally, in EIAs, more site-specific factors such as mine face orientation and location, bitumen quality and mine face age may have been factored into the prediction of emissions.

Assumptions incorporated into emissions calculations herein were likely simplified relative to calculations completed in EIAs. These simplified assumptions include scaled mine face surface area on the basis of production forecasts and information provided in EIAs and limited quantity of emissions data available to validate EF for planned, proposed and approved facilities. Additionally, emissions reported in EIAs from mine faces were reported as daily emissions and required conversion to annual emissions for comparison to emissions calculated herein. Details on what daily emissions represented (e.g., average, median, maximum or other emissions) in EIAs were not provided. The calculation of emissions using EF considered average annual emissions. Hence, the overestimation could be related to differences in the method of calculating emissions as well as the conversion daily emissions reported in EIAs to annual emissions.

4.4.2 Emissions from Tailings Ponds

Figure S summarizes the predicted increase in surface areas of the tailings ponds between 2006 and 2022 on the basis of planned, proposed, approved and operational mining facilities. The surface areas of the tailings pond are estimated to grow to approximately 1.6 times the surface area that existed in 2006 (80 km² to 140 km²).

There are two groups of EFs, Suncor's and Syncrude's, that can be used to predict emissions from tailings ponds. Both Syncrude's and Suncor's EFs are based on measured emissions monitoring data from 1997 (Golder and Connor, 1998). The differences in EFs are generally attributed to the water quality in the tailings ponds. As illustrated previously in Table H, the water quality of Mildred Lake Base mine and Suncor mine tailings differ. The concentrations of NA, toluene and benzene in Suncor tailings pond water are greater than in Syncrude's tailings pond water, and thus it is assumed that this would apply for the emissions from their tailings ponds. It is also worth noting that although both operators can have equivalent solvent recovery requirements, quantities of solvent discharged with tailings will still differ according to the facilities' production rate.

A review of the proposed extraction processes and the tailings management techniques for non-operational facilities has shown that generally tailings management aligns with those techniques used by Syncrude. This is supported by statements in Golder and Connor's report (1998), which indicated that EFs

from Syncrude were used to predict emissions from tailings ponds of other existing and future mines (Table 5).

Daily emissions predicted between 2006 and 2022 are summarized in Table 6 with detailed calculations presented in Tables 4-III and 4-IV in Appendix 4. Figure T summarizes the predicted increase in THC, CH₄, benzene, RSC, PAHs and VOC emissions between 2006 and 2022. It is estimated that:

- THC emissions will increase from approximately 7.4×10^4 to 2.2×10^5 t/yr;
- CH₄ emissions will increase from approximately 5.0×10^4 to 1.4×10^5 t/yr;
- Benzene emissions will increase from approximately 29 to 98 t/yr;
- RSC emissions will approximately increase from approximately 344 to 805 t/yr;
- PAH emissions will increase from approximately 2.4×10^3 to 7.2×10^3 t/yr; and
- VOC emissions will increase from approximately 2.5×10^4 to 7.1×10^4 t/yr

Figure S: Predicted Increase in Surface Areas of Tailings and Bitumen Production Capacity (2006-2022)

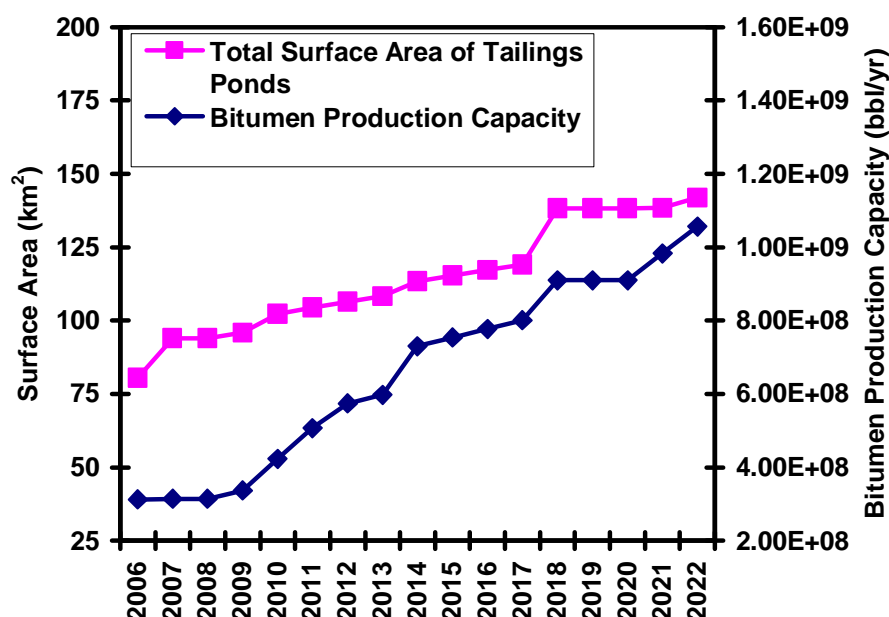
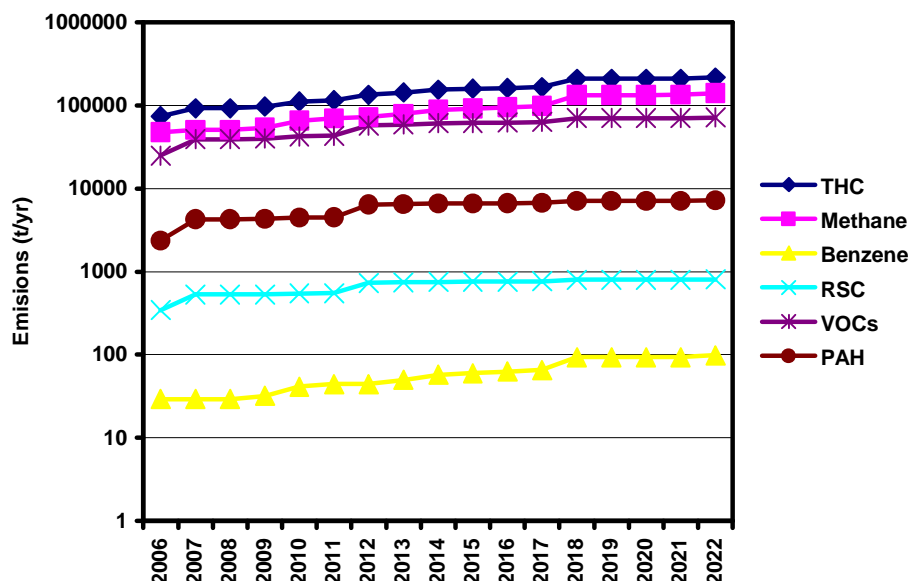




Figure T: Predicted Increase in Emissions from Tailings Ponds (2006-2022)



The tailings pond emissions predicted herein were validated by comparing estimated emissions to emissions reported in EIAs using a ratio. If the ratio exceeded 1, this was considered to indicate that calculated tailings pond emissions overestimated emissions relative to those presented in EIAs. Conversely, a ratio less than 1 was considered to indicate that calculated tailings pond emissions underestimated emissions relative to those presented in EIAs. This comparison is presented in Table O.

Table P Ratio of Tailings Ponds Emissions Estimated Using EF to Tailings Emissions Reported in EIAs

Mines	VOC	RSC	Benzene	CH ₄
Shell Jack Pine Mine	0.34	0.34	-	0.83
Shell Pierre River Mine	0.02	0.02	-	-
Shell Muskeg River Mine	0.12	0.01	-	-
Syncrude Mildred Lake Mine	5.14	-	1.25	9.53
CNRL Horizon Mine	0.25	0.02	0.09	1.39
Suncor Millennium Mine	1.29	-	-	-
Total E&P Joslyn North Mine	0.08		0.0008	3.02
Imperial Oil-Kearl Mine	0.36	0.36	-	0.87
Synenco Northern Lights	4.31	0.80	-	-

Generally, the ratio of predicted emissions compared to emissions presented in EIAs was less than 1 for tailings ponds, suggesting that predictions using EF typically underestimate emissions relative to those emissions presented in EIAs. Exceptions include VOCs from Syncrude Mildred Lake, Suncor Millenium Mine and Synenco Northern Lights, Benzene from Syncrude Mildred Lake and methane from Syncrude Mildred Lake, CNRL Horizon and Total E&P Joslyn North Mine. These predictions may have used alternative methods to correct predicted emissions based on facility-specific factors.

It should be noted that EF used to estimate tailings ponds emissions herein were based on data from Suncor and Syncrude from 1997 and considered tailings ponds surface area reported in EIAs. In EIAs, it is anticipated that more current emissions data may have been considered, that were not provided by operators for evaluation. Additionally in EIAs, more site-specific factors such as ambient and water temperature, concentration of methanogens, type of diluent, agitation rate from outfalls and/or mixing in tailings ponds may have been factored into emissions in EIAs.

Assumptions incorporated into emissions calculations herein were likely simplified relative to calculations completed in EIAs. These simplified assumptions include scaled tailings pond surface area on the basis of production forecasts and information provided in EIAs, and limited quantity of emissions data available to validate EF for planned, proposed and approved facilities. Additionally, emissions reported in EIAs from tailings ponds were reported as daily emissions and required conversion to annual emissions for comparison to emissions calculated herein. Details on what daily emissions represented (e.g., average, median, maximum or other emissions) in EIAs were not provided. The calculation of emissions using EF considered average annual emissions. Hence, the underestimation could be related to differences in the method of calculating emissions as well as the conversion of daily emissions reported in EIAs to annual emissions.

4.4.3 Total Emissions

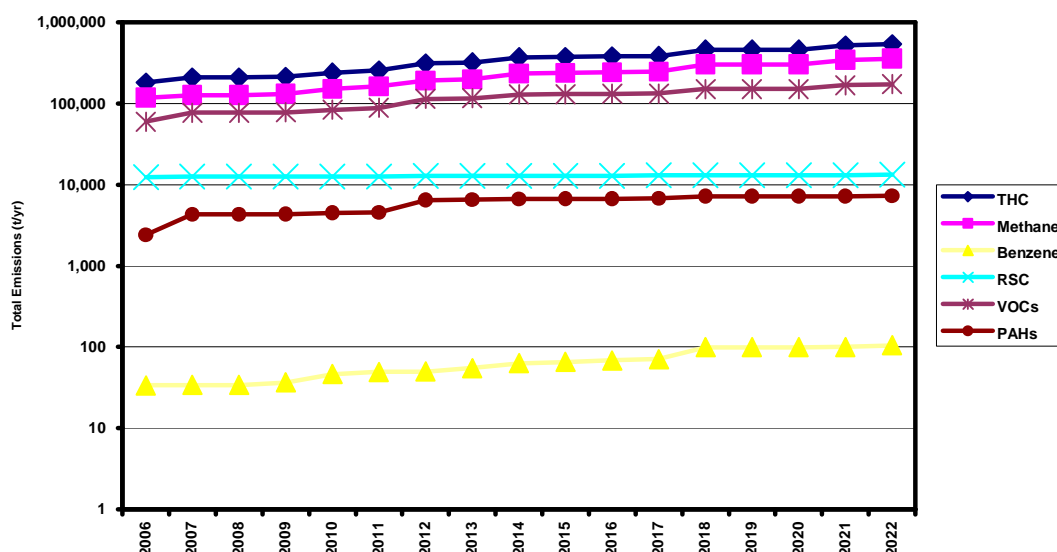
Table 7 (after the text) summarizes the predicted total emissions quantities from mine faces and tailings ponds. Percentage increase in emission from mine faces, tailings ponds and overall facility is presented in Table Q. Figure U summarizes the predicted increase of THC, CH₄, benzene, RSC, PAHs and VOC emissions, respectively, from mine faces and tailings ponds between 2006 and 2022.



Table Q Predicted Total Emissions Increase (Percent) Between 2006 and 2022

PPC	2006 Emissions from Mine Faces (t)	Percent Increase - Mine Face Emissions	2006 Emissions from Tailings Ponds (t)	Percent Increase - Tailings Ponds Emissions	2006 Total Emissions from Mine Faces and Tailings Ponds (t)	Percent Increase - Total Emissions
THC	1.1×10^5	274	7.4×10^4	234	2.1×10^5	256
CH ₄	7.0×10^4	281	5.0×10^4	277	1.2×10^5	279
Benzene	5	138	29	337	34	309
RSC	1.2×10^4	103	344	152	1.2×10^4	105
PAH	35	283	2.4×10^3	168	2.4×10^3	169
VOC	3.5×10^4	267	2.5×10^4	183	5.9×10^4	224
Overall Average Increase	-	238	-	197	-	204

Figure U Predicted Increase in Exposed Emissions from Mine Faces and Tailings Ponds (2006-2022)



It is estimated that:

- THC will increase from approximately 1.8×10^5 to 5.3×10^5 t/yr;
- CH_4 emissions will increase from approximately 1.2×10^5 to 3.5×10^5 t/yr;
- Benzene emissions will increase from approximately 34 to 105 t/yr;
- RSC emissions will increase from approximately 1.2×10^4 to 1.3×10^4 t/yr;
- PAH emissions will increase from approximately 2.4×10^3 to 7.3×10^3 t/yr; and
- VOC emissions will increase from approximately 5.9×10^4 to 1.7×10^5 t/yr.

4.5 Correlating Annual Emissions with Annual Bitumen Production

Figures Q and S indicate that the surface areas of mine faces and tailings ponds can be approximately correlated with cumulative annual bitumen production. This suggests that since emissions from mine faces and tailings ponds are partially dependent on surface area, that cumulative annual emissions from mine faces and tailings ponds can be calculated from cumulative annual bitumen production. The emissions from mine faces and tailings ponds were plotted as a function of the cumulative annual bitumen production capacity in Figures V and W, respectively to test this correlation.



Generally a strong correlation was observed, although the linear trend line ($y = mx + b$) may appear to more closely follow data points as a result of presentation on a logarithmic scale. It is worth noting that on the basis of the assumptions incorporated into calculations herein, it could be that the correlation is stronger than would generally be expected because of simplified assumptions incorporated into the estimation of total emissions. Specifically, these assumptions include scaled mine face and tailings pond surface area on the basis of production forecasts and information provided in EIAs, and the limited quantity of emissions data available to validate emissions factors for planned, proposed and approved facilities.

The correlations presented herein could conceivably be used to estimate or predict emissions from oil sands mining facilities in the future. However, the assumptions included in the prediction and intrinsic to the EFs used to estimate emissions would require validation prior to application of these correlations. Additionally, it is identified that these correlations would generally be applicable to the industry as a whole, rather than individual facilities since facility-specific factors may result in different emissions rates and quantities not accounted for herein.

Based on the methodologies employed for this work, it appears that emissions from mine faces are closely correlated to the cumulative annual bitumen production. Table R summarizes the PPC emissions from mine faces as a function of the cumulative annual bitumen production. The coefficients of correlation ranged from 0.96-0.97 for target PPCs, indicating that linear equations selected as trendlines adequately describe the relationship between the calculated emissions data and theoretical bitumen production.

Table R Correlations of Mine Face Emissions with Cumulative Annual Bitumen Production

PPC	Correlation	Coefficient of Correlation (R^2)
THC	$\text{THC (t/yr)} = 2.7 \times 10^{-4}[\text{B(bbl/yr)}] + 1.7 \times 10^4$	0.96
CH ₄	$\text{CH}_4 \text{ (t/yr)} = 1.8 \times 10^{-4}[\text{B(bbl/yr)}] + 8.8 \times 10^3$	0.96
VOC	$\text{VOC (t/yr)} = 8.4 \times 10^{-5}[\text{B(bbl/yr)}] + 6.8 \times 10^3$	0.96
RSC	$\text{RSC (t/yr)} = 5.3 \times 10^{-7}[\text{B(bbl/yr)}] + 1.2 \times 10^4$	0.96
PAH	$\text{PAH (t/yr)} = 9.0 \times 10^{-8}[\text{B(bbl/yr)}] + 5.8$	0.97
Benzene	$\text{Benzene (t/yr)} = 2.4 \times 10^{-9}[\text{B(bbl/yr)}] + 3.9$	0.96

Note: B is the cumulative annual bitumen production.

Table S summarizes the emissions from tailings ponds as a function of the cumulative annual bitumen production. The coefficient of correlation between the emissions of PPCs and the cumulative annual bitumen production ranged between 0.82 and 0.96.

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Table S Correlations of Tailings Ponds Emissions with Cumulative Annual Bitumen Production

PPC	Correlation	Coefficient of Correlation (R ²)
THC	$\text{THC (t/yr)} = 1.8 \times 10^{-4} [\text{B (bbl/yr)}] + 3.1 \times 10^4$	0.96
CH ₄	$\text{CH}_4 \text{ (t/yr)} = 1.3 \times 10^{-4} [\text{B (bbl/yr)}] + 4.7 \times 10^3$	0.93
VOC	$\text{VOC (t/yr)} = 4.6 \times 10^{-5} [\text{B (bbl/yr)}] + 2.4 \times 10^4$	0.94
RSC	$\text{RSC (t/yr)} = 4.3 \times 10^{-7} [\text{B (bbl/yr)}] + 4.1 \times 10^2$	0.84
PAH	$\text{PAH (t/yr)} = 5.0 \times 10^{-6} [\text{B (bbl/yr)}] + 2.4 \times 10^3$	0.82
Benzene	$\text{Benzene (t/yr)} = 1.0 \times 10^{-7} [\text{B (bbl/yr)}] - 6.5$	0.92

Note: B is the cumulative annual bitumen production.

Figure V Correlation of Mine Face Emissions with Cumulative Annual Bitumen Production Capacity.

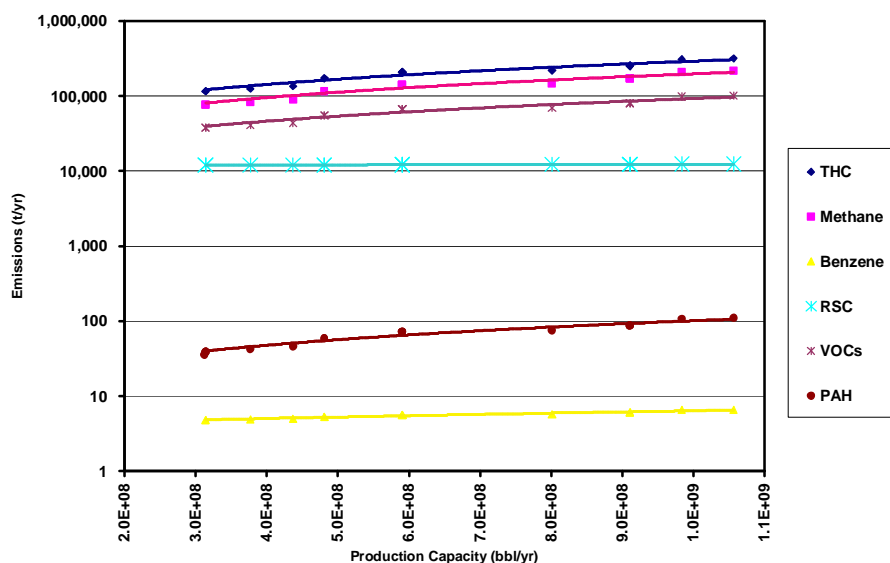
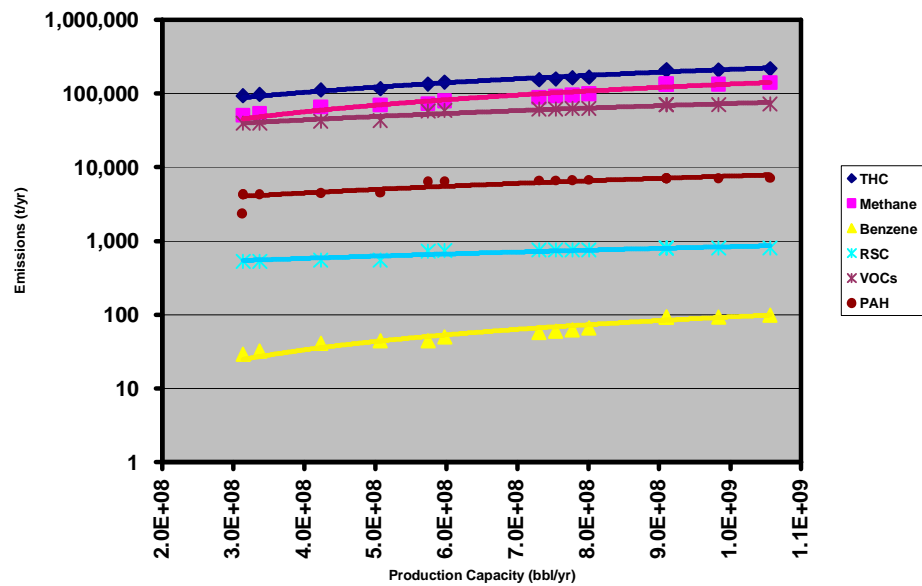




Figure W Correlation of Tailings Ponds Emissions with Cumulative Annual Bitumen Production Capacity



5. CONTROL OPTIONS FOR REDUCING EMISSIONS OF VOCS, BENZENE, METHANE AND THC FROM MINE FACES AND TAILINGS PONDS

A review of existing and proposed technologies to reduce CH₄, benzene, VOCs and THC emissions was completed for mine faces and tailings ponds. The review identified that generally technologies to reduce emissions from mine faces are non-existent and that very limited technologies are directly applicable to tailings ponds emissions. Current technologies for reduction of tailings ponds emissions include solvent recovery systems which are used to strip the diluent solvents from the tailings and collect the vaporized solvents for reuse in bitumen extraction. As a consequence, these systems reduce VOCs emissions from tailings ponds. An alternative to solvent recovery from the tailings is through active reduction of PPCs in tailings ponds water through water treatment technologies. Eliminating PPCs in tailings and process water will reduce the emissions of benzene, CH₄, VOCs and THC to the atmosphere.

In accordance with the AENV zero water discharge policy, and AENV Approval and mine permit requirements, tailings and other process affected waters (such as runoff) are stored in on-site and/or external tailings ponds. This process has been in place since the beginning of oil sands operations. As indicated previously, it is estimated that tailings ponds contribute roughly 60% of the fugitive emissions of VOCs, benzene, CH₄ and THC from oil sands mining facilities. As oil production increases over the next decade, emissions reductions are expected to become a critical issue for oil sands operators, both in terms of sustaining bitumen production, and minimizing the impacts from discharge of process affected waters in the tailings ponds.

Currently air emissions control in the oil sands industry relates primarily to solvent recovery systems. Additionally, tailings ponds can be used to reduce emissions of specific PPCs. However, the presence of methanogenic bacteria in tailings ponds, while reducing THC, benzene and VOC emissions, increases RSC and CH₄ emissions. These techniques represent current best practices. The use of emerging technologies for oil sands emissions control has been explored, but generally not implemented as a result of technical and economic challenges. The primary technical challenge for treatment of oil sands process water and tailings is associated with the high concentrations of suspended solids, such as sand, clay and other fines. Economic considerations relate to the quantity of tailings and process water produced (13,000–16,000 t/h) that would require treatment (CNRL, 2002; Total E&P, 2006; Imperial Oil, 2005; Shell, 1997; Shell 2002; Shell 2005; Suncor 2005; Syncrude 1998; Synenco 2006).

A review of potential technologies to control emissions from tailings ponds mainly focused on the tailings discharged to the settling ponds. Improving the water quality of the discharged tailings will ultimately reduce the VOC, benzene, and CH₄ and THC emissions to the atmosphere. However, as discussed, potential limitations are associated with the current state of knowledge for water treatment of water with high suspended solids. Allen (2008a) identified four emerging water treatment processes that have demonstrated significant advances with respect to water treatment of the produced water in the oil sands industry including:



- adsorption;
- membrane process;
- biological treatment; and
- advanced oxidation.

Additional candidate treatment technologies were compiled from literature review.

This chapter describes the solvent and recovery systems and considers available and conventional as well as emerging water treatment technologies. It includes a review of recent developments and application of the technologies in the oil industry, previous research on the treatment of oil sands water, and examines emerging technologies in the oilfield for treatment and management of produced water and their applicability to oil sands PPCs.

5.1 Mine Face Emissions Reduction

Technologies to reduce mine face emissions are currently unavailable. However, options for emissions reductions can be recommended. One possible option may include cap and cover of the mine face. An overburden cap/ cover can be applied to cap the areas of the mine face that are not currently mined. This method may not be a favourable option to the mine operators since it may increase the operational costs of the ore mining process; however, in other industries (i.e. landfills) it has been successfully applied to limit atmospheric release of PPCs.

5.2 Solvent Recovery Systems

Solvent recovery systems used to recover solvents from tailings produced from froth treatment processes include tailings solvent recovery units (TSRUs) and vapour recovery units (VRUs) (Figure X). A third component of the solvent recovery system strips diluent from bitumen prior to upgrading. Since solvent is recycled for subsequent extraction, this component of the solvent recovery system has not been described herein. The units recover and recycle the solvents from the tailings streams and vapour produced in the froth treatment process. The recovery systems not only reduce the use of solvents but also CH₄, benzene, VOCs and THC emissions from tailings ponds. Information describing the solvent recovery systems was compiled from the description of the processing options for oil sands mining facilities provided in EIAs.

The froth treatment tailings contain small quantities of bitumen and solvent. The latter is removed in the TSRU, by subjecting the tailings to elevated temperature, partial vacuum and agitation. The recovered solvent is recycled to the froth treatment process.

The TSRU consists of 2 separation columns in series designed to operate so that the tailings discharged from the second separation column contain less than 4 volumes of solvent per 1000 volumes of bitumen produced by the mining facility. This results in overall solvent recovery in excess of 99%.

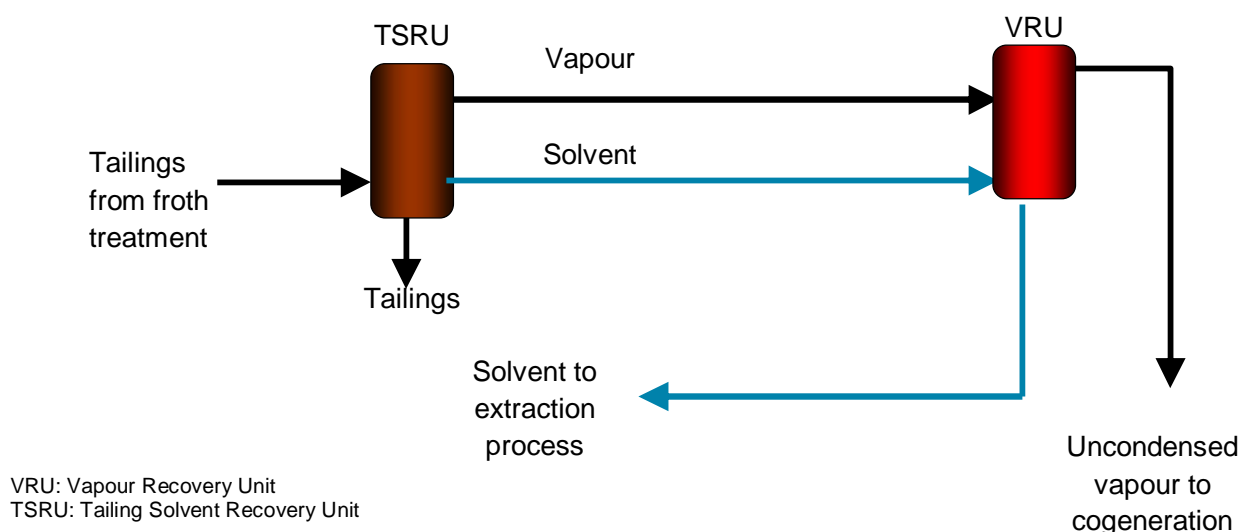
In the first column, froth treatment tailings are heated by direct steam injection to strip the solvent from the tailings. Tailings from the first column will then be injected to the second column which operates under

partial vacuum to strip the solvent from the tailings. The solvent from both columns is condensed in an overhead system and recycled back to the froth treatment unit. The tailings are then deposited in the tailings ponds.

Solvent vapours arising from TSRU are collected in a VRU. Condensed solvent is returned to solvent storage. Non-condensable vapours are used as supplementary fuel in the steam generators at cogeneration plants.

PPC removal efficiencies and operational costs of solvent recovery systems were not presented, and were not available from the oil sands mining production reports and journals. For removal efficiency, however, it was assumed that VOC removal is almost equivalent to solvent recovery. This assumption parallels those made in the EIAs and is thought to be valid since, as a worst case, it would overestimate predicted emissions. The assumption is such that VOC emitted from tailings ponds are equal to the solvent loss from the tailings ponds.

Figure X Solvent Recovery System



5.3 Wastewater Treatment Technologies

Water treatment technologies can be categorized into primary, secondary, and tertiary processes. Primary treatment comprises the physical processes of solid-liquid, liquid-liquid, and or gas-liquid separation, and includes processes such as sedimentation, flotation, filtration, and aeration. These separation processes are often facilitated by chemical treatments such as coagulation and flocculation particularly where suspensions are stable and resistant to sedimentation. Secondary treatment processes refer to biological treatment, or methods involving the use of microorganisms to stabilize wastewater water through the removal of nutrients and organic compounds. Biological treatment technologies include aerated lagoons, activated sludge, and fixed-film bioreactors. These processes are designed to reduce BOD but do not



effectively remove dissolved inorganic species and recalcitrant organic compounds. Tertiary treatment, also referred to as advanced treatment, encompasses a wide range of processes that target dissolved and particulate species that are not effectively removed by primary and secondary methods. Advanced treatment technologies include chemical precipitation, advanced oxidation, membranes, and ion exchange, adsorption, and treatment wetlands.

Depending on the treatment objectives, a treatment train may be established containing of primary, secondary and tertiary processes. In the oil industry, wastewater treatment begins with oil and suspended solids removal, followed by further clarification with coagulants and flocculants, biological treatment to remove organic compounds and the use of tertiary processes to demineralize and further detoxify the effluent (Mujeriego and Asano, 1999).

There are numerous references and technical handbooks reviewing wastewater treatment theory and system design. It is not the intention of this chapter to discuss the basic theory of wastewater treatment, but rather to discuss the treatment processes, development and applications of the technologies in the oil sands industry.

5.3.1 Sedimentation, Coagulation and Flocculation

Sedimentation is one of the earliest water treatment processes. Sedimentation, also known as clarification, refers to the downward settling of particles through the water column to clarify a surface layer of water. Sedimentation is most commonly used as a pretreatment technology to remove suspended solids and precipitates, flocs, and other aggregates generated by other treatment processes. The accumulated sludge is subsequently processed via biological or non-biological means using thickening, digestion, dewatering, filtration, centrifugation, incineration, and/or drying beds (Mujeriego and Asano, 1999). This method reduces the amount of suspended solids in the produced tailings, and thus will improve the removal efficiencies of other treatment technologies used after sedimentation. In addition, sedimentation also reduces the contaminants introduced to the tailings, specifically those adsorbed to the suspended solids, which can otherwise volatilize from the tailings ponds.

The three main categories of clarifiers used in sedimentation are horizontal flow, solids contact, and inclined surface (Allen, 2006). Horizontal flow tanks are either rectangular or circular, and are designed to allow for consistent flow with low turbulence. Circular flow patterns can be used to generate centrifugal forces that increase the settling velocities of particles or the coalescence of oil. Centrifugal-action desanders and coalescers are currently used in the oil sands industry (Allen, 2006). Settled solids are subsequently scraped from the tank bottom by sludge removal mechanisms. In solids-contact clarifiers, influent solids are trapped by a sludge blanket in the tank, which is scraped and undergoes further treatment before discarding. Inclined surface clarifiers contain angled plates or tubes which increase settling rates by reducing the distance that the particles have to travel. The latter is a preferred technology, since it reduces the settling time, and process time.

Coagulation and flocculation are chemical processes that facilitate sedimentation, flotation and/or filtration of suspended solids, oil, colloids, and/or trace metals (Nenov, 1995; Ebeling et al. 2003). Coagulation refers to the destabilization of colloidal or particulate suspensions. Flocculation refers to bridging between

groups of particulates or added polymers to form larger aggregates. Coagulation and flocculation incorporate the use of organic and/or inorganic agents and/or the use of electrochemical methods to remove the suspended solids, oil, colloids, and/or trace metals. An overview of these methods can be found in Appendix 5.

5.3.2 Aeration and Stripping

Aeration refers to the addition of a gas for chemical treatment (e.g., disinfection or oxidation), or to promote the loss of VOCs to the atmosphere through air stripping. It has been proven as a treatment technology for VOCs in oil-field produced water. However, for this technology to be useful for accomplishing the goal of reducing VOC emissions to the atmosphere, the VOCs must be recovered and further treated or destroyed by combustion. The main types of aeration systems are diffused-air, surface aerator, spray, and packed-tower systems (Allen, 2006), which are discussed in more detail in Appendix 5.

5.3.3 Flotation

Flotation processes rely on air bubbles to separate low density solids or liquids from wastewater. The mining industry was the first industry to apply this technology to solids from ore slurries; flotation has since been applied in wastewater and drinking water treatment. Standard applications of flotation include the separation of oil and grease, floc, metal ions, and algal blooms from aqueous streams (Bennett, 1988). Flotation processes typically remove 60-95% of suspended solids, including sand, clay and fines, and 65-98% of oil and grease (Allen, 2006).

Flotation is a key process for the deoiling of produced water. In addition to the aided flotation processes described above, oil may be separated by natural flotation in settling tanks, or artificial gravity generated by rotational forces. Widespread technologies include the American Petroleum Institute (API) separator, corrugated plate interceptors (CPI), hydrocyclones, and centrifugation, induced gas flotation (IGF), and dissolved air flotation (DAF), dissolved air precipitation (DAP), and electrolytic flotation. Chemical aids (flocculants, de-emulsifiers) are often used to improve the deoiling performance of these processes. Information on flotation processes and factors affecting their performance is presented in Appendix 5.

5.3.4 Filtration

Filtration refers to the use of a water-permeable barrier that restricts the passage of solids or liquids. Non-membrane filtration processes can be broadly classified into granular media, and precoat cartridge filtration. In addition to multi-layer granular media filters, a wide range of materials have been used in single-layer filters for oily water treatment, including hay, polyurethane foam, glass fibre, slag fibre, pitch coke, ligneous materials, and peat. Filters are formed from these materials by encapsulating them in wire or synthetic polymer mesh. In filtration-coalescence filters, emulsified oil droplets adsorb to filter media that promote coalescence, which is followed in turn by desorption of larger oil droplets. Micro-, ultra-filtration and nanofiltration are three filtration methods used in wastewater treatment. Micro- and ultrafiltration are pressure driven membrane processes that reject particles as small as 0.1 μm and 0.01



µm, respectively (Allen, 2008b). Nanofiltration is a process that has a molecular weight cutoff as low as 300-400 Dalton (Da). Da is a unit of mass used to express atomic and molecular masses. Adsorbents such as activated carbon, fly ash, and synthetic polymers have also been incorporated into deoiling filters. Filtration processes and media used are discussed in Appendix 5

5.3.5 Adsorption

Adsorption is defined as the accumulation of one substance on the surface of another substance and is an important retention mechanism in many water treatment processes, including coagulation, chemical precipitation, filtration, and ion exchange. As a water treatment process, adsorption involves the addition of an adsorbent material (e.g., activated carbon) to a reaction vessel to bind specific pollutants, followed by separation from the aqueous phase by filtration. The adsorbent can be present as a slurry, which increases surface area and improves efficiency of regeneration. Alternatively, the adsorbent can be present in a fixed-bed system, which involves an immobilized adsorbent with liquid passed through the fixed-bed to facilitate adsorption. In both cases, adsorbent is typically regenerated through removal, concentration and treatment of the adsorbent. A secondary vessel is required with either type of system to allow for regeneration to occur while concurrently treating newly produced processed water. Adsorbents are used in a wide array of treatment processes, but are particularly suited to the removal of organic carbon compounds, dyes, and heavy metals.

Both organic and inorganic adsorbents are used in water treatment. The most common organic adsorbent is activated carbon, which is produced from a range of materials including anthracite and bituminous coal, lignite, pine, peat, and coconut shells (Pollard et al., 1992). Activated carbon is prepared in a two-step process involving carbonization, in which all non-carbon elements are removed from the base material, and activation, whereby a catalyst is used to clear away tarry substances and produce a porous structure with a large surface area (100-1,500 m²/g).

There are two main forms of activated carbon used in wastewater treatment; granular activated carbon (GAC), which is often used in filter beds, and powdered activated carbon (PAC), which is added to reaction vessels as a free-floating adsorbent. A third type, cloth or fibrous activated carbon (FAC), has been shown to outperform granular activated carbon in certain applications, however, treatment units have to be redesigned to accommodate FAC, which increases the costs of using the system. (Ahsan et al., 2001). Activated carbon can be reused, but must be regenerated via thermal, chemical, or biological processes. Other materials such as bark, lignin, charcoal, cement, zeolite, bentonite, fly ash, peat, steel plant slag organic matter and alumina can be used as alternatives to activated carbon. Costs are generally decreased, although substances such as zeolite may be less cost effective than activated carbon, depending on whether it is synthetic. Appendix 5 provides an overview of these adsorption technologies.

5.3.6 Biological Treatment

Biological treatment refers to the use of microorganisms to stabilize BOD through nutrient absorption and oxidation of organic pollutants. In aerobic systems, the by-products of microbial oxidation are carbon dioxide, inorganic species (e.g., chloride), water, and energy. The energy released from the oxidation of

organic compounds is used by the microorganisms for growth. Where dissolved oxygen concentrations are low, sulphate or nitrate may be used as oxygen sources. In anaerobic systems organic compounds are broken down via hydrolysis and/or methanogenesis reactions (Allen, 2006).

Application of conventional biological treatment to more complex industrial effluents has been hindered to some degree by the relative sensitivity of microorganisms to feed water salinity and toxic organic chemicals. Improvements on suspended growth design have come in the form of fixed growth or fixed biofilm systems, fluidized bed reactors, and sequential batch biofilm reactors (Allen, 2008b). These developments are discussed in Appendix 5.

Recent advances in bioreactor technology have addressed the problem of microbial toxicity through combining GAC/PAC with fluidized-bed reactor (FBR). The combination of activated carbon and microbial biofilm improves the removal of toxic organic compounds, mitigating their toxic effects (Allen, 2008b). The addition of GAC/PAC FBR, reported a 99% removal of BTEX (Allen, 2008b).

For the oil sands industry, advances in biological treatment may lead to new alternatives for removal of naphthenic acids. Newer designs may consume 25% of the operational energy used in activated sludge systems while producing 55-75% less waste sludge. Consequently, costs for high rate processes may be lower than conventional biological treatment technologies.

5.3.7 Advanced Oxidation

Chemical oxidation processes degrade pollutants through a series of ionic or radical reactions involving an oxidant compound that either accepts electrons or donates an electron-accepting group. The most frequently used oxidants in water and wastewater treatment include chloride (Cl^-), hydrogen peroxide (H_2O_2), ozone (O_3), and permanganate (MnO_4^-) or exposure to ultra violet light (UV) (Allen, 2008b). Photocatalytic and sonochemical oxidation are the two primary chemical oxidation techniques that have demonstrated the potential to degrade chemical compounds associated with oilfield produced water. Chemical oxidation is most commonly used for compounds that are not amenable to biological treatment due to their toxicity or recalcitrant nature. Examples of these species include cyanide, formaldehyde and aromatic compounds (Gogate and Pandit, 2004). Since these compounds can form a component of produced water, chemical oxidation is applicable for treating organic compounds in the oilfield produced water.

Table T provides a summary of the results from the studies which investigated advanced oxidation methods on treating oilfield produced waters. A more detailed discussion on the different advanced oxidation methods can be found in Appendix 5.

Table T Advanced Oxidation Studies on Oilfield Produced Waters

Process	Wastewater	Findings
Electrochemical oxidation $\text{H}_2\text{O}_2 + \text{UV} + \text{Phenol}$ solution	Oily wastewater activated carbon	70% removal of COD 100% removal of phenol 87% removal of TOC High energy consumption (25 kWh/m^3)



Process	Wastewater	Findings
Ozone-initiated oxidation process	Oilfield produced water	97% removal of BTEX
Photocatalysis with TiO ₂	Oilfield produced water	40% removal of TOC (pH 10.5) 59% removal of ammonia (pH 6.25) 64% removal of phenols (pH 10.5)
Photocatalysis with TiO ₂ + H ₂ O ₂	Oilfield produced water	TOC degradation targeted toxic, high molecular weight compounds H ₂ O ₂ had a negative effect on the treatment
Photoelectrocatalysis with TiO ₂ and H ₂ O ₂	Oilfield produced water	>99% removal of COD (with H ₂ O ₂) 100% removal of mutagenicity Degradation rates inversely correlated with pH
Solar photocatalytic oxidation (TiO ₂ , O ₂ , sodium persulphate)	Industrial wastewater	62% removal of phenol Sodium persulphate enhanced 98% removal of TOC
Solar photocatalytic oxidation (TiO ₂ , H ₂ O ₂)	Contaminated groundwater	>70% removal of BTEX with solar light immobilized TiO ₂ slurry; H ₂ O ₂ addition and increased solar collector area improved degradation rates
Sonochemistry + Fenton's reagent (FeSO ₄)	Phenol solution	>95% degradation of phenol after 2 h, enhanced by FeSO ₄ , and optimized at
Ultrasonic irradiation + FeSO ₄	PAH solution	Complete destruction of most compounds after 2 h; degradation enhanced by Fenton's reagent, Degradation decreased by increases in temperature and salinity

5.4 Emerging Technologies for Oil Sands Emission Reduction

Water treatment technologies may play an important role in the reduction of emissions from tailings ponds in the oil sands industry. By removing the organic compounds such as NA, VOCs and PAH from process water, emissions will likely be reduced. Water treatment options reviewed herein present several means of removing target compounds from oil sands process water. NA are of particular interest since it has been shown that their degradation by microorganisms, the tailings ponds can result in the production of GHG. Candidate technologies for the removal of NA may include adsorption, nanofiltration, ion exchange, biological treatment, and/or photocatalytic oxidation.

Over the past several decades, treatment of oilfield produced waters has evolved in response to increasingly stringent environmental regulations and concerns over limited water resources (Table U). These driving factors have expanded the water treatment needs of the oil sands industry from the basic requirement of oil and suspended solids removal, to the more challenging objectives of boiler feed water treatment for recycling of produced water, demineralization of oilfield brines for disposal via deep well injection, detoxification for environmental discharge, and reclamation of waste streams for agricultural or potable reuse (Allen, 2006). Conventional treatments are insufficient to meet these objectives, forcing operators to consider the use of advanced treatment processes. In some cases, the application of tertiary technologies which remain constrained by the complex nature of petroleum wastewaters. Petroleum

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wastewaters include emulsified oils, surfactants, high salinity, hardness, trace metals and toxic soluble organic compounds. Many of the advances and innovations in the water treatment industry have resulted directly from modifications to established technologies to increase their effectiveness on difficult industrial effluents such as these.

Since the emerging treatment technologies have not been tested on oil sands produced waters, results of their performances on oilfield water are discussed. Oilfield water differs from oil sands produced water in pH, mineral and suspended solids content. However, in most cases they contain similar PPCs, such as VOCs, CH₄, RSC, THC, benzene and PAHs. In a review of emerging treatment technologies for processed oilfield water, Allen (2006 and 2008b) categorized the status of conventional and tertiary treatment technologies in the oil and gas industry (Table U). Allen (2006 and 2008b) used the term "established" to refer to a wastewater treatment process already in place. He used the term "emerging" to refer to technologies that are in the pilot/field testing stages. Established technologies include: oil separators, induced gas flotation, deep bed filtration (deoiling), aeration and sedimentation (iron removal), chemical precipitation and ion exchange (softening, silicate), distillation (desalination), activated carbon and biological treatment (soluble organics). Emerging technologies in the oil industry include: microfiltration, ultrafiltration (deoiling), fixed film bioreactors (soluble organics) and advanced oxidation processes such as photocatalytic oxidation (Bessa et al., 2001).

Previous assessments of candidate water treatments in the oil and gas industry offer insight into the suitability of emerging technologies to the oil sands. A technical comparison of four water treatment processes for the removal of soluble organic constituents in produced water was conducted. The comparison considered the performances of each treatment and was based on oilfield produced water where TOC and TDS were considered the primary pollutants of concern. Chemical oxidation was the most efficient technology for decreasing contaminant levels and was rated highly for its ability to degrade pollutants to carbon dioxide and water. However, when energy requirements were considered, chemical oxidation ranked poorly relative to activated carbon and biological oxidation. Although both of these methods reduced concentrations of target pollutants, these technologies also result in the production of solid waste.

Table U Summary of Potential Treatment Technologies for Oil Sands Industry

Process	Oil sands target pollutants	Problems associated with treatment of produced water	Significant technological advances	Oil sands process water considerations
Adsorption	Aromatic Hydrocarbons Naphthenic acids Oil Trace metals	Incomplete pollutant removal, fouling from oil; low adsorption capacity; regeneration and	Development of synthetic polymers and resins (non-ionic/ionic) with improved adsorption, regeneration properties; organic-	Acidification required to adsorb naphthenic acids; ionic strength affects electrostatic



Process	Oil sands target pollutants	Problems associated with treatment of produced water	Significant technological advances	Oil sands process water considerations
		disposal costs	modified clay adsorbents	interactions
Filtration				
Micro/ultrafiltration	Bitumen Suspended solids	Fouling from oil and solids; membrane durability and replacement costs; disposal of retentate	Surface chemistry modifications to improve filtration of oily water; antifouling measures (e.g., aeration, ultrasound, backpulse)	Sub micron clay particles may permeate membranes; fouling from bitumen; alkaline pH improves permeate flux
Nanofiltration/ Reverse osmosis/ Electrofiltration	Aromatic hydrocarbons Hardness Naphthenic acids TDS Trace metals	Fouling from oil, organics; biofouling; scale-up costs; disposal of retentate; water recovery	Ultra-low pressure membranes to reduce energy consumption; membrane modifications to reduce fouling from organics	Fouling from bitumen; alkaline pH promotes removal of anionic pollutants; high ionic strength can cause salt leakage
Biological Treatment				
	Ammonium Aromatic hydrocarbons Naphthenic acids Oil	Effect of feed water toxicity on microbial population; incomplete pollutant removal	Extractive membrane bioreactor and GAC-FBR to promote microbial growth and facilitate degradation of soluble organic compounds	Effects of toxicity and salinity on biofilm or activated sludge
Advanced Oxidation				
	Ammonium Aromatic hydrocarbons Naphthenic acids	Incomplete pollutant removal; influence of water chemistry on reaction rates; energy efficiency; operational costs; scale-up problems	Solar photocatalytic degradation of organic compounds; photoelectrocatalytic process to reduce the effect of radical scavengers in produced water	Radical scavengers (Cl^- , HCO_3^-) in process water; oxidation processes are optimized at low pH

(Source: Allen, 2008b)

Through small scale experiments, consultation with experts, and a literature review, Hansen and Davies (1994) selected a short list of potential treatment options and conducted analysis of their performance on target pollutants in the Norwegian oil industry process waters. The candidate treatment options considered included ion exchange, GAC, ultrafiltration, air stripping, adsorption on zeolite, and biological treatment. Air stripping was an effective method for removal of aromatic hydrocarbons such as benzene, toluene, and xylene, aliphatic hydrocarbons, and naphthalenes (90-95%; Table V). Activated carbon removed the majority of naphthalenes (95-100%) and dispersed oil (75-100%), but only a small fraction of the production chemicals (25%). The most effective methods for phenol and fatty acids were ion exchange

and biological treatment, respectively. Ultrafiltration proved to be effective only for benzene, toluene, xylene and dispersed oil. Hansen and Davies (1994) concluded that at least two water treatment technologies would be required to sufficiently remove all target pollutants from produced water.

Table V Summary of Assessments of Water Treatment Technologies for Norwegian Oil Industry Process Water

Treatment	Removal rates (%)			Cost (USD ⁽¹⁾ \$/m ³)
	Aliphatics	Naphthalenes	Phenol	
Air stripping	95	90-95	-	0.21
Ion exchange	-	-	95-100	1.02
Ultrafiltration	-	10	15	-
Activated carbon	15	95-100	-	2.29
Biological treatment	-	-	14-30	0.64
Zeolite	60	70	40	-

(Source: Hansen and Davies, 1994)

⁽¹⁾ United States dollars (2004 base year)

⁽²⁾ The m³ within the cost term refers to m³ of treated process water.

5.5 Oil Sands Water Treatment Research

Generally, water treatment research in the oil sands has been limited to conventional methods rather than advanced wastewater treatment technologies. Numerous treatment processes were tested on oil sands tailings between 1970 and 1990, including chemical flocculation and centrifugation, pH adjustment filtration, microfiltration, settling, coagulation and flocculation, activated carbon, gypsum and bentonite (Allen, 2006). The research primarily focused on improving settling rates and separation of bitumen from wastewaters, although several studies discussed the treatment of other chemical constituents in tailings pond water.

Research on improving tailings pond water examined the treatment methods of acidification, coagulants/flocculants (alum), and activated carbon on suspended solids, organic compounds, and toxicity (Allen, 2006). Acidifying tailings to pH 6 or lower rapidly induced a clear liquid zone and reduced sludge volume to 20-30% of the initial volume. Acidification was advantageous over other methods because it reduced organic carbon concentrations. However, acidification of alkaline process water resulted in significant salinity. Alum treatment was more attractive from the standpoint that it resulted in less salinity than acidification and had a treatment pH of 8.2. Activated carbon was examined, and resulted in removal of a significant fraction of the organic compounds (73%), but did not reduce toxicity or concentrations of heavy metals, some of which the authors noted were at or above applicable guidelines (i.e., lead,



cadmium, and mercury). Other treatments included lime precipitation, which increased settling rates but did not reduce concentrations of dissolved organic substances, and dilution with municipal supplied water, which caused some flocculation and improved settling.

A comparison of the performances of basic physical and chemical treatment methods on tailings pond water, including settling, centrifugation, sand filtration, aeration, and shifts in pH on tailings pond water quality revealed that settling and centrifugation effectively separated bitumen and suspended solids from the water. However, settling and centrifugation had no effect on dissolved solids, and resulted in only slight reductions in dissolved organic carbon concentration (~5-10%) and toxicity to fish (although toxicity to zooplankton improved considerably). Sand filtration had modest effects on dissolved organic carbon (-10%), total solids (-20%) and bitumen concentrations. Aeration for 72 h removed odours but had only negligible effects on all other parameters. In contrast to the physical treatments, acidification to pH below 4 with sulphuric acid induced rapid settling and produced a non-turbid, colorless supernatant with significant reductions in toxicity to fish and lower concentrations of dissolved organic carbon (-30%), which has been oxidized by the sulphuric acid. However, sulphate and calcium concentrations increased by 2- and 10-fold, respectively, following acidification.

More recent studies have examined detoxification of process water through adsorption and biological treatments. The treatment of CT release water using activated carbon combined with tertiary treatments (e.g., acidification and sand filtration) reduced the NA concentration by almost 50%. Subsequent filtration through a granular activated carbon column further decreased NA by 75% and reduced toxicity to aquatic organisms. Biodegradation of NA by microorganisms indigenous to tailings ponds was demonstrated in microcosm experiments (Herman et al., 1994), and resulted in almost 30% removal of NA.

5.6 Potential Technologies for Target Compounds in Oil Sands Process Water

5.6.1 Oils

Candidate technologies for oil removal include coagulation/flocculation, skim tanks, induced gas flotation, adsorption, sand filtration, micro- and ultrafiltration, biological treatment, and wetlands. The selection of deoiling technologies is dependent on influent oil concentrations. Skim tanks are used to treat high influent concentrations of free floating oil but are not effective on small droplets or oil-in-water emulsions (Allen, 2006). Granular media filters can reduce oil concentrations to 5-10 mg/L but will not remove soluble oil. To further reduce oil residuals and remove emulsified oil requires the use of adsorbents or micro- and ultrafiltration membranes (Chen et al., 1991; Karakulski et al, 1995). Alternatively, biological treatment, often in combination with chemical additives, may be applied. Advanced methods such as membrane filtration and membrane bioreactors may only be required for highly solubilized oils and where target concentrations are less than 1 mg/L. Membrane processes can lower operating costs over conventional processes, contingent on proper selection of membrane material and operational parameters (Ramirez and Davis, 1998).

Granular media filters or adsorbents used in combination with chemical precipitation may be sufficient to achieve target oil residuals for environmental or industrial usage. Chemical precipitation has been shown to destabilize and remove emulsified oil (Semerjian and Ayoub, 2003). Pre-treatment of produced water containing mostly solubilized oil and grease (16 mg/L) with walnut shell media, warm lime, and a pressure filter were sufficient to enable the operation of ion exchange and reverse osmosis units, although the membranes required cleaning three times per week.

5.6.2 Methane (through removal of Naphthenic acids)

Removal of NA and aromatic organic compounds, which are sources of CH₄ emissions, corresponded to removal rates exceeding 95% (Allen, 2008b). Proven technologies for the removal of naphthenic acids include nanofiltration, acidification and GAC, bioremediation, and anion exchange (Allen, 2006). Other technologies potentially capable of removing naphthenic acids include anionic flocculants, reverse osmosis, electrodialysis, advanced oxidation, and fixed film biological treatment.

A review of membrane processes provides numerous examples in which low molecular weight acids and organic compounds were significantly reduced by nanofiltration or reverse osmosis membranes (Kiso et al, 2001; Levine et al, 1999). In one such study, nanofiltration removed 95% of NA from fresh tailings waters (Kiso et al., 2001).

5.6.3 Aromatic Compounds

Although relatively low concentrations of aromatic compounds have been detected in tailings pond water, historical data indicate exceedances of CCME surface water quality guidelines. An exceedance of these guidelines could become a concern in end-pit lakes or water based reclamation scenarios (Allen, 2008a). Proven technologies for the removal of organics such as phenols, toluene, and PAH from process water include inorganic adsorbents, activated sludge, GAC-FBR, membrane bioreactor (Allen, 2006), nanofiltration, reverse osmosis, UV-oxidation, ozone oxidation, and photocatalytic oxidation. Mean removal rates of benzene, phenol, and toluene are highly variable, requiring further investigations.

5.7 Influence of Tailings Water Chemistry on Water Treatment Performance

Pollutant removal rates are a function of the technologies applied, but also tailings water chemistry and other operational parameters. The following section examines the influence of process water chemistry and other aspects of oil sands operations on candidate treatment processes (Table W). Primary consideration has been given to pH, TDS, suspended solids, oil content and temperature.

5.7.1 pH

Feed water pH influences the performance of most water treatment processes, through its effects on pollutant speciation, charge density on active surfaces (e.g., adsorbents, ion exchange resins, membranes), oxidation reactions and radical production, precipitation (lime softening, flocculation), and



microbial activity. Tailings pond water pH ranges from approximately 8-8.4 and is buffered with high concentrations of calcium carbonate (approximately 600-800 mg/L). The alkaline pH of process water is beneficial to some treatment technologies, and inhibitory to others. Weak acid cation exchange requires an alkaline pH, as does ozonation (radical production is optimized at pH 8.5-12.4). Electrostatic repulsion of anionic solutes by nanofiltration membranes is optimized at elevated pH due to the ionization of acid functional groups on the membrane surface, which increases the negative surface charge. Thus alkaline conditions facilitate the nanofiltration of naphthenic acids, which dissociate at elevated pH. In addition, the negative surface charge inhibits membrane fouling from negatively-charged particulates and oil droplets, which in turn reduces membrane cleaning and replacement costs.

Treatment processes that are either dependent on or optimized by low feed water pH include activated carbon adsorption, air stripping, coagulant salts, Fenton's reagent, photocatalytic and ultrasonic oxidation of organics, and weak base anion resins (see Appendix 5). Fenton's process is optimized at a pH of 3.4, and degradation rates for organic compounds have been shown to decrease with increasing pH. The effect of pH on a treatment process can be pollutant specific. In the case of acids and bases, dissociation constants can be used to predict how they will respond to treatments at a given pH. Naphthenic acids dissociate in alkaline conditions, therefore acidification is required for treatment processes that are only effective on the non-dissociated species (e.g., adsorption to GAC) (Allen, 2008b). However, generally acidification of process waters for the purposes of water treatment is undesirable because of the consequential increase in TDS and decrease in bitumen recovery as a result of decreased pH.

5.7.2 TDS

TDS impact water treatment processes in several ways. Elevated salinity can reduce membrane performance through charge screening of surface active groups, increased concentration polarization, and increased salt leakage. High TDS concentrations can negatively affect biological treatments through acute or chronic toxic effects. However, high ionic strength is beneficial to acoustic cavitations and electrochemical processes such as electrocoagulation and electrolytic oxidation (see Appendix 5). Currently, tailings pond water is brackish (2,000-3,000 ppm NaCl) and therefore unlikely to cause the problems associated with high salinity. However more saline water (e.g., basal aquifer water used in the processing and/or extraction process) and CT release water may impact treatment processes.

Individual dissolved ions can also influence treatment processes. High concentrations of divalent cations present a scaling concern and also have a charge screening effect. Sulphate ions interfere with anion exchange and have been shown to affect ammonium and carbon removal rates in treatment wetlands. Chloride and bicarbonate ions are radical scavengers that can reduce reaction rates in advanced oxidation processes. Sulphate, chloride, and bicarbonate are dominant anions in tailings pond water; however it is unclear whether they occur at concentrations sufficient to have an impact on these processes.

5.7.3 Suspended solids, oil, and temperature

Other operational characteristics of process waters that could affect water treatment processes include fine clay suspensions, residual bitumen, surfactants, and temperature. Fine clay particles and bitumen droplets present a fouling risk to adsorbents, ion exchange resins, and membranes. Surfactants in process water can influence membrane performance by attaching to functional groups on the membrane surface, increasing hydrophobicity (and fouling from oil). Temperature effects have been shown for membrane processes (permeate flux increases with temperature), and sonolytic cavitation (optimum temperature of 10-15 °C).

Tailings produced from the oil sands extraction and cleaning process have an elevated suspended solids content, which can alter the effectiveness of several treatment technologies such as adsorption, filtration, ion exchange, and oxidation processes. Surface charges on the suspended solids, such as clays, can affect the ion exchange process, decreasing the removal efficiency. In addition, if suspended solids contain organic material, adsorption of target organic pollutants will be affected, since the pollutants can preferentially select the suspended solids over the adsorbent used. Hence, it is essential that sedimentation or clarification of the tailings be used to reduce the suspended solids content prior to the use of other treatment methods.



Table W Influence of Chemical and Physical Characteristics of Oil Sands Process Water on Water Treatment Processes

Treatment	Suspended Solids ¹	pH	Salinity	Comments	
				Pros	Cons
Aeration and Air Stripping					
Air stripping	Volatility of some organic compounds can be reduced due to association with suspended solids.	Volatility of some organics is pH dependent; dissociated compounds will not be volatilized	Ionic strength influences Henry's Law constant of volatile compounds	N/A	-Concentrations of volatile compounds in process water are too low to justify costs -Capture of volatilized compounds would be difficult for the scale of the system required for tailings treatment.
Adsorption					
Activated carbon	Suspended solids can interfere with activated carbon adsorption of organics.	Acidification is required to adsorb naphthenic acids; alkaline Tailings pond water requires large dose of acid, increases TDS	Ionic strength influences electrostatic interactions between adsorbents and oil droplets	-Demonstrated removal of toxicity from oil sands tailings pond water after acidification and sand filtration -Removed toxicity from production water in Utah tar sands	-Low adsorptive capacity for organic compounds (0.1 g/g carbon) results in high costs given high water volumes in oil sands operations

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Treatment	Suspended Solids ¹	pH	Salinity	Comments	
				Pros	Cons
Coagulation and flocculation					
Chemical precipitation	N/A	-Optimum pH for softening is 9.3 to 10	N/A	-Low cost, widely used	-Potential interference from organic acids -Sludge disposal
Coagulation/ flocculation	Suspended solids removed through coagulation / flocculation process. Additional volume of coagulating / flocculating agents may be required with higher suspended solid content.	-pH influences the formation of hydrolysis by-products, deprotonation of functional groups on ionic polymers -Complexing capacity of synthetic flocculant PAA decreases with increasing pH	-Salinity influences optimal pH for hydrolyzed metal salts -Electrocoagulation: power consumption inversely proportional to ionic strength	-Effective pre-treatment for destabilizing oil emulsions and colloidal suspensions	-Sludge disposal
Flotation					
Flotation	N/A	-pH influences electro potentials of emulsified oil droplets and behaviour of coagulants, flocculants, surfactants	N/A	N/A	-Oxygenation of water promotes corrosion -Addition of surfactant to enhance particle hydrophobicity and Floatability



Treatment	Suspended Solids ¹	pH	Salinity	Comments	
				Pros	Cons
Filtration					
Membranes Microfiltration and ultrafiltration	Suspended solids can reduce removal efficiency of membranes by clogging the filtration system.	-Alkaline pH improves permeate flux during filtration of produced water	-High salinity lowers rejection of salts -Reduced energy requirement to actively induce concentration gradient.	-Produces low oil and grease residuals (i.e., <1 mg/L)	-Low temperatures reduce flux -Suspended solids and oil droplets cause fouling; poor rejection of dissolved organics - Energy costs due to high pressure
Nanofiltration and reverse osmosis	Clogging of filtration processes by suspended solids can cause operational malfunctions.	-Alkaline pH increases negative charge density on membranes, improving rejection rates for anions, dissolved organic carbon -Oil solubility is positively correlated with pH, thus fouling reduced at high pH	-High ionic strength and hardness reduce membrane surface charge; high potential for scaling from carbonates, sulphates, hydroxides; fouling from clay colloids -High sulphate concentrations can cause negative rejection of chloride ions	-Demonstrated removal of naphthenic acids and hardness	-Pre-treatment required, saline retentate requires disposal. -Energy costs due to high pressure
Electrodialysis	Surface charges of suspended solids can affect the electrodialysis process.	N/A	-Efficiency declines with increasing salinity recommended for brackish waters rather than saline	N/A	-Desalination is positively correlated with temperature -Increase in feed volume decreases pollutant removal rates

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Treatment	Suspended Solids ¹	pH	Salinity	Comments	
				Pros	Cons
Advanced oxidation					
Fenton's reagent	Oxidation of organic suspended solids will reduce oxidation of organics.	-Ideal pH is 3.4; higher pH reduces decomposition	-Chloride and bicarbonate are radical scavengers; high concentrations in TPW may reduce reaction rate	-Proven to degrade carboxylic acids	-Highly corrosive; acidification and neutralization required
Ozone	Ozone can be depleted due to oxidation of organic suspended solids, interfering with the oxidation of target organic compounds.	-Radical production initiated by hydroxide ion -Ideal pH = 8.5-12.4	-Radical scavengers may reduce reaction rates	N/A	N/A
Photocatalysis	Under some circumstances, suspended solids can adsorb photons, decreasing efficiency of the photocatalytic process. Adsorption of photons is dependent on the nature of suspended solids and wavelength of light.	-Low pH is preferable for degradation of phenols	-Radical scavengers may reduce reaction rates	-Proven to degrade carboxylic acids -Renewable energy potential (sunlight)	-No large-scale applications



Treatment	Suspended Solids ¹	pH	Salinity	Comments	
				Pros	Cons
Acoustic cavitation	N/A	-Low pH promotes degradation of carboxylic acids	-Salinity improves cavitation; radical scavengers may reduce reaction rates	-Destroys high molecular wt organics without sludge production	-Optimal temperature: 10-15°C -High costs -No large-scale applications
Electrochemical oxidation	N/A	N/A	-High ionic strength required	N/A	N/A
Ion exchange	Surface charge of suspended solids can interfere with the ion exchange process, reducing removal efficiency.	-Strong acid and base resins function over a wide pH range; weak acid resins require neutral to alkaline pH; weak anion resins require acidic pH	-Exchange of monovalent ions increases with feed water ionic strength; sulphate can block other anions; less sensitive to feed water hardness and scaling than reverse osmosis -High sodium concentration may interfere with removal of Ca and Mg	-Synthetic resins remove naphthenic acids; widespread commercial application; effective removal of organic acids, DOC; reduces ions to low residuals; operates over a wide temperature range	-Bentonite and zeolite exchangers have low capacity for naphthenic acids -Suspended solids can inhibit efficiency of ion exchange.

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Treatment	Suspended Solids ¹	pH	Salinity	Comments	
				Pros	Cons
Biological Treatment					
Biological treatment	<p>Suspended solids can adsorb target organic compounds making the less available for microorganisms to biodegrade.</p> <p>Suspended solids can accumulate in sludge, increasing overall volume requiring management.</p>	<p>-pH 6-8 is suitable for microbial activity</p> <p>-pH 7 is optimal for anaerobic processes</p>	<p>-Microorganisms must be adaptable to high salinity</p>	<p>-Widespread application in petroleum-industry effluents</p> <p>-Proven effective on VOCs, other soluble organic compounds</p> <p>-Anaerobic processes reduce sludge volume, degrade halogenated species</p>	<p>-Trickling filters require less surface area, but are less economical than aerated lagoons (for large volumes)</p>

N/A: Not Available

¹Suspended solids removal may be required for technologies presented herein as discussed in column 2 of the table. Suspended solids removal will improve efficiency of specific processes by reducing interference and adsorption of target compounds, and/or through preventing plugging or fouling of adsorbents, membranes, etc.



5.8 Water Treatment Costs

Water treatment costs for a range of processes and wastewater were compiled from the literature (Table X). In the following section treatment costs are compared among processes and applications, with the acknowledgement that cost comparisons are complicated by differences in flow rate, feed water chemistry, and pre-treatment requirements. Note that total costs refer to amortized capital costs plus operating and maintenance costs. Cost estimates are expressed in USD.

Table X Water Treatment Costs

Treatment	Wastewater type	Flow rate ⁽¹⁾ (m ³ /d)	Base Year	Total + O&M costs (USD/m ³) ⁽³⁾
Adsorption				
Activated carbon	Agricultural runoff	65,000-90,000	2003	0.08
	Off-shore produced water (North Sea)	21,000	1994	2.29
	Groundwater (drink. water treatment)		1997	0.03-1.67
	Surface water (drink. water treatment)		1999	0.11
	Groundwater contaminated with MTBE	55	2004	0.8-4.6.
	Industrial and municipal wastewater	5,500	2004	0.52 ^a
	Polymer-modified bentonite adsorbent		1997	1.19
Electrosorption	Oily wastewater (100 ppm oil)		1990	1.17
Air stripping				
Counter current air stripping	Off shore produced water (North Sea)	21,000	1994	0.21
	Groundwater		1997	0.02-0.18
	Groundwater contaminated with methyltertbutyl ether, BTEX	55,000	2004	1.4-2.0
Oxidation				
Advanced oxidation	Groundwater		1997	0.04-18.5
	Phenol solution		2000	2.26
	Groundwater	55	2004	0.2-14.6
	Groundwater contaminated with methyltertbutyl ether	5,500		
Biological treatment				

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Treatment	Wastewater type	Flow rate ⁽¹⁾ (m ³ /d)	Base Year	Total + O&M costs (USD/m ³) ⁽³⁾
Activated sludge	Oilfield produced water		2002	1.08
Membrane bioreactor	Sewage	21,000	1994	0.64
	Sewage	38,000	2004	0.125
	Municipal wastewater	58	2004	0.22 770 ^d
Chemical treatment				
Acid/alum treatment	Machining and cutting oil	45.6	1986	3.67
Chemical and biological processes	Municipal wastewater	58	2004	0.27 974 ^d
Chemical treatment	Metal fabrication (0.5-5% oil and grease)	272-8 17	1978	0.73
Coagulation	Kaolinite suspension	4,000	1982	0.112-0.138
	Bentonite suspension/ oil in water dispersion	500-6,000	1998	0.88
Electrocoagulation	Textile wastewater		2004	0.34-1.02
	Textile wastewater		2004	0.86-1.71
	Railroad industry; O&G = 100 mg/L		1990	1.93-1.99
Lime softening	Groundwater	3,800-38,000	1995	0.25-0.106
Warm lime softening	Oilfield produced water			0.35-0.64
Filtration				
Slow sand filtration	Agricultural runoff	65,000-90,000	2003	0.015
Sand filtration	Municipal wastewater	3,785	1998	0.21
Microfiltration	Kaolin suspension	4,000	1982	0.12
Crossflow microfiltration	Bentonite suspension/ oil in water dispersion	500-6,000	1998	0.31-0.44
Microfiltration	Agricultural runoff	65,000-90,000	2003	0.06
Microfiltration/ ultrafiltration		2,400	2003	0.15-0.34
Ceramic membrane (0.8 micron) with backpulsing	Bentonite suspension; oil in water dispersion	1,892-18,920	1997	0.14-0.3
Hollow fibre ultrafiltration	Railroad industry; O&G = 100 mg/L		1990	1.48-1.56
Tubular ultrafiltration	Railroad industry; (O&G = 100 mg/L)		1990	1.03-1.24
	Machining and	45.6	1986	2.94



Treatment	Wastewater type	Flow rate ⁽¹⁾ (m ³ /d)	Base Year	Total + O&M costs (USD/m ³) ⁽³⁾
Ultrafiltration	cutting oil Agricultural runoff	65,000- 90,000	2003	0.07
Ultrafiltration (including pre-treatment)	Fatty acid effluent (O&G = 3,000- 4,000 mg/L)	230-400	1989	2.65
Nanofiltration	Groundwater	20,000	2003	0.23
	Groundwater	60,000	2001	0.16
		6,000		0.24
Ion exchange				
Caustic softening and weak acid cation exchange	Oilfield produced water	19,000	1992	0.38-0.50
Ion exchange	Agricultural runoff	65,000- 90,000	2003	0.26
	Industrial wastewater	1,134	1996	0.088
	Artificial wastewater	2,184	2002	0.44
	Off-shore produced water (North Sea)	21,000	1994	1.02
	Surface water		1999	0.05

(Source: Allen, 2006 and sources within)

⁽¹⁾ Design flow rate of the treatment process.

⁽²⁾ Tailings production at oil sands facility is approximately 13,000 – 16,000 t/h. This has not been converted to m³/d since density of tailings is unknown.

⁽³⁾ m³ in the cost term refers to m³ of treated water.

The total costs and operational and maintenance costs vary according to technology type and wastewater type. More energy intensive technologies which require pre-treatment (such as ultrafiltration) will have higher operational and maintenance costs. Technologies with the lowest total costs may be energy intensive or have pre-treatment requirements, but lower capital costs. Examples of treatments with low capitals costs include ion exchange used to treat surface water; ultrafiltration used for agricultural runoff water treatment, microfiltration for agricultural runoff water treatment and advanced oxidation treatment used for groundwater treatment. Technologies with the highest operational and maintenance costs were acid/alum treatment and tabular ultrafiltration used for treating machining and cutting oil wastewater.

The wastewater type will have an effect on the cost of the technology used, thus information on wastewater type, and chemical physical properties are necessary to accurately compare the cost of the technologies used in treating that water. Because of the drastic difference between the treatment volume of the aforementioned pilot and field-scale studies and the volume of tailings requiring treatment in the oil sands, it is difficult to identify what actual costs would be for implementation in the oil sands industry. Activated carbon and filtration methods likely provide some of the lower cost options for oil sands tailings treatment, provided that suspended solids can be managed appropriately. However, as these techniques have higher associated operational and maintenance costs, it is unclear, on the scale of oil sands

operations, whether this would be achievable. Hence, more research is required on evaluation of the cost of implementing these wastewater treatment technologies in oil sands mining operations.

5.9 GHG Emissions

Selection of an appropriate water treatment technology should include sustainability considerations to promote water and energy conservation and reduced emissions of CO₂ and other pollutants. Water treatment processes can result in the release CO₂ through oxidation of organic compounds as well as through combustion of fossil fuels for energy supply. Allen (2006) has compiled average CO₂ emissions associated with select water treatment processes (Table Y). Studies reviewed did not include other GHG such as CH₄, O₃, and nitrous oxide. Emissions from ion exchange process were the highest at approximately 4395 tonnes of CO₂ (tCO₂)/year, followed by sand filtration, microfiltration, activated carbon and aerobic degradation.

Table Y Greenhouse Gas Emissions of Various Water Treatment Processes

Treatment	kWh/m ³	kWh/day ⁽¹⁾	tCO ₂ /year ⁽²⁾	Energy cost ⁽³⁾
Aerobic degradation	-	-	617	-
Activated carbon	0.56	11,200	1,758	784
Microfiltration	0.64	12,800	2,009	896
Ion exchange	1.4	28,000	4,395	1,960
Sand filtration	1.14	22,800	3,578	1,596

(Source: Allen, 2006)

(1)Daily energy consumption is based on a water treatment capacity of 20,000 m³/day

(2)kWh converted to kg CO₂ by multiplying the energy consumption by a factor of 0.43 (Allen, 2006)

(3)energy cost is based on electricity cost of \$0.07/kWh (Canadian)

5.10 Life Cycle Assessment

Life cycle assessment (LCA) is a method for investigating the environmental impacts of a product or system over its entire life cycle, it includes consideration of extraction of raw materials, processing, manufacture, use and end life (Dixon et al., 2003). Vlasopoulos et al. (2006) used a life cycle approach to assess the performance and environmental impacts of 20 treatment technologies for petroleum industry wastewaters. Environmental impacts considered included climate change, abiotic depletion, photo-oxidant formation, acidification, eutrophication, and quantity of waste produced (



Table Z). The study was based on cleaning 10,000 m³ per day of process water. Comparisons were made within treatment stages, which consisted of deoiling (Stage 1), biological treatment (Stage 2), further deoiling and demineralization (Stage 3) and further demineralization (Stage 4). The authors also considered the potential for agricultural and industrial reuse of the treated effluent.

The available technologies can be grouped into 4 different treatment stages depending on their ability to treat the oily wastewater as well as on their requirements regarding the influent water quality.

- Stage 1: Technologies in this stage typically include hydrocyclones and dissolved air flotation and are aimed at significant removal of oil and grease to levels acceptable to downstream treatment stages;
- Stage 2: Technologies in this stage include biological processes, such as trickling filters or activated sludge, or physical treatment, such as air stripping or adsorbents are employed to further reduce oil and grease concentration to levels suitable for disposal or further treatment;
- Stage 3: Technologies at this stage require good influent water quality for efficient and economic operation. This stage typically includes activated carbon or organoclay technologies as well as membrane technologies, such as ultrafiltration or nanofiltration, to further reduce the oil and grease concentration to levels suitable for Stage 4 of treatment; and
- Stage 4: Technologies at this stage typically include ion exchange processes and are used to remove dissolved pollutants such as sodium and total dissolved solids to produce high quality water for reuse.

The assessment assumed a flow rate of 10,000 m³/d based on available data. Among Stage 1 technologies (dissolved air flotation and hydrocyclones), dissolved air flotation was considered to have a lower environmental impact than hydrocyclones, although the latter produces less sludge. Activated sludge treatment had the highest environmental impact of Stage 2 technologies, largely due to energy consumption, whereas adsorbents, microfiltration, biological contactors, and trickling filters, had the lowest environmental impacts. When contrasted with comparable Stage 1 and 2 technologies (e.g., dissolved air flotation and adsorbents), microfiltration had the lowest environmental impact due to its low energy consumption. Stage 3 technologies with high environmental impact include ozonation, nanofiltration, and ultrafiltration, whereas slow sand filtration and dual media filtration had the lowest impacts (though in terms of permeate quality they are not strictly comparable to the former technologies).

Table Z Summary of Quantity, Quality and Treatment/Disposal Methods of Treated Petroleum Industry Produced Water.

Technology	Stage	Waste	Quantity (m ³ /d)	Disposal
Dissolved air flotation	1	Oily sludge	220	Oil recover, incineration, landfill
Hydrocyclone	1	Oily sludge	50	Oil recovery, incineration, landfill
Activated sludge	2	Microbiological sludge	850	Recycling, incineration, landfill
Air stripping	2	Spent carbon	50 kg/d ⁽¹⁾	Incineration, landfill
Microfiltration	2	Oily sludge	230	Oil recovery, incineration, landfill
Trickling filter	2	Microbiological sludge	370	Anaerobic digestion, land application, landfill
Granular activated carbon	3	Spent carbon	50 kg/d	Incineration, landfill
Nanofiltration	3	Oily brine with sodium and other TDS, antifouling chemicals	800	Landfill
Organoclay	3	Spent organoclay	95 kg/d	Incineration, landfill
Ultrafiltration	3	Backwash sludge	285	Landfill
Ion exchange	4	Acidic sludge	25	Landfill

⁽¹⁾ kilogram per day
(Source: Vlasopoulos et al. 2006)

5.11 Ranking Technologies

Current technologies in oil sands mining to reduce air emissions include solvent recovery systems and tailings ponds. While these represent the current available technologies with the greatest positive impact on emissions reduction, the focus of this contract is to identify emissions reduction technologies that will



further reduce emissions relative to the status quo. Hence, while they represent efficient technologies that do result in emissions reductions, they have not been included in the ranking since they are already in use at this time.

In addition to solvent recovery systems and tailings ponds, there is a variety of wastewater treatment technologies that can reduce concentrations of PPCs in process water and tailings associated with oil sands mining facilities. Solvent recovery systems and tailings ponds have an advantage on the water treatment technologies since both processes are a vital part of the oil sand mining facilities, thus they are expected to remain in place, even if viable wastewater treatment technologies are identified.

In this section wastewater treatment technologies which can potentially be applied to reduce concentrations of PPCs in tailings ponds, were ranked. The ranking was based on the applicability of the technology to the oil sands mining industry, operational costs, GHG emissions and PPC removal efficiency.

The ranking provided herein was completed as preliminary task and may require additional consideration prior to implementation. The seven technologies compared were selected on the basis of available information on operating costs, removal efficiency, CO₂ emissions and by-product/waste handling. The evaluation did not consider associated VOC emissions or capital costs associated with installation. Hence, this comparison should not be used as an indication that the seven technologies evaluated represent the most appropriate technologies for treatment of oil sands tailings. These technologies and others discussed in Section 5.1, 5.2, 5.3 and Appendix 5 require additional consideration and field testing on process waters and tailings from tailings pond of oil sands mining facilities to evaluate the actual associated costs, removal efficiency, GHG emissions, and by-products and waste generated as well as applicability to the oil sands industry.

Technologies on reducing mine face emissions are not available. However, further investigations are required to evaluate methods or practices for mining that can potentially reduce VOC, THC, PAH, CH₄ and RSC emissions.

5.11.1 Methodology

Technologies where information on cost, GHG emissions and removal efficiencies was available were considered. This screening mechanism reduced the wastewater treatment technologies from 29 potential technologies (Appendix 5) to 7 technologies that may be applicable based on the current state of knowledge. Technologies retained for ranking considering these criteria include:

- activated carbon;
- polymer-modified bentonite adsorbent;
- activated sludge;
- microfiltration;
- hollow fibre ultrafiltration;

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- nanofiltration; and
- ion exchange.

The other 22 technologies had incomplete information on one or more criteria used in the ranking and hence have not been included herein. The final seven technologies with complete data were subsequently ranked as follows:

- The applicability of each technology in the oil sand mining industry was evaluated based on the information compiled from Sections 5.2 to 5.9 and Appendix 5. Technologies that are potentially applicable to oil sands facilities for treatment of tailings ponds were initially assigned 100 points. Those which were not applicable were not assigned points;
- Once the technologies that are potentially applicable were determined the score was adjusted by adding or removing points based on several factors;
- Information of the pre-treatment requirements prior to application of the technology was compiled. For each pre-treatment that is required to successfully apply the technology, 5 points were deducted;
- Information on the by-products and/or waste associated with the technologies was compiled. Initially technologies were assigned 50 points. For technologies which produced waste, 10 points were deducted from the initial 50 points. For technologies which produced emissions of GHG or produced of hazardous waste, 5 points were deducted. If incineration was required then an additional 10 points were deducted. If the waste required landfilling an additional 10 points was deducted;
- Operational costs associated with each technology were compiled. The technologies with the lowest operational cost were ranked highest. Technologies with the highest operational cost were ranked lowest. Once the technologies were ranked for operational cost, they were assigned a score from 10 to 70 depending on the ranking. The higher ranking was assigned the highest score for each category;
- Removal efficiencies of the technologies were compiled. The technologies with the highest removal efficiencies were ranked highest. Technologies with the lowest removal efficiency were ranked lowest. Once the technologies were ranked for removal efficiency, they were assigned a score from 10 to 70 depending on the ranking. The higher ranking was assigned the highest score for each category;
- GHG emissions from the treatment process of each technology were evaluated. The technologies with the lowest GHG emissions were ranked highest; technologies with the highest GHG emissions were ranked lowest. Once the technologies were ranked for GHG emissions they were assigned a score from 1 to 7 depending on the ranking. The higher ranking was assigned the highest score for each category; and
- The scores from each category were subsequently summed. Technologies with the highest points were ranked highest; technologies with the lowest points were ranked lowest.



5.11.2 Applicability

This section summarizes the results of the assessment of applicability of the seven technologies (Table AA). Generally, technologies require that tailings be pre-treated through sedimentation along with additional technologies prior to application. Activated carbon, polymer-modified bentonite and activated sludge generally require only sedimentation and acidification. Microfiltration and hollow fibre ultrafiltration can also be used, however, several pre-treatment steps are required to enhance their removal efficiency. Nanofiltration and ion exchange technologies were considered not applicable due to fouling from bitumen as well as their reduced removal efficiencies due to high ionic strength process water and tailings.

Table AA Applicability of Wastewater Treatment Methods to the Oil Sands Mining Industry

Wastewater Treatment Method	Applicability Points	Pre-treatment Required	Deductions	Total Points
Activated sludge	100	Requires sedimentation and application of chemical additives.	-10	90
Polymer-modified bentonite adsorbent	100	Requires sedimentation and acidification of tailings.	-10	90
Activated carbon	100	Requires sedimentation and acidification of tailings.	-10	90
Microfiltration	100	Requires sedimentation, application of chemical additives; and aeration.	-15	85
Hollow fiber ultrafiltration	100	Requires sedimentation, application of chemical additives; and aeration.	-15	85
Nanofiltration	0	-		0
Ion exchange	0	-		0

5.11.3 By-Products /Waste

The seven technologies result in the production of by-products/wastes which can be recycled/reused, disposed of in a landfill and/or incinerated (Table BB). The activated carbon method produces spent carbon which can be reused for up to 10 times by regeneration using thermal desorption or solvent vapour extraction. Both regeneration methods produce GHG and an organic waste stream, which requires further

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treatment. Using polymer-modified bentonite adsorbent will also produce spent bentonite which can be reused after regeneration. The polymer-modified bentonite can be reused up to 6 times. Regeneration includes using organic solvents such as alcohols and ketones, producing another waste stream which requires further treatment prior to disposal. For both activated carbon and polymer-modified bentonite methods, the use of organic solvents presents a number of environmental and safety problems associated with their use. Included among them are the necessity for having: processing systems which have fire and explosion safeguards; equipment for capturing any vapours that might otherwise escape to the atmosphere; and equipment for separating, purifying and recycling the organic solvents. These requirements all add considerably to the expense of utilizing any regeneration process which might require the use of organic solvents.

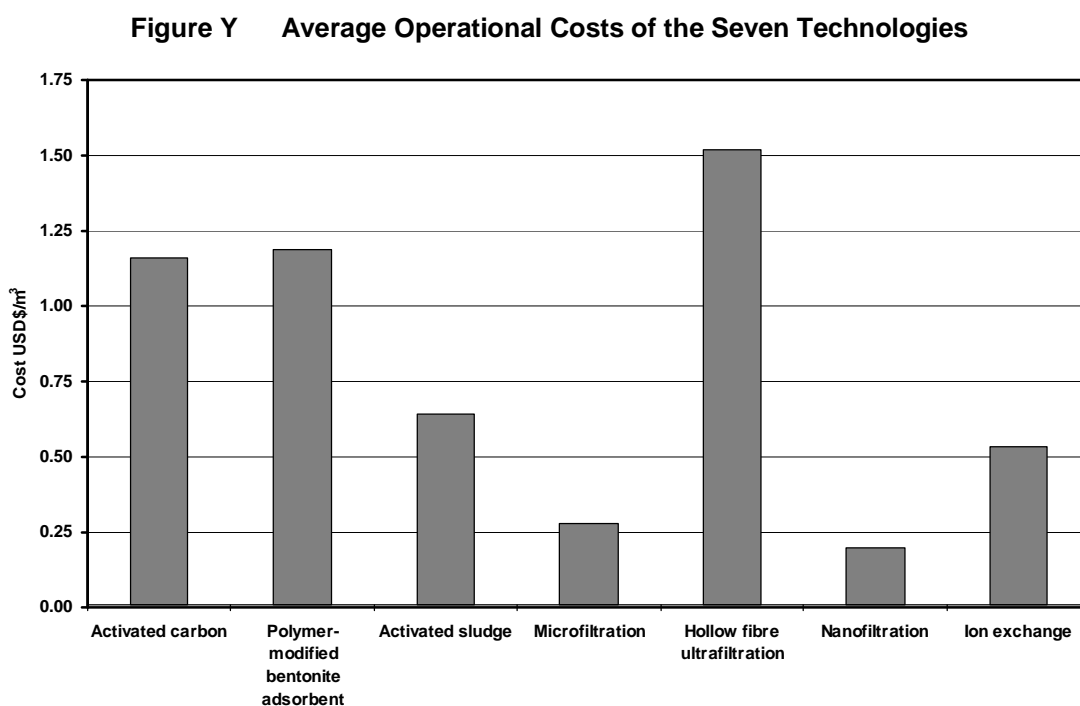


Table BB Ranking and Points Allocation of the Wastewater Treatment Technologies By-products/Waste Generation and Handling

Wastewater Treatment method	Waste/by-product				Disposal		Total
	Type	Points	Waste Production	Recycling/ regeneration process of waste	Points	Method	Points
Activated carbon	Spent Carbon	50	-10	Thermal desorption and solvent vapor extraction emitting GHG and hazardous waste	-5	Landfill and incineration	-20
Polymer-modified bentonite adsorbent	Spent bentonite	50	-10	Organic solvents used producing hazardous waste	-5	Incineration and landfill	-20
Nanofiltration	Anti-fouling agents and brine	50	-10	High cost of regeneration	0	Landfill	-10
Ion exchange	Acidic Sludge	50	-10	Reagents used as regenerants include sodium hydroxide, hydrochloric acid, methanol and bentonite; High cost of regeneration	-5	Landfill	-10
Activated sludge	Sludge	50	-10	-	0	Recycle, incineration and landfill	-20
Microfiltration	Sludge	50	-10	High cost of regeneration 0	0	Recycle, incineration and landfill	-20
Hollow fiber ultrafiltration	Sludge	50	-10	High cost of regeneration 0	0	Recycle, incineration and landfill	-20
⁽¹⁾ Mature fine tailings							
⁽²⁾ Consolidated tailings							

5.11.4 Operational Costs

Figure Y summarizes the operating costs of the selected seven technologies. Nanofiltration had the lowest operating cost, while hollow fibre ultrafiltration had the highest operating costs. Table CC summarizes the ranking and points for each of the technologies.



Note: These technologies were selected because information on operational cost, removal efficiency and GHG emissions were available.

Table CC Ranking and Points Allocation of the Wastewater Treatment Technologies Operating Costs

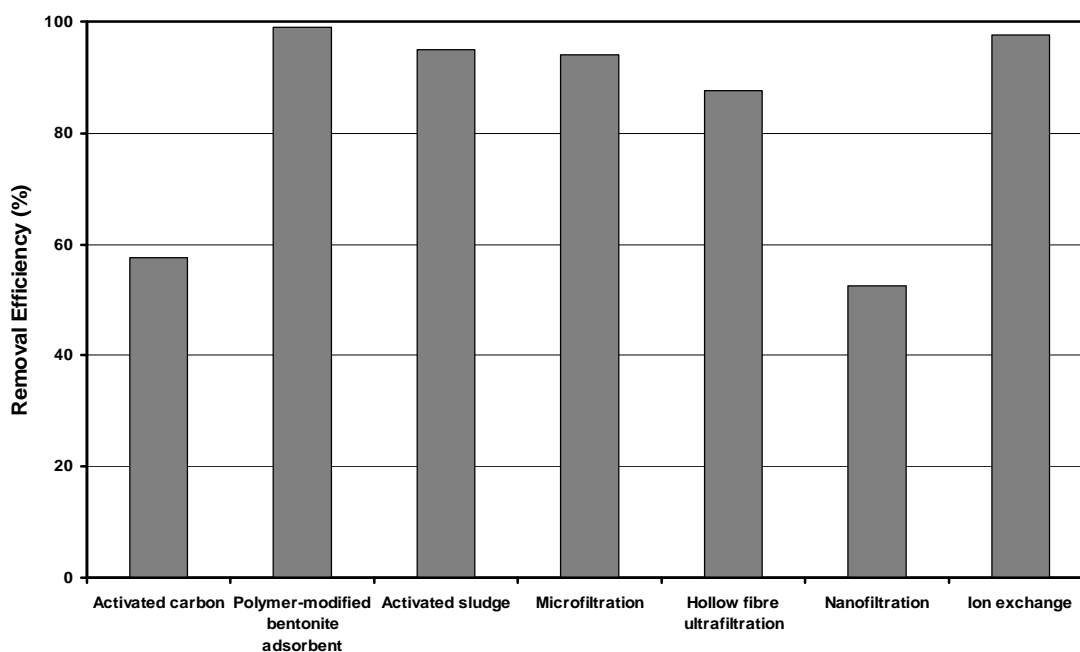
Wastewater treatment technology	Rank	Points
Nanofiltration	1	70
Microfiltration	2	60
Ion exchange	3	50
Activated sludge	4	40
Activated carbon	5	30
Polymer-modified bentonite adsorbent	6	20
Hollow fiber ultrafiltration	7	10



5.11.5 Removal Efficiency Ranking

Removal efficiencies of each of the seven technologies were compared (Figure Z). The polymer-modified bentonite adsorbent technique which is an adsorption technology had the best removal efficiency for PPCs at almost 100%, while nanofiltration had the lowest removal efficiency for PPCs at almost 53%. Table DD summarizes the ranking and points for each of the seven technologies.

Figure Z Average Removal Efficiencies of PPCs by the Seven Technologies



Note: These technologies were selected because information on operational cost, removal efficiency and GHG emissions were available.

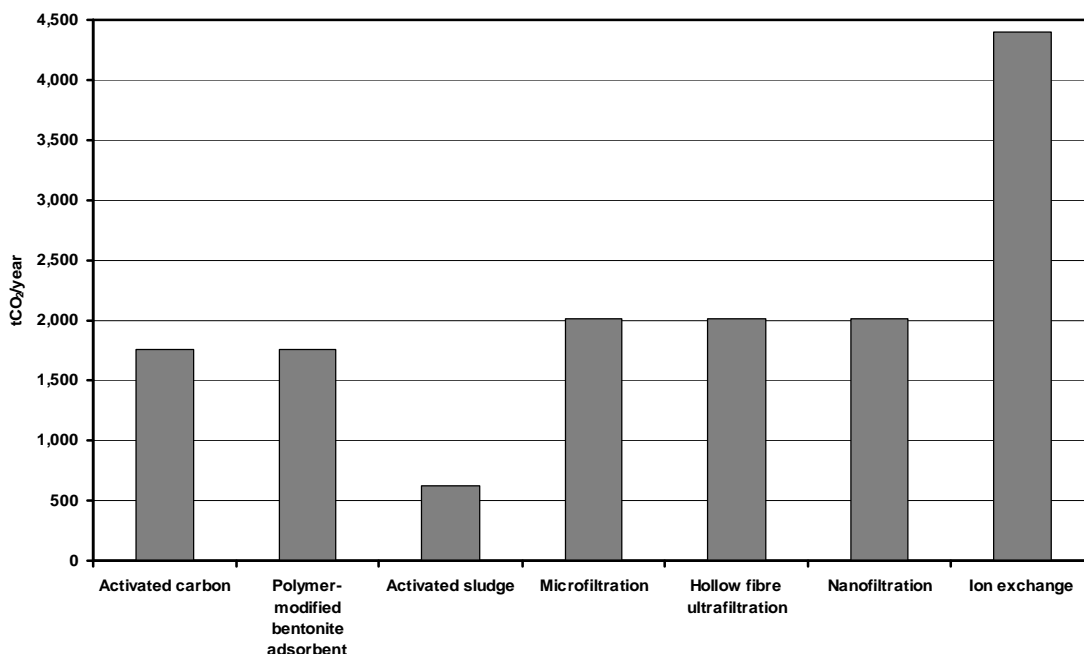
Table DD Ranking and Points Allocation of the Wastewater Treatment Technologies PPC Removal Efficiencies

Technology	Rank	Points
Polymer-modified bentonite adsorbent	1	70
Ion exchange	2	60
Activated sludge	3	50
Microfiltration	4	40
Hollow fiber ultrafiltration	5	30
Activated carbon	6	20
Nanofiltration	7	10

5.11.6 GHG Emissions Ranking

The GHG emissions were obtained from the information presented in Table Y on general GHG emissions from wastewater treatment technologies. Figure AA summarizes the annual CO₂ emissions for each of the seven technologies (only data available; Allen, 2006). Details on methane emissions were not available. The ion exchange technology had the highest annual CO₂ emissions at approximately 4,400 tCO₂/year, while the activated sludge technology had the lowest associated emissions at approximately 600 tCO₂/year (Table EE).

Figure AA Average Annual CO₂ by each of the Seven Technologies



Note: These technologies were selected because information on operational cost, removal efficiency and GHG emissions were available.

Table EE Ranking and Points Allocation of the Treatment Technologies CO₂ Emissions

Wastewater treatment technology	Rank	Points
Activated sludge	1	7
Activated carbon	2	6
Polymer-modified bentonite adsorbent	2	6
Microfiltration	4	4
Hollow fiber ultrafiltration	4	4
Nanofiltration	4	4



Wastewater treatment technology	Rank	Points
Ion exchange	7	1

5.11.7 Overall Ranking

Considering applicability to the oil sands industry, waste/by-products generated, removal efficiency operating costs and GHG emissions, the seven technologies were ranked overall. Table FF summarizes the overall score and associated ranking of each technology. The highest ranking technology was microfiltration, due to relatively high removal efficiency, relatively low GHG emissions and operating costs. The lowest ranking technology was the nanofiltration, which had the lowest removal efficiency and most important, compared to the other technologies, was generally not applicable to the oil sands mining industry.

Table FF Total Points and Overall Ranking of the Wastewater Treatment Technologies

Wastewater Treatment Technology	Points						Rank
	Applicability	By-product/waste	Operating costs	Removal efficiency	GHG emissions	Total	
Activated carbon	90	15	30	20	6	161	4
Polymer-modified bentonite adsorbent	90	15	20	70	6	201	3
Activated sludge	90	20	40	50	7	207	2
Microfiltration	85	20	60	40	4	209	1
Hollow fiber ultrafiltration	85	20	10	30	4	149	6
Ion exchange	0	35	50	60	6	151	5
Nanofiltration	0	30	70	10	4	114	7

6. DATA GAPS

A review of the information on THC, VOC, PAH, CH₄, and RSC emissions from mine faces and tailings ponds, the methods to predict future emissions using EFs, and the technologies which can potentially be used to reduce these emissions resulted in the identification of data gaps. These data gaps need to be identified in order to target research initiatives and facilitate the prediction of current and future emissions from oil sands mining facilities.

The following are the data gaps identified while completing this study:

- Emissions data from more recent monitoring programs were only available in aggregate format. Data is required on individual emissions sources and should be reviewed to confirm emissions estimates;
- EFs developed on the basis of monitoring data were not available for dates later than 1997, except for Suncor tailings ponds EFs based on 2007 air monitoring data from Millennium Mine;
- EFs for individual PPCs were generally not available, and therefore emissions of certain pollutants could not be quantified and/or predicted;
- Information on the progression of mine face and/or tailings pond surface area throughout the life of the project is not currently documented in publicly available sources;
- The various types of tailings ponds used for individual projects are not well documented;
- Verification and validation of EFs by secondary test methods is not currently available;
- Cost analysis on solvent recovery systems and tailings ponds used in oil sand facilities is not published in EIAs or oil sands production reports;
- PPCs removal efficiencies of solvent recovery systems are not currently available;
- Technologies presented are not necessarily specific to oil sands operations, and information on their performance, cost, and removal efficiency for treatment of tailings from oil sands mining facilities is lacking;
- Recent publications on the application of emerging technologies to tailings pond water are relatively scarce. Research on process water and tailings treatment for oil sands facilities should become a priority;
- Limited data are available on site specific cost estimates for candidate technologies;
- Influence of process water chemistry and other operational parameters specific to the oil sands industry on the performance and efficiency of emerging treatment technologies is generally not available;
- Residual bitumen in process water presents both operational and environmental concerns. Research in deoiling treatment is not comprehensive;



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- Data on site specific cost estimates for candidate technologies to determine if implementation of the technologies would be cost effective is scarce;
 - The influence of process water chemistry and other operational parameters specific to the oil sands industry on the performance and efficiency of emerging treatment technologies has not been studied;
 - Many emerging technologies focus on removal of aromatic compounds (e.g. BTEX). However, because these compounds occur at relatively low concentrations in oil sands process water these treatments may not be necessary or efficient. Further research is required to determine the fate of aromatic compounds in oil sands process water;
 - Mine face emissions reduction technologies have not been established;
 - Emissions technologies which directly capture air emissions from mine faces and tailings ponds are not available.

7. CONCLUSIONS

A review of EIAs, NPRI, research publications, energy reports, and air monitoring and emissions studies was completed. The review focused on compiling details on air emission from mine faces and tailings ponds of oil sands mining facilities. The review included evaluation of current data available on emissions from operating mine facilities, existing methods to predict emissions for future oil sands mining facilities and potential technologies available to mitigate emissions.

The review considered emissions of the following PPCs emitted from mine faces and tailings ponds at oil sands mining facilities:

- VOCs which included xylenes, toluene, n-hexane, butanes, cyclohexane, nonane, octane, decane, propanes, ethylene, ethylene glycol, propylene, benzene, 1,2,4-trimethylbenzene, 1,3-butadiene, C₂-C₈ aliphatic, C₉-C₁₆ aliphatic C₁₆₊ aliphatic, C₆-C₈ aromatic (excluding benzene), C₉-C₁₆ aromatic, aldehydes, ketones, acrolein and formaldehyde;
- PAHs which included acenaphthene, acenaphthylene, benzo(a)phenanthrene and cumene;
- RSC which included H₂S, COS, CS₂, mercaptans and thiophenes;
- THC; and
- CH₄.

The identified PPCs are mainly sourced to fugitive emissions from exposed mine faces and tailings ponds. Tailings pond emissions can occur from settling basin ponds and consolidated tailings surfaces. Mine face emissions can occur from exposed mine faces. THC, VOC, benzene, and RSC emissions can result from the volatilization of residual amounts of diluent contained in the tailings discharged to settling basins as well as from volatilization of hydrocarbons from mine faces. CH₄ is emitted from tailings ponds due to the biodegradation of organic compounds, including NA, bitumen and diluents in the tailings. The emission magnitude from tailings ponds largely depends on the composition of the tailings, temperature of the pond surface, photolysis, hydrolysis and volatilization. Emission rates will increase proportionally to these parameters.

Emissions of PPCs from mine faces and tailings ponds can be predicted using EFs. EFs were originally developed for Suncor's Millennium Mine (tailings ponds) and Syncrude Mildred Lake Mine (tailings ponds and mine faces). The EFs are based on monitoring data collected in 1997 using flux chamber measurements on mine faces and tailings ponds.

The EFs were used to predict emissions between 2006 and 2022 for mine faces and tailings ponds. For mine faces, emissions of various PPCs were estimated to increase by between 150 – 300% as a result of increasing bitumen production (from approximately 3.1x10⁸ bbl/yr to 1.1 x10⁹ bbl/yr) over the same period. Surface areas of mine faces were estimated to increase from 90 km² to approximately 260 km². It is estimated that:



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- THC will increase from approximately 1.1×10^5 to 3.1×10^5 t/yr;
 - Benzene emissions will increase from approximately 5 to 7 t/yr;
 - CH_4 emissions will increase from approximately 7.0×10^4 to 2.1×10^5 t/yr;
 - RSC will increase from approximately 1.19×10^4 to 1.20×10^4 t/yr;
 - PAHs emissions will increase from approximately 35 to 110 t/yr; and
 - VOC emissions will increase from approximately 3.5×10^4 to 1.0×10^5 t/yr.

Generally, predictions of emissions from mine faces using EFs typically overestimate emissions relative to those emissions presented in EIAs. Exceptions include VOCs from CNRL Horizon and Suncor facilities and RSC from CNRL and Suncor North Steep Bank. Suncor does not use EF to predict emissions, but rather measured data collected from their facility. It is unclear why the discrepancy with CNRL, relative to other facilities, exists.

The general overestimation of emissions from mine faces using EFs could be due to EIAs considering more current emissions that were not provided by operators for evaluation. Additionally, in EIAs, more site-specific factors such as mine face orientation and location, bitumen quality and mine face age may have been factored into the prediction of emissions.

Tailings ponds surface areas are estimated to increase from approximately 80 km^2 to 140 km^2 , between 2006 and 2022. As a result, it is estimated that:

- THC emissions will increase from approximately 7.4×10^4 to 2.2×10^5 t/yr;
- CH_4 emissions will increase from approximately 5.0×10^4 to 1.4×10^5 t/yr;
- Benzene emissions will increase from approximately 29 to 98 t/yr;
- RSC emissions will increase from approximately 344 to 805 t/yr;
- PAH emissions will increase from approximately 2.4×10^3 to 7.2×10^4 t/yr; and
- VOC emissions will increase from approximately 2.5×10^4 to 7.1×10^4 t/yr

Predicting emissions from tailings ponds using EFs typically underestimate emissions relative to those emissions presented in EIAs. Exceptions include VOCs from Syncrude Mildred Lake, Suncor Millennium Mine and Synenco Northern Lights, Benzene from Syncrude Mildred Lake and methane from Syncrude Mildred Lake, CNRL Horizon and Total E&P Joslyn North Mine. These predictions may have used alternative methods to correct predicted emissions based on facility-specific factors.

The underestimation could be attributed to EIAs considering more current emissions data that were not provided by operators for evaluation. Additionally in EIAs, more site-specific factors such as ambient and water temperature, concentration of methanogens, type of diluent, agitation rate from outfalls and/or mixing may have been factored into emissions in EIAs.

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The review has identified the absence of technologies to directly mitigate emissions from mine faces. One proposed method to reduce emissions from mine faces is to cap and cover mine faces using available overburden when mining is not taking place. It is expected that this would reduce exposure of the mine surface containing PAHs, and VOCs to the atmosphere, thus reducing volatilization and emissions.

Two methods are currently in use to reduce THC, VOCs, benzene, RSC and CH₄ emissions from tailings ponds. These include the solvent recovery systems, which have target diluent reduction exceeding 99% from tailings, and use of tailings ponds. Solvent recovery systems recover solvents from the various tailings streams prior to discharge into tailings ponds, which correspondingly results in reduction of THC, VOCs, benzene and RSC. Tailings ponds, through methanogenesis, can reduce emissions of target PPCs such as VOCs, THC and RSC. However, concurrently this process can increase CH₄ emissions. Potential wastewater treatment technologies have been identified to reduce emissions by treating process waters and tailings.

Of 29 potential wastewater treatment technologies that can be applied to the oil sand mining industry, 7 were ranked due to readily available information on applicability, operational cost, GHG emissions and by-product/waste production and removal efficiencies. The ranking of technologies, in ascending order, was as follows:

1. Microfiltration;
2. Activated sludge;
3. Polymer-modified bentonite adsorbent;
4. Activated Carbon
5. Ion exchange;
6. Hollow fiber ultrafiltration; and
7. Nanofiltration.



8. RECOMMENDATIONS

This review has identified several key points where further improvements are required. The following recommendations are based on the findings and data gaps presented in this review.

- Current emissions from existing oil sands mining technologies should be readily available to evaluate the contribution of mine faces and tailings ponds emissions on the total emissions from mining facilities. Emissions monitoring programs should include monitoring air emissions from mine faces and tailings ponds rather than general air quality in the area of the facility;
- Available EFs for mine faces are based on historical monitoring programs, completed in the late 1990s, at Syncrude's Mildred Lake Basin Mine. EF should be re-evaluated considering more current monitoring studies and incorporating current information on chemical, physical and biological processes which influence the emissions of VOC, THC, benzene, CH₄, PAHs and RSC from mine faces to improve the accuracy of emissions estimates;
- Available EFs for tailings ponds are based on historical monitoring programs, completed in the late 1990s, at Suncor's Millennium Mine and Syncrude's Mildred Lake Basin Mine. Similarly to EFs for mine faces, EFs from tailings ponds should be updated considering more current monitoring studies and incorporating current information on chemical, physical and biological processes which affect emissions of VOC, THC, benzene, CH₄ from mine face and tailings ponds to produce more accurate emissions estimates;
- Recent EFs for tailings ponds are available for Suncor mining facilities based on data collected in 2007, but do not include as many PPCs as historical EFs produced in 1997. EFs for a wider variety of PPCs, including VOCs and CH₄ from Suncor, Syncrude and other operators (as mines begin production) should be compiled to improve the quality of EFs, and provide emissions estimates more representative of the anticipated increase in oil sands mining facilities;
- Studies on EFs should focus on different mining, extraction and tailings management processes in order to develop factors that more accurately predict emissions associated with specific tailings ponds configurations and operational processes;
- Air emissions standards for mine faces and tailings ponds emissions should be developed;
- Monitoring water quality of the tailings ponds is essential to understanding emissions associated with tailings ponds. Routine monitoring programs that target parameters of importance to ambient air quality emissions should be developed;
- Current research on factors affecting the tailings quality is essential to improve understanding of the relation between tailings quality and emissions from tailings ponds;
- Research on treatment of process water and tailings should become a greater priority which focuses on prevention of freshwater resource depletion and improves water recycling technologies. The research should be directed by the concept of water reclamation and reuse, with a focus on the following subject areas:

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- Membrane fouling potential of residual bitumen and fine clay particles in tailings pond water. It remains unclear how the economics of commercial scale micro- and ultrafiltration of oil sands process water would compare with more conventional deoiling treatments;
- Influence of process water chemistry on treatment performance, including membrane rejection of dissolved organic compounds, ion exchange interference, adsorption of soluble organic compounds, production of radicals in advanced oxidation processes, and influence of toxicity on microbial communities in biological and wetland treatments;
- Comprehensive economic analysis of alternative and conventional technologies for water softening (nanofiltration and electrodialysis) and detoxification (membranes, biological treatment, advanced oxidation, wetlands) including pre-treatment costs;
- Preliminary research on photocatalytic and sonochemical oxidation processes for the degradation of naphthenic acids;
- Life-cycle assessment of candidate technologies based on the environmental impacts, land use, energy consumption, performance criteria, and costs.



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9. CLOSURE

We trust that this report satisfies your current requirements and provides suitable documentation for your records. If you have any questions or require further details, please contact the undersigned at any time.

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ENVIRONMENT CANADA

**REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
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Tables

Table 1

[illegible]

⁽¹⁾Emissions reported as tCO₂E/year

⁽²⁾ Emissions reported as total fugitive emission from plant, mine faces and tailings ponds

Table 2
Emissions Data from NPRI

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

Substance	CAS	per year	Mildred Lake Mine-Syncrude			Aurora North Mine-Syncrude			Muskeg River Mine-Shell			Millennium-Suncor		
			Fugitive	Total	Estimate code	Fugitive	Total	Estimate code	Fugitive	Total	Estimate code	Fugitive	Total	Estimate code
Phenanthrene	85-01-8	kg	NR	NR		NR	NR		NR	NR		29.09	52.48	M3
Fluorene	86-73-7	kg	NR	NR		NR	NR		NR	NR		15.29	24.52	M3
Acenaphthene	83-32-9	kg	NR	NR		NR	NR		NR	NR		3.08	19.70	O
Pyrene	129-00-0	kg	NR	NR		NR	NR		NR	NR		8.89	10.63	O
Benzo(a)phenanthrene	218-01-9	kg	NR	NR		NR	NR		NR	NR		5.35	6.05	O
Acenaphthylene	208-96-8	kg	NR	NR		NR	NR		NR	NR		0.52	5.90	O
Xylenes	1330-20-7	tonnes	469.67	478.24	O	NR	NR		0.73	0.73	E1	278.75	289.34	O
RS	NA - M14	tonnes	35.23	223.46	O	4.72	4.74	O	NR	NR		94.18	411.24	M3
Toluene	108-88-3	tonnes	195.13	211.23	O	26.21	26.37	M3	NR	NR		184.14	198.80	M3
Carbonyl sulphide	463-58-1	tonnes	19.97	146.04	O	NR	NR		NR	NR		18.49	54.63	M3
Hydrogen sulphide	7783-06-4	tonnes	16.55	129.49	O	NR	NR		NR	NR		7.40	30.53	M3
n-Hexane	110-54-3	tonnes	103.58	111.01	O	NR	NR		0.21	232.13	M3	179.84	241.78	M3
Ethylene	74-85-1	tonnes	0.70	77.26	O	NR	NR		NR	NR		NR	NR	
Ethylene Glycol	107-21-1	tonnes	NR	NR		NR	NR		0.86	3.76	E1	NR	NR	
Ethylbenzene	100-41-4	tonnes	66.37	69.60	E1	NR	NR		NR	NR		52.72	58.58	M3
Propylene	115-07-1	tonnes	5.95	69.12	E1	NR	NR		NR	NR		NR	NR	
Cyclohexane	110-82-7	tonnes	55.77	56.71	O	NR	NR		0.00	0.96	E1	24.93	217.77	M3
Benzene	71-43-2	tonnes	39.90	54.34	O	NR	NR		0.00	3.00	E1	8.92	19.08	M3
1,2,4-Trimethylbenzene	95-63-6	tonnes	53.19	54.01	O	NR	NR		3.52	3.52	E1	58.84	59.49	M3
Carbon disulphide	75-15-0	tonnes	8.21	12.43	O	NR	NR		NR	NR		7.40	58.69	M3
Cumene	98-82-8	tonnes	10.68	11.02	O	NR	NR		NR	NR		NR	NR	
1,3-Butadiene	106-99-0	tonnes	2.20	6.90	O	NR	NR		NR	NR		NR	NR	
VOCs	NA - M16	tonnes	10176.21	11313.10	M3	15753.00	16418.00		7.83	2521.27	E1	20988.88	27600.34	M3

Notes:

NR: Not Reported

NPRI are from Environment Canada (2007)

Fugitive data is not categorized by emission source.

Estimate Code is the identification of the method used to quantify the substance:

M3: source Testing

E1: Site specific emission factor

E2: Published emission factor

O: Engineering estimates

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Table 3
Emissions Factors Used To Predict Emissions from Mine Faces of Operating,
Approved and Publicly Disclosed Oil Sands Mining Projects

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds
and Mining Faces and Options for Reducing Emissions

Mines	Area (m2)	Area (km2)	General, [kg/km²/d]			Human Health, [kg/km²/d]									Photochemical, [kg/km²/d]													
			Total hydrocarbon (C ₁₋₁₂)	Methane (C ₁)	C ₂ *	C ₂ to C ₄ alkanes and alkenes	C ₅ to C ₈ Alkanes and alkenes	C ₉ to C ₁₂ alkanes and alkenes	Cyclohexane	Benzene	C ₆ to C ₈ non-benzene aromatics	Total aldehydes	Total ketones	RSC	Methane (C ₁)	Ethane (C ₂)	C ₃ to C ₄ alkanes	C ₅ to C ₆ alkanes	C ₉ to C ₁₂ alkanes	C ₁₃₊ alkanes	Ethylene (C ₂)	C ₃ to C ₄ alkenes	C ₅ to C ₆ alkenes	C ₉ to C ₁₂ alkenes	C ₁₃₊ alkenes	Benzene (C ₆)	C ₆ to C ₈ non-benzene aromatics	C ₉ to C ₁₂ aromatics
Shell Jackpine Phase 1 and Jackpine Mine Expansion-Mine Area 1	1.65E+07	16	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Shell Jackpine Phase 1 and Jackpine Mine Expansion-Mine Area 2	9.37E+06	9	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Shell Jackpine Phase 1 and Jackpine Mine Expansion-Mine Area 3	4.56E+06	5	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Shell Pierre River Mine Area-Mine Area 1	3.40E+07	34	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Shell Pierre River Mine Area-Mine Area 2	9.51E+06	10	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Shell Pierre River Mine Area-Mine Area 3	3.65E+06	4	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Albian Sands Muskeg River and Muskeg River Mine Expansion-Mine Area 1	4.50E+06	5	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Albian Sands Muskeg River and Muskeg River Mine Expansion-Mine Area 2	4.53E+06	5	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Syncrude Mildred Lake-North Mine Area(1)	8.14E+06	8	3,749	2,759	990	10	12	956	0	0.076	0.97	0	0	4.47	2,759	7	3	907	36.6	8.80	0	0.61	5.40	18.7	2.28	0.08	0.97	0.50
Syncrude Mildred Lake West Base Mine Area(1)	3.68E+06	4	4420	2641	1779	36	27	1,698	2	-	0.72	0	0	6.34	2,641	31	4	1,621	63.7	13.01	0	0.91	9.11	31.3	3.23	0.00	0.72	0.59
Syncrude Aurora North Mine Area	6.00E+06	6	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Syncrude Aurora South Mine Area	6.00E+06	6	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Petro-CanadaOil Sands Inc. Fort Hills-Mine Area	8.00E+06	8	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Canadian Natural Horizon-Mine Area	7.28E+06	7	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Millennium-Mine Area 1	1.69E+07	17	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Millennium-Mine Area 2	1.22E+07	12	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Millennium-Mine Area 3	1.06E+07	11	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Millennium-Mine Area 4	1.61E+06	2	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Millennium-Mine Area 5	1.12E+07	11	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Millennium-Mine Area 6	8.84E+06	9	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor North Steepbank Extension-Area 1	3.42E+06	3	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor North Steepbank Extension-Area 2	2.76E+06	3	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor North Steepbank Extension-Area 3	1.80E+06	2	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Voyageur South-Mine Area 1	9.03E+06	9	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Voyageur South-Mine Area 2	1.03E+06	1	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Voyageur South-Mine Area 3	4.30E+06	4	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Suncor Voyageour South Mine Face	1.59E+07	16	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Total E&P Joslyn North Mine	6.59E+06	7	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Imperial Oil Kearl-Mine Area 1	3.03E+06	3	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Imperial Oil Kearl-Mine Area 2	6.73E+06	7	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Imperial Oil Kearl-Mine Area 3	3.11E+06	3	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Imperial Oil Kearl-Mine Area 4	7.97E+06	8	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Imperial Oil Kearl-Mine Area 5	7.78E+06	8	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39
Synenco Northern Lights-Mine Area	3.60E+06	4	3,308	2,274	1,034	35.1	19.8	967	0.78	0.030	0.78	0	0	6.60	2274	26.5	7.1	922	40.1	8.42	0	1.5	5.57	19.9	2.23	0.03	0.78	0.39

Notes:
EF for all mine faces are the mean EF for Syncrude's Mildred Lake EF, except for Syncrude's Mildred Lake North Mine and West Base Areas which used their measured EF from Table

Table 4

Predicted Emissions from Mine Faces of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects

CLIENT: Environment Canada
PROJECT NO.: B2179 0000
PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds
and Mining Faces and Options for Reducing Emissions

Mines	Year of Maximum	Production	Area (km2)	General, [t/yr]			Human Health, [t/yr]										Photochemical, [t/yr]													
	Operation	Capacity (bbld)		Total hydrocarbon (C ₁₋₁₂)	Methane (C ₁)	C ₂₊	C ₂ to C ₄ alkanes and alkenes	C ₅ to C ₈ Alkanes and alkenes	C ₉ to C ₁₂ alkanes and alkenes	Cyclohexane	Benzene	C ₆ to C ₉ non-benzene aromatics	Total aldehydes	Total ketones	RSC	Methane (C ₁)	Ethane (C ₂)	C ₃ to C ₄ alkanes	C ₅ to C ₈ alkanes	C ₉ to C ₁₂ alkanes	C ₁₃₊ alkanes	Ethylene (C ₂)	C ₃ to C ₄ alkenes	C ₅ to C ₈ alkenes	C ₉ to C ₁₂ alkenes	C ₁₃₊ alkenes	Benzene (C ₆)	C ₇ to C ₉ non-benzene aromatics	C ₉ to C ₁₂ aromatics	
Shell Jackpine Phase 1 and Jackpine Mine Expansion-Mine Area 1	2010	100,000	16	19,883	13,668	6,215	211	119	5,812	5	0.2	5	-	-	40	13,668	159	43	5,542	241	51	-	9	33	120	13	0	5	2	
Shell Jackpine Phase 1 and Jackpine Mine Expansion-Mine Area 2	2012	100,000	9	11,308	7,774	3,535	120	68	3,306	3	0.1	3	-	-	23	7,774	91	24	3,152	137	29	-	5	19	68	8	0	3	1	
Shell Jackpine Phase 1 and Jackpine Mine Expansion-Mine Area 3	2014	100,000	5	5,509	3,787	1,722	58	33	1,610	1	0.0	1	-	-	11	3,787	44	12	1,536	67	14	-	2	9	33	4	0	1	1	
Shell Pierre River Mine Area-Mine Area 1	2018	200,000	34	41,038	28,210	12,827	435	246	11,996	10	0.4	10	-	-	82	28,210	329	88	11,438	497	104	-	19	69	247	28	0	10	5	
Shell Pierre River Mine Area-Mine Area 2			10	11,477	7,889	3,587	122	69	3,355	3	0.1	3	-	-	23	7,889	92	25	3,199	139	29	-	5	19	69	8	0	3	1	
Shell Pierre River Mine Area-Mine Area 3			4	4,408	3,030	1,378	47	26	1,289	1	0.0	1	-	-	9	3,030	35	9	1,229	53	11	-	2	7	27	3	0	1	1	
Albian Sands Muskeg River and Muskeg River Mine Expansion-Mine Area 1	2002	155,000	5	5,433	3,735	1,698	58	33	1,588	1	0.0	1	-	-	11	3,735	44	12	1,514	66	14	-	2	9	33	4	0	1	1	
Albian Sands Muskeg River and Muskeg River Mine Expansion-Mine Area 2	2010	115,000	5	5,475	3,764	1,711	58	33	1,600	1	0.0	1	-	-	11	3,764	44	12	1,526	66	14	-	2	9	33	4	0	1	1	
Syncrude Mildred Lake-North Mine Area(1)	1978	290,700	8	11,139	8,197	2,941	30	36	2,840	-	0.2	3	-	-	13	8,197	21	9	2,695	109	26	-	2	16	56	7	0	3	1	
Syncrude Mildred Lake West Base Mine Area(1)			4	5,937	3,547	2,390	48	36	2,281	3	-	1	-	-	9	3,547	42	5	2,177	86	17	-	1	12	42	4	-	1	1	
Syncrude Aurora North Mine Area	2006	116,300	6	7,245	4,980	2,264	77	43	2,118	2	0.1	2	-	-	14	4,980	58	16	2,019	88	18	-	3	12	44	5	0	2	1	
Syncrude Aurora South Mine Area			6	7,245	4,980	2,264	77	43	2,118	2	0.1	2	-	-	14	4,980	58	16	2,019	88	18	-	3	12	44	5	0	2	1	
Petro-CanadaOil Sands Inc. Fort Hills-Mine Area	2011	165,000	8	9,659	6,640	3,019	102	58	2,824	2	0.1	2	-	-	19	6,640	77	21	2,692	117	25	-	4	16	58	7	0	2	1	
Canadian Natural Horizon-Mine Area	2017	577,000	7	8,793	6,044	2,748	93	53	2,570	2	0.1	2	-	-	18	6,044	70	19	2,451	107	22	-	4	15	53	6	0	2	1	
Suncor Millennium-Mine Area 1	1967	294,000	17	20,439	14,050	6,389	217	122	5,975	5	0.2	5	-	-	41	14,050	164	44	5,697	248	52	-	9	34	123	14	0	5	2	
Suncor Millennium-Mine Area 2			12	14,679	10,091	4,588	156	88	4,291	3	0.1	3	-	-	29	10,091	118	32	4,091	178	37	-	7	25	88	10	0	3	2	
Suncor Millennium-Mine Area 3			11	12,779	8,785	3,994	136	76	3,736	3	0.1	3	-	-	25	8,785	102	27	3,562	155	33	-	6	22	77	9	0	3	2	
Suncor Millennium-Mine Area 4			2	1,947	1,338	608	21	12	569	0	0.0	0	-	-	4	1,338	16	4	543	24	5	-	1	3	12	1	0	0	0	
Suncor Millennium-Mine Area 5			11	13,475	9,263	4,212	143	81	3,939	3	0.1	3	-	-	27	9,263	108	29	3,756	163	34	-	6	23	81	9	0	3	2	
Suncor Millennium-Mine Area 6			9	10,677	7,340	3,337	113	64	3,121	3	0.1	3	-	-	21	7,340	86	23	2,976	129	27	-	5	18	64	7	0	3	1	
Suncor North Steepbank Extension-Area 1	2007	4,000	3	4,134	2,842	1,292	44	25	1,208	1	0.0	1	-	-	8	2,842	33	9	1,152	50	11	-	2	7	25	3	0	1	0	
Suncor North Steepbank Extension-Area 2			3	3,332	2,290	1,041	35	20	974	1	0.0	1	-	-	7	2,290	27	7	929	40	8	-	2	6	20	2	0	1	0	
Suncor North Steepbank Extension-Area 3			2	2,174	1,495	680	23	13	636	1	0.0	1	-	-	4	1,495	17	5	606	26	6	-	1	4	13	1	0	1	0	
Suncor Voyageur South-Mine Area 1	2012	120,000	9	10,902	7,495	3,408	116	65	3,187	3	0.1	3	-	-	22	7,495	87	23	3,039	132	28	-	5	18	66	7	0	3	1	
Suncor Voyageur South-Mine Area 2			1	1,249	858	390	13	7	365	0	0.0	0	-	-	2	858	10	3	348	15	3	-	1	2	8	1	0	0	0	
Suncor Voyageur South-Mine Area 3			4	5,189	3,567	1,622	55	31	1,517	1	0.0	1	-	-	10	3,567	42	11	1,446	63	13	-	2	9	31	3	0	1	1	
Suncor Voyageour South Mine Face			16	19,256	13,237	6,019	204	115	5,629	5	0.2	5	-	-	38	13,237	154	41	5,367	233	49	-	9	32	116	13	0	5	2	
Total E&P Joslyn North Mine	2022	200,000	7	7,957	5,470	2,487	84	48	2,326	2	0.1	2	-	-	16	5,470	64	17	2,218	96	20	-	4	13	48	5	0	2	1	
Imperial Oil Kearl-Mine Area 1	2018	300,000	3	3,656	2,513	1,143	39	22	1,069	1	0.0	1	-	-	7	2,513	29	8	1,019	44	9	-	2	6	22	2	0	1	0	
Imperial Oil Kearl-Mine Area 2			7	8,129	5,588	2,541	86	49	2,376	2	0.1	2	-	-	16	5,588	65	17	2,266	99	21	-	4	14	49	5	0	2	1	
Imperial Oil Kearl-Mine Area 3			3	3,760	2,584	1,175	40	23	1,099	1	0.0	1	-	-	8	2,584	30	8	1,048	46	10	-	2	6	23	3	0	1	0	
Imperial Oil Kearl-Mine Area 4			8	9,629	6,619	3,010	102	58	2,815	2	0.1	2	-	-	19	6,619	77	21	2,684	117	25	-	4	16	58	6	0	2	1	
Imperial Oil Kearl-Mine Area 5			8	9,393	6,457	2,936	100	56	2,746	2	0.1	2	-	-	19	6,457	75	20	2,618	114	24	-	4	16	57	6	0	2	1	
Synenco Northern Lights-Mine Area	2010	57,250	4	4,347	2,988	1,359	46	26	1,271	1	0.0	1	-	-	9	2,988	35	9	1,212	53	11	-	2	7	26	3	0	1	1	

Notes:
EF for all mine faces are the mean EF for Syncrude's Mildred Lake EF, except for Syncrude's Mildred Lake North Mine and West Base Areas which used their measured EF from Table

Table 5
Emissions Factors Used To Predict Emissions from Tailings of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands

Tailings Ponds and Mining Faces and Options for Reducing Emissions

Mines	Area (m2)	Area (km2)	General, [kg/km ² /d]			Human Health, [kg/km ² /d]										Photochemical, [kg/km ² /d]													Comments
			Total hydrocarbon (C ₁₋₇)	Methane (C ₁)	C ₂ +	C ₂ to C ₄ alkanes and alkenes	C ₅ to C ₆ Alkanes and alkenes	C ₆ to C ₁₂ alkanes and alkenes	Cyclohexane	Benzene	C ₁₀ to C ₁₄ non-benzene aromatics	Total aldehydes	Total ketones	RSC	Methane (C ₁)	Ethane (C ₂)	C ₃ to C ₄ alkanes	C ₅ to C ₆ alkanes	C ₆ to C ₁₂ alkanes	C ₁₀ alkenes	Ethylene (C ₂)	C ₃ to C ₄ alkenes	C ₅ to C ₆ alkenes	C ₆ to C ₁₂ alkenes	C ₁₀ alkenes	Benzene (C ₆)	C ₁₀ to C ₁₄ non-benzene aromatics	C ₁₀ to C ₁₄ aromatics	
Shell Jackpine Phase 1 and Jackpine Mine Expansion-Tailings Pond ⁽¹⁾	3.28E+06	3	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Process uses caustic free warm water. Produces coarse, fine and thickened tailings. Uses conventional
Shell Pierre River Mine Area-Tailings Pond ⁽¹⁾	1.75E+05	0	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Process uses caustic free warm water. Produces coarse, fine and thickened tailings. Uses conventional
Albian Sands Muskeg River and Muskeg River Mine Expansion ⁽¹⁾	1.29E+05	0	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Process uses caustic free warm water. Produces coarse, fine and thickened tailings. Uses conventional
Albian Sands Muskeg River Mine Expansion ⁽¹⁾	-	-																											
Syncrude Mildred Lake-Basin Tailings Pond ⁽¹⁾	1.16E+07	12	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Syncrude Facility
Syncrude Mildred Lake-Basin Beach Tailings Pond ⁽²⁾	1.85E+07	18	24.1	8.1	16.0	0	0	14.7	0	0.026	0.34	0	0	3.32	8.1	0	0	14.1	0.53	0.21	0	0	0	0.06	0	0.03	0.34	0.79	Syncrude Facility
Syncrude Mildred Lake East Mine In-Pit Tailings Ponds ⁽³⁾	1.02E+07	10	1774	1705	69	0	5	60	0	0	3	0	0	4	1,704.6	0	0	64.13	0.83	0.18	0	0	0.10	0.03	0	0.24	2.63	1.32	Syncrude Facility
Syncrude Mildred Lake-West Mine In-Pit Tailiongs Ponds ⁽³⁾	6.25E+06	6	1774	1705	69	0	5	60	0	0	3	0	0	4	1,704.6	0	0	64.13	0.83	0.18	0	0	0.10	0.03	0	0.24	2.63	1.32	Syncrude Facility
Syncrude Mildred Lake-Soutwest Sand Storage Area ⁽⁴⁾	2.30E+07	23	333.1	6.9	326.2	0	0	324.6	0	-	1.48	0	0	8.81	6.9	0	0	321	3.95	-	0	0	0	0	0	0	1.48	0.12	Syncrude Facility
Syncrude Mildred Lake-Soutwest Sand Storage Pond ⁽⁵⁾	1.96E+06	2	365.4	45.6	319.8	0	1	290	0	0	2	0	0	7	45.6	0	0	276.76	14.51	2.54	0	0.01	0	0.03	0	0.16	1.8	23.97	Syncrude Facility
Syncrude Aurora North-Tailings Pond	3.61E+06	4	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Syncrude Facility
Syncrude Aurora South-Tailings Pond	3.61E+06	4	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Syncrude Facility
Petro-CanadaOil Sands Inc. Fort Hills-Tailings Pond	2.50E+05	0	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Tailings emissions are based on Syncrude flux chamber emissions measurment
Canadian Natural Horizon-Tailings Pond	1.69E+07	17	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Conventional storage of tailings similar to Syncrude
Suncor Millennium-Tailings Ponds ⁽⁶⁾	1.60E+06	2	18,367	2,869	15,498	0	4	8,874	3,225	2,181	0	1,034	0	0	184	0	2,869	0	4	8,111	2,133	358	0	0	2,712	965	0	33	Suncor Facility
Suncor SouthTailings Ponds	1.35E+07	13	18,367	2,869	15,498	0	4	8,874	3,225	2,181	0	1,034	0	0	184	0	2,869	0	4	8,111	2,133	358	0	0	2,712	965	0	33	Suncor Facility
Suncor Voyageour South-Tailings Pond	2.05E+07	21	18,367	2,869	15,498	0	4	8,874	3,225	2,181	0	1,034	0	0	184	0	2,869	0	4	8,111	2,133	358	0	0	2,712	965	0	33	Suncor Facility
Total E&P Joslyn North Mine-Tailings Pond	3.43E+06	3	6,051	4,957	1,094	0	73	957	2	4	38	0	0	5	4,957	0	0	977	39	3	0	0	11	2	0	4	38	19	Conventioan storage of tailings similar to Syncrude
Imperial Oil Kearl-Tailings Pond	1.92E+07	19	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Uses cold water extaction and high temperature froth treatment similar to Syncrude process. Conventional
Synenco Northern Lights-Tailings Pond	4.59E+06	5	6051	4957	1094	0	73	957	2	4	38	0	0	5	4,956.8	0	0	977.06	39.19	3.01	0	0	11.46	2.21	0.18	3.97	38.21	18.68	Conventional storage of tailings similar to Syncrude

Notes
(1) Used EF from Syncrude's Mildred Lake Settling Basin for water surfaces
(2) Used EF for dry surfaces from Syncrude's Mildred Lake Tailings Surfaces
(3) EF for Syncrude's West & Eat In-Pit ponds
(4) EF for Syncrude's Southwest Sand Storage Area-dry surfaces
(5) EF for Syncrude's Southwest Sand Storage Area-watersurfaces
(6) EF are mean of Fugitive HC and RS Emission Factors for Selected Suncor Tailings Surfaces

Table 6
Predicted Emissions from Tailings of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

Mines	Operation	Production	Area (km ²)	General, [t/yr]			Human Health, [t/yr]										Photochemical, [t/yr]												
	Year	Capacity (bbl/d)		Total hydrocarbon (C ₁₊)	Methane (C ₁)	C ₂₊	C ₂ to C ₄ alkanes and alkenes	C ₅ to C ₈ Alkanes and alkenes	C ₉ to C ₁₂ alkanes and alkenes	Cyclohexane	Benzene	C ₉ to C ₁₀ non-benzene aromatics	Total aldehydes	Total ketones	RSC	Methane (C ₁)	Ethane (C ₂)	C ₃ to C ₄ alkanes	C ₅ to C ₈ alkanes	C ₉ to C ₁₂ alkanes	C ₁₃₊ alkanes	Ethylene (C ₂)	C ₃ to C ₄ alkenes	C ₅ to C ₈ alkenes	C ₉ to C ₁₂ alkenes	C ₁₃₊ alkenes	Benzene (C ₆)	C ₉ to C ₁₀ non-benzene aromatics	C ₉ to C ₁₂ aromatics
Shell Jackpine Phase 1 and Jackpine Mine Expansion-Tailings Pond	2014	30,000	3	7,234	5,926	1,308	-	87	1,144	2	5	46	-	-	6	5,926	-	-	1,168	47	4	-	-	14	3	0	5	46	22
Shell Pierre River Mine Area-Tailings Pond	2021	20,000	0	386	317	70	-	5	61	0	0	2	-	-	0	317	-	-	62	3	0	-	-	1	0	0	0	2	1
Albian Sands Muskeg River and Muskeg River Mine Expansion	2002	155,000	0	285	233	52	-	3	45	0	0	2	-	-	0	233	-	-	46	2	0	-	-	1	0	0	0	2	1
Albian Sands Muskeg River Mine Expansion	2012	115,000	0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Synchrude Mildred Lake-Basin Tailings Pond	1978	290,700	12	25,531	20,915	4,616	-	308	4,037	8	17	161	-	-	22	20,915	-	-	4,123	165	13	-	-	48	9	1	17	161	79
Synchrude Mildred Lake-Basin Beach Tailings Pond			18	163	55	108	-	-	99	-	0	2	-	-	22	55	-	-	95	4	1	-	-	-	0	-	0	2	5
Synchrude Mildred Lake East Mine In-Pit Tailings Ponds			10	6,629	6,369	259	-	19	225	-	1	10	-	-	14	6,369	-	-	240	3	1	-	-	0	0	-	1	10	5
Synchrude Mildred Lake-West Mine In-Pit Tailings Ponds			6	4,047	3,889	158	-	11	138	-	1	6	-	-	8	3,889	-	-	146	2	0	-	-	0	0	-	1	6	3
Synchrude Mildred Lake-Soutwest Sand Storage Area			23	2,801	58	2,743	-	-	2,730	-	-	12	-	-	74	58	-	-	2,699	33	0	-	-	-	-	-	-	12	1
Synchrude Mildred Lake-Soutwest Sand Storage Pond			2	261	33	229	-	1	207	-	0	1	-	-	5	33	-	-	198	10	2	-	0	-	0	-	0	1	17
Synchrude Aurora North-Tailings Pond	2006	116,300	4	7,973	6,531	1,442	-	96	1,261	3	5	50	-	-	7	6,531	-	-	1,287	52	4	-	-	15	3	0	5	50	25
Synchrude Aurora South-Tailings Pond			4	7,973	6,531	1,442	-	96	1,261	3	5	50	-	-	7	6,531	-	-	1,287	52	4	-	-	15	3	0	5	50	25
Petro-CanadaOil Sands Inc. Fort Hills-Tailings Pond	2011	165,000	0	552	452	100	-	7	87	0	0	3	-	-	0	452	-	-	89	4	0	-	-	1	0	0	0	3	2
Canadian Natural Horizon-Tailings Pond	2017	577,000	17	37,269	30,531	6,738	-	450	5,893	12	24	235	-	-	32	30,531	-	-	6,018	241	19	-	-	71	14	1	24	235	115
Suncor Millennium-Tailings Ponds	1967	294,000	2	10,696	1,671	9,025	-	2	5,167	1,878	1,270	-	602	-	-	107	-	1,671	-	2	4,723	1,242	209	-	-	1,579	562	-	19
Suncor South Tailings Ponds	2007	4,000	13	90,502	14,137	76,365	-	20	43,723	15,890	10,747	-	5,092	-	-	909	-	14,139	-	20	39,964	10,511	1,765	-	-	13,363	4,756	-	164
Suncor Voyageour South-Tailings Pond	2012	120,000	21	137,489	21,477	116,012	-	31	66,423	24,139	16,326	-	7,736	-	-	1,381	-	21,479	-	31	60,712	15,969	2,682	-	-	20,301	7,225	-	249
Total E&P Joslyn North Mine-Tailings Pond	2022	200,000	3	7,569	6,201	1,369	-	91	1,197	3	5	48	-	-	7	6,201	-	-	1,222	49	4	-	-	14	3	0	5	48	23
Imperial Oil Kearl-Tailings Pond	2018	300,000	19	42,317	34,666	7,651	-	511	6,691	14	28	267	-	-	37	34,666	-	-	6,833	274	21	-	-	80	15	1	28	267	131
Synenco Northern Lights-Tailings Pond	2010	57,250	5	10,137	8,304	1,833	-	122	1,603	3	7	64	-	-	9	8,304	-	-	1,637	66	5	-	-	19	4	0	7	64	31

Table 7
Predicted Total Emissions from Mine Face and Tailings
Ponds of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

Mines	General, [t/yr]			Human Health, [t/yr]									Photochemical, [t/yr]													
	Total hydrocarbon (C ₁₊)	Methane (C ₁)	C ₂₊	C ₂ to C ₄ alkanes and alkenes	C ₅ to C ₉ Alkanes and alkenes	C ₁₀ to C ₁₂ alkanes and alkenes	Cyclohexane	Benzene	C ₆ to C ₉ non-benzene aromatics	Total aldehydes	Total ketones	RSC	Methane (C ₁)	Ethane (C ₂)	C ₃ to C ₄ alkanes	C ₅ to C ₉ alkanes	C ₁₀ to C ₁₂ alkanes	C ₁₃₊ alkanes	Ethylene (C ₂)	C ₃ to C ₄ alkenes	C ₅ to C ₉ alkenes	C ₁₀ to C ₁₂ alkenes	C ₁₃₊ alkenes	Benzene (C ₆)	C ₆ to C ₉ non-benzene aromatics	C ₁₀ to C ₁₂ aromatics
Total 2008 Emissions	179,692	117,375	55,981	1,073	15,091	40,684	2,217	34	1,351	-	22	12,276	112,107	767	5,078	44,603	3,638	622	3	71	3,047	1,557	65	67	1,858	535
Total 2022 Emissions	532,547	354,320	171,891	3,316	35,372	125,388	6,664	105	4,134	-	22	13,157	349,053	2,454	5,538	136,568	11,141	1,928	3	166	9,026	4,793	210	205	5,649	1,614

Appendix 1 Toxicity Profiles of COPCs

APPENDIX 1

Toxicity Profiles for Potential Contaminants of Concern (PCOCs)

1. INTRODUCTION

PCOCs in ambient air were identified from the review of previous Environmental Impact Assessments (EIAs) conducted in the Oil Sands region. The PCOCs were categorized as carcinogenic compounds (known, probable, or possible) and non-carcinogenic compounds (inadequate data, not assessed, not listed) by the United States Environmental Protection Agency Integrated Risk Information System (US EPA IRIS, 2009). The following sections include descriptions of physical and chemical properties of COPCs, potential routes of exposure to human receptors and potential adverse health effects associated with exposure.

1.1 Known Carcinogens (Group A)

1.1.1 Benzene

Benzene is a colorless liquid with a sweet odour. It evaporates quickly into air and is slightly soluble in water. Benzene can be released into the environment from industrial sources as well as natural sources. The majority of industrial releases of benzene occur as a result of its use in the manufacture of other chemicals (i.e., styrene, cumene, cyclohexane) or products (i.e., rubbers, lubricants, dyes, detergents, drugs, pesticides). Once in the environment, benzene can undergo photooxidation, photodegradation or biodegradation to produce degradation/transformation products such as formaldehyde, nitrophenols, hydroquinones and catechol. Benzene is not thought to bioaccumulate or biomagnify (Agency for Toxic Substances and Disease Registry [ATSDR], 2007a).

Benzene is classified as a known carcinogen (Health Canada [HC], 2007) based on sufficient epidemiological and experimental evidence (ATSDR, 2007a). Specifically, benzene is known to have effects on the blood and bone marrow, with a primary carcinogenic endpoint of leukemia.

1.1.2 1,3-Butadiene

1,3-Butadiene is a colourless gas with a mild gasoline-like odour. 1,3-Butadiene is typically found at low levels in urban air samples; however, it degrades quickly in the atmosphere. Under sunny conditions, approximately half of the concentration of 1,3-butadiene in air will degrade in around two hours. Sunlight is not necessary for the degradation of 1,3-butadiene; however, sunlight does assist in the degradation. Under winter conditions with short days and reduced sunlight, approximately half of the concentration of 1,3-butadiene in air will again degrade in around two hours (ATSDR, 1992). Due to lack of information, the fate of 1,3-butadiene in soil or water is unclear. In addition, reliable methods for detecting 1,3-



butadiene in soil or groundwater are not available. If 1,3-butadiene were spilled into water or onto soil, based on its physical properties, it is expected to evaporate quickly into the atmosphere (ATSDR, 1992a). Studies regarding the time of degradation of 1,3-butadiene in soil or in water have not been conducted.

Large quantities of 1,3-butadiene are produced every year from petroleum. It is used to make rubber, and is typically used to make vehicle tires in addition to other rubber and plastics. 1,3-Butadiene is also found in small amounts in gasoline. Low concentrations of 1,3-butadiene may be trapped within the plastics or rubber. These concentrations are not expected to cause health problems. Low concentrations of 1,3-butadiene are also found in vehicle exhaust at approximately 10 parts per billion (ppb) and in gasoline vapours at 4 ppb. 1,3-Butadiene is also found in cigarette smoke and may also be found in the smoke of wood fires (ATSDR, 1992a).

Exposure to 1,3-butadiene is through breathing air, drinking water, or eating contaminated food. Workers in plants producing rubber, plastics, and resins are most likely to be exposed to 1,3-butadiene. Epidemiology studies indicate the possibility of higher than normal mortality rates from cancer and certain cardiovascular diseases (mainly chronic rheumatic and arteriosclerotic heart diseases) among workers in rubber plants. Workers exposed to 1,3-butadiene gas during the manufacture of rubber complained of irritation of the eyes, nasal passages, throat and lungs. In some, coughing, fatigue, and drowsiness developed. All symptoms disappeared when the gas was removed. Exposure levels were not stated in the study (ATSDR, 1992a).

Occupational exposure to in styrene-butadiene rubber plants was linked to increased incidences in respiratory, bladder, stomach, and lymphato-hematopoietic cancers. Because workers were exposed to mixtures of various chemicals, the contribution of 1,3-butadiene exposure to the development of these effects was unclear. The lack of historic exposure data to 1,3-butadiene and possible exposure to other chemicals are the main confounding factors of epidemiological studies of 1,3-butadiene exposed workers. In addition, though adjustments for age, calendar time, and race were done in most studies, there was no adjustment for smokers (ATSDR, 1992a).

1.2 Possible Carcinogens

1.2.1 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are a group of chemicals that are formed during the incomplete combustion of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat. There are in excess of 100 different PAHs which generally occur as complex mixtures, for example, as part of combustion products such as soot, rather than single compounds. Structurally, PAHs consist of two or more fused aromatic rings, with varying degrees of substitution. PAHs can occur

naturally or as a result of anthropogenic sources. Additionally, single PAH compounds can be manufactured for research purposes (ATSDR, 1995).

As pure chemicals, PAHs generally exist as colorless, white, or pale yellow-green solids with a faint, pleasant odour. PAHs can be used in medicines and to make dyes, plastics, and pesticides. Additionally, PAHs may be contained in asphalt used in road construction, in substances such as crude oil, coal, coal tar pitch, creosote, and roofing tar. PAHs are found throughout the environment in the air (e.g., attached to dust particles), water, soil, and sediments.

The PAHs summarized below are the most commonly studied PAHs. Generally, this is because:

- they are suspected to be more harmful than other PAHs;
- they exhibit harmful effects that are thought to be representative of other PAHs;
- there is higher probability of exposure to these PAHs; and,
- they are generally present on sites as a result of anthropogenic sources more frequently and at higher concentrations.

The most commonly studied PAHs are as follows:

- acenaphthene;
- benz(a)anthracene;
- benzo(a)pyrene;
- benzo(b&g)fluoranthene;
- benzo(g,h,i)perylene;
- chrysene;
- dibenz(a,h)anthracene;
- fluoranthene;
- fluorene;
- indeno(1,2,3-c,d)pyrene;
- phenanthrene; and,
- pyrene.

PAHs enter the environment commonly as releases to air from volcanoes, forest fires, residential wood burning, and exhaust from automobiles and trucks. They can enter surface waters through discharges



from industrial and waste water treatment plants, and can be released to soils at hazardous waste sites through accidental spills (ATSDR, 1995).

The movement of PAHs in the environment depends on properties such as solubility and volatility, both of which are typically limited. Volatility of PAHs is more variable than solubility and thus some PAHs may be present in air as vapours or adsorbed to particulate matter. When suspended in air, PAHs may travel long distances before deposition on the earth's surface by rainfall or particle settling. PAHs may volatilize into the atmosphere from surface waters; however, the majority adsorb to solid particles and are deposited on the bottoms of rivers or lakes. In soils, PAHs typically bind tightly to soil particles. PAHs may volatilize from surface soils to the atmosphere, and PAHs in soils may solubilize and migrate into groundwater (ATSDR, 1995).

PAHs will undergo degradation to form recalcitrant products through reactions with sunlight and chemicals present in the atmosphere. These reactions generally occur within days to weeks. Biodegradation in soil and water generally takes longer than chemical conversion, requiring weeks to months or even years (ATSDR, 1995).

PAHs are ubiquitous in the environment; thus exposure can occur through a variety of sources. Typically, exposure to PAHs occurs as an exposure to a mixture rather than individual compounds. Exposure is most likely to occur from vapours or to PAHs sorbed to dust or other particulate matter. Sources may include cigarette smoke, vehicle exhausts, asphalt roads, coal, coal tar, wildfires, agricultural burning, residential wood burning, municipal and industrial waste incineration, and/or hazardous waste sites (ATSDR, 1995).

Background concentrations of these representative PAHs (listed above) in the atmosphere are reported to range between 0.02 and 1.2 nanograms (ng)/m³ in rural areas and between 0.15 and 19.3 ng/m³ in urban areas. Exposure to PAHs in soils may occur in proximity to areas where coal, wood, gasoline, or other products were burned historically. Former manufactured-gas factory sites and wood-preserving facilities may also contain elevated residual concentrations of PAHs. PAHs have been identified in drinking water sources at relatively low concentrations, ranging from 4 to 24 ng/L (ATSDR, 1995).

In the average home, PAHs are present in tobacco smoke, smoke from wood fires, creosote-treated wood products, cereals, grains, flour, bread, vegetables, fruits, meat, processed or pickled foods, and contaminated cow's milk or human breast milk. Food grown in contaminated soil or air may also contain PAHs. Cooking meat or other foods at high temperatures, such as grilling or charring, increases the PAH content in foods. However, despite the large number of potential sources, the typical human diet contains less than 2 ppb of total PAHs (ATSDR, 1995).

PAHs can enter the body through the lungs, when inhaling air containing PAH vapours, such as smoke, or inhaling PAHs sorbed to particulate matter. It is unknown how rapidly or completely lungs absorb PAHs. Ingestion of drinking water and ingestion of food, soil, or dust particles that contain PAHs are other

exposure pathways; however, when PAHs are swallowed, absorption is generally slow. PAHs can also enter the body through dermal contact with soils or products containing of PAHs. The rate of dermal absorption may be influenced by the presence of other compounds. PAHs can enter all body tissues that contain fat, thus they are often stored in the kidneys, liver, and in adipose tissue. Lower concentrations of PAHs can also be stored in the spleen, adrenal glands, and ovaries. Once PAHs have entered the body they are metabolized by all tissues and produce a variety of metabolic products. The toxicity of the metabolites varies, with some being more toxic than the parent compounds, and others being less toxic than the original PAH (ATSDR, 1995).

PAHs can be harmful to human health under certain circumstances. Several PAHs, including benz(a)anthracene, benzo(a)pyrene, benzo(b&j)fluoranthene, chrysene, dibenz(a,h)anthracene, and indeno (1,2,3-c,d)pyrene have been found to induce tumour formation in laboratory animals when exposed through inhalation, ingestion or dermal contact. Humans exposed by inhalation or dermal contact for prolonged periods have also been found to develop cancer (ATSDR, 1995).

1.2.2 Naphthalene

Naphthalene is a white solid that can readily sublime, with a strong, unpleasant odour. It is found in fuels such as petroleum and coal and is used in mothballs and moth flakes. Naphthalene is also a combustion product of both wood and tobacco. It is also used in the manufacture of polyvinyl chloride and toilet deodorant blocks (ATSDR, 2005).

Naphthalene enters the environment from industrial and domestic sources and from accidental spills. It can dissolve in water to a limited degree and can weakly bind to soils and sediments. Exposure to air, moisture and sunlight result in photolytic degradation within 24 hours of initial exposure. Naphthalene is not known to bioconcentrate or bioaccumulate.

Exposure to large amounts of naphthalene may damage or destroy red blood cells, causing hemolytic anemia. Symptoms of this disease include fatigue, lack of appetite, restlessness and pale skin. High exposure dose may also result in acute effects such as nausea, vomiting, diarrhea, blood in the urine and yellowing of the skin. No studies have documented the cancerous effects in humans due to inhalation, oral or dermal exposure of naphthalene (ASTDR, 2005).

1.2.3 Toluene

Toluene is a clear, colourless liquid that can occur naturally or as a result of industrial processes. In its natural form, toluene is found in the tolu tree and in crude oil. In industry, it is used as a solvent, in gasoline processing and other fuel manufacturing, in paints, lacquers, adhesives and rubber (ATSDR, 2000).



Toluene commonly enters the environment through leaks from underground storage tanks or leachate from landfills. Upon entering soils, toluene can be rapidly biodegraded under aerobic and anaerobic conditions into metabolic by-products identified as intermediates in the Krebs cycle or completely mineralized. Generally, in soils with high organic carbon content, leaching of toluene is not problematic and complete mineralization will occur. In soils with low organic carbon content, leaching of toluene into surface waters or groundwater occurs readily. Once in surface waters, toluene may undergo photolysis reactions, producing cresols and benzaldehyde, which will subsequently degrade to simple hydrocarbons. In both surface waters and groundwater, biodegradation can occur and is enhanced by the presence of nutrients, such as sulphate, nitrate, potassium and phosphate. In groundwater, toluene tends to be more persistent than in soils.

Toluene may adversely affect the human brain. Exposure to toluene can cause headaches and sleepiness, and can impair someone's ability to think clearly depending on the amount and duration of exposure, genetic susceptibility, and age. Low to moderate chronic exposure in the workplace can cause tiredness, confusion, weakness, memory loss, nausea, and loss of appetite. Long-term chronic exposure may result in hearing and colour vision loss. Research is inconclusive as to whether low levels of toluene result in permanent effects on the brain or body over the long term. Acute exposure to toluene may cause death by interfering with breathing and beating of the heart. Repeated acute inhalation of toluene is reported to cause permanent brain damage, speech problems, vision and hearing problems, loss of muscle control, and loss of memory (ATSDR, 2000).

Inhalation of toluene has not been conclusively linked to a particular type of cancer. Workers in the majority of studies used to assess the carcinogenic potential of toluene were exposed to mixtures of solvents, thus information from these studies is inadequate, predominantly because of the lack of consistent findings across the studies and the likelihood that many of the studied groups were exposed to mixtures of chemicals. No studies have documented the cancerous effects in humans due to oral or dermal exposure of toluene (ASTDR, 2000).

1.2.4 Xylenes

Xylenes are a mixture of isomers composed of a single aromatic ring substituted with two methyl groups in the ortho, meta or para positions. All xylene isomers are colourless, flammable liquids with a sweet odour, and are highly volatile with low solubility in water. Xylenes are primarily a synthetic chemical, produced from petroleum products, although they do exist naturally in petroleum, coal tar and are formed during forest fires. Industrial applications of xylenes include as a solvent, a cleaning agent, paint thinner, in varnishes, plastics, synthetic fibres, and in coatings of fabrics and papers. Xylenes are also found in small amounts in airplane fuel and gasoline (ATSDR, 2007b).

Xylenes typically enter the environment through accidental spills or leaks. Xylenes are thought to be removed from soils and water through volatilization. Xylenes may adsorb to soil organic matter (SOM), and while sorption is weak, it does increase proportionally to the organic carbon content in a soil. If

xylenes adsorb to SOM, additional processes such as leaching, can result in transportation into groundwater. In the atmosphere, xylenes are readily degraded by photooxidation processes. Biodegradation of xylenes in soil and water will occur once volatilization has occurred. Aerobic biodegradation of xylenes is generally more efficient than anaerobic biodegradation. Metabolites of biodegradation of xylenes include: methylated homologs of benzy succinic acid; benzy fumaric acid; and E-phenylitaconate. Iron-reducing conditions enhance biodegradation rates of xylenes.

Short-term, acute exposure to xylenes can cause irritation of the skin, eyes, nose, and throat, difficulty in breathing, impaired function of the lungs, delayed response to visual stimulus, impaired memory, stomach discomfort, and possible changes in the liver and kidneys. Both short- and long-term acute exposure can also cause adverse effects to the nervous system (e.g., headaches, lack of muscle coordination, dizziness, and confusion). Cancerous effects of inhalation of xylenes in humans is limited to four studies. In the studies, individuals were potentially exposed to mixtures of compounds, thus chronic inhalation of xylenes could not conclusively be linked to particular type of cancer. Studies of workers exposed to solvents suggest a possible relationship between coal-based xylenes and leukemia; however, these studies were inconclusive based on limited data. No studies have documented the cancerous effects in humans due to oral exposure of toluene (ASTDR, 2007b).

1.3 Not Classifiable (Group D)

1.3.1 Cumene (Isopropylbenzene)

Cumene occurs as a colorless flammable liquid that is insoluble in water. It has a sharp, penetrating, gasoline-like odour, with an odour threshold of 0.088 parts per million (ppm). Cumene is a constituent of crude oil and finished fuels. It is released to the environment as a result of its production and processing from petroleum refining, the evaporation and combustion of petroleum products, and by the use of a variety of products containing cumene. It is used as a thinner for paints, lacquers, and enamels and as a component of high octane fuels. Cumene is also used in the manufacture of phenol, acetone, acetophenone, and methylstyrene (US EPA, 2007a).

The most probable route of human exposure is by the inhalation of contaminated air from the evaporation of petroleum products. Exposure may also occur through the consumption of contaminated food or water.

Acute (short-term) inhalation exposure to cumene may cause headaches, dizziness, drowsiness, slight incoordination, and unconsciousness in humans. Cumene has a potent central nervous system (CNS) depressant action characterized by a slow induction period and long duration of narcotic effects in animals. Cumene is a skin and eye irritant. No information is available on the chronic (long-term), reproductive, developmental, or carcinogenic effects of cumene in humans. Animal studies have reported increased liver, kidney, and adrenal weights from inhalation exposure to cumene. The US EPA has classified cumene as a Group D, not classifiable as to human carcinogenicity (US EPA, 2007a).



1.3.2 Ethylbenzene

Ethylbenzene is a colourless liquid with a gasoline-like odour. It is naturally occurring in coal tar and petroleum and is found in many products including paints, inks, pesticides, glues, varnishes, asphalt, fuels and tobacco products. In addition to being commonly used as a solvent, ethylbenzene is used in the production of many different chemicals, including: styrene; acetophenone; cellulose acetate; diethylbenzene; ethyl anthraquinone; ethylbenzene sulfonic acids; propylene oxide; and α -methylbenzyl alcohol (ATSDR, 2007c).

Releases of ethylbenzene into the environment can occur from a number of sources. Common sources of groundwater impacts include industrial discharge, leaking petroleum pipelines and/or underground storage tanks, and migration from landfills through leachate. In the atmosphere, ethylbenzene undergoes rapid photolytic degradation via reactions with hydroxyl radicals. In surface waters, naturally occurring compounds in the water can interact with ethylbenzene to promote transformations, such as photooxidation and biodegradation processes which may both play a role in influencing the fate of ethylbenzene in surface waters and groundwater. In soil, biodegradation is the primary degradation pathway. Ethylbenzene sorbs weakly to soil particle, thus the potential for ethylbenzene to leach from soils into groundwater is high. Major degradation products of photooxidation, aerobic and anaerobic transformation processes in soils, sediment, and water include acetophenone, benzaldehyde and various substituted phenolic compounds.

Exposure to ethylbenzene may be through inhalation, oral, or dermal routes. Acute and intermediate-duration exposure to inhaled ethylbenzene is associated with respiratory irritation and affects on the liver and the blood system. Chronic exposure to inhalation of ethylbenzene is associated with adverse effects to the liver, kidney, and endocrine system. No association has been found between the occurrence of cancer in humans and occupational exposure to inhalation of ethylbenzene. No studies are available for oral and dermal exposure to ethylbenzene, including cancerous effects (ATSDR, 2007c). Ethylbenzene is included in Group D (not classifiable as to human carcinogenicity).

1.3.3 Heptane

Heptane is a colourless, flammable liquid with a mild, gasoline-like odour. Heptane is used as a carrier and penetrating solvent for adhesives, in azeotropic distillations, in rubber tire manufacturing, as a reference fuel for testing gasoline engine knock and in the synthesis of toluene, alkylbenzene, gasoline and petroleum solvents (Occupational Safety and Health Administration [OSHA], 2009).

When released into the soil and water heptane is expected to quickly evaporate or biodegrade to certain extent; however, from soil, heptane is not expected to leach into groundwater. In the atmosphere, heptane is expected to be degraded through reactions with photochemically produced hydroxyl radicals. The half life in the air is between 1 and 10 days.

Exposure to heptane can occur through inhalation, ingestion and eye or skin contact. Short term exposure to heptane can induce vertigo, nausea, loss of coordination, and hilarity. Additionally, it may cause stupor, loss of appetite and a gasoline taste in the mouth. Skin contact causes redness and blistering. Eye irritation can occur at higher airborne concentrations of heptane. Chronic exposure is associated with repeated contact with the skin and causes drying, cracking, and dermatitis (OSHA, 2009).

Heptane is currently classified as a non-carcinogen (International Agency for Research on Cancer [IARC], 2009). An oral reference dose (RfD) of 4.4 mg/kg-d and a reference concentration (RfC) of 3.5 mg/m³ have been developed for heptane (State of Michigan Department of Environmental Quality [Mich DEQ], 2008).

1.4 Inadequate Data to Assess

1.4.1 Cyclohexane

Cyclohexane is a colourless, flammable liquid with a sweet odour. Cyclohexane evaporates quickly into the atmosphere. Reported odour thresholds for cyclohexane range from 0.21 to 880 mg/m³ (van Gernert and Nettenbreijer, 1977).

Cyclohexane is manufactured in large quantities for its use as a chemical intermediate and solvent (Hazardous Substances Data Bank [HSDB], 2001a). Ninety percent of this use is in the manufacture of adipic acid and caprolactam for the manufacture of nylon. Because it is a component of petroleum, its primary release is via fugitive emissions from petroleum refining, vaporization of gasoline, oil spills and in gasoline exhaust ([HSDB], 2001a). Cyclohexane occurs naturally in petroleum crude oil, in volcanic gases and in cigarette smoke (USEPA, 1994).

Cyclohexane is extremely volatile, existing in the vapour phase in air. It is estimated to have a half-life of 45 hours. Cyclohexane reacts primarily with photo-chemically produced hydroxyl radicals. Volatilization from soil and surface water is the most probable removal mechanism, though in aquatic systems it may partition out to organic particles and sediment. The half-life of cyclohexane in water is from 3 hours to 3.6 days. In soils, it is moderately mobile based on a K_{oc} (octanol/water coefficient) of 160 (HSDB, 2001a).

Cyclohexane is extremely resistant to biodegradation. Bioconcentration is considered to be low, with a reported bioconcentration factor of 89 (HSDB, 2001a)

Overexposure to cyclohexane vapours (for short or long periods) can cause effects ranging from headaches to anesthesia, tremors, and convulsions (USEPA, 1994). At sufficient concentrations, vapours are irritating to the eyes, mucous membranes, upper respiratory tract and skin. Cyclohexane also may be irritating to the nose and throat, and is reported as mildly irritating to the skin (Canadian Centre for Occupational Health and Safety [CCOHS], 1994).



The 24-hour exposure limit for cyclohexane of 100,000 $\mu\text{g}/\text{m}^3$ recommended by the Ontario Ministry of Environment and Energy (OMEE) was used as an acute exposure limit in the current assessment (OMEE, 1994). This exposure limit was estimated based on health considerations, but the specific basis was not provided.

A chronic exposure limit for cyclohexane was estimated by Cantox Environmental due to an absence of regulatory limits. An RfD of 100 $\mu\text{g}/\text{kg}/\text{day}$ was developed based on the absence of liver and kidney effects in rabbits exposed via inhalation to 100 $\text{mg}/\text{kg}/\text{day}$ cyclohexane for 10 weeks (Treon et al., 1943). A 1,000-fold safety factor (10-fold to account for sensitive individuals in the population, 10-fold for inter-species variability, and 10-fold for using a subchronic rather than a chronic study) was incorporated to derive the human exposure limit. This RfD was used for the assessment of both oral and inhalation exposures.

1.4.2 Hexane

Hexane is a colourless, volatile liquid with a faint gasoline-like odour. It is flammable and insoluble in water. Reported odour thresholds for hexane range from 23 to 875 mg/m^3 (van Gernert and Nettenbreijer, 1977).

Hexane is a component of many petroleum products and is a combustion product of polyvinyl chloride (HSDB, 2001b). It is also used as a solvent, in low temperature thermometers, calibrations, polymerization reaction mediums, as a paint diluent, and as an alcohol denaturant. Documented materials responsible for the release of n-hexane to the environment include printing pastes, paints, varnishes, adhesives and other coatings (HSDB, 2001b). Hazardous waste disposal sites, landfills, and waste incinerators also release n-hexane into the environment.

Hexane is a constituent in the paraffin fraction of crude oil and natural gas.

Hexane is extremely volatile, existing in the vapour phase in air. It is estimated to have a half-life of 2.9 days. Hexane reacts primarily with photo-chemically produced hydroxyl radicals; reactions with nitrate radicals occur mostly at night. Volatilization from soil and surface water is the most probable removal mechanism, though in aquatic systems it may partition out to organic particles and sediment. The half-life of hexane in water is from 2.7 hours to 6.8 days. In soils, it is only slightly mobile based on a Koc (octanol/water coefficient) of 1250 to 4100 (HSDB, 2001b; ATSDR, 1999).

Bioconcentration is unlikely based on low bioconcentration factors of 2.24 and 2.89 (HSDB, 2001b; ATSDR, 1999).

Acute (short-term) overexposure to hexane vapour can cause dizziness, giddiness, nausea, headache and irritation of the eyes, nose and throat (USEPA, 1994). Chronic inhalation exposure at sufficient

concentrations is associated with polyneuropathy, characterized by numbness in the extremities, muscular weakness, blurred vision, headache and fatigue (USEPA, 1994).

An acute exposure limit for n-hexane of $17,600 \mu\text{g}/\text{m}^3$ was estimated from the 8-hour time-weighted average (TWA) exposure limit recommended by American Conference of Governmental Industrial Hygienists (ACGIH, 1997) for occupational exposures to n-hexane ($176,000 \mu\text{g}/\text{m}^3$). A 10-fold safety factor was applied to this TWA to account for sensitive individuals.

The chronic exposure limit for n-hexane was based on the USEPA assessment of hexane which determined an inhalation RfC for n-hexane of $200 \mu\text{g}/\text{m}^3$. The USEPA RfC was based on an epidemiological inhalation study which demonstrated neurotoxic electro-physiological alterations at an air concentration of $204 \text{ mg}/\text{m}^3$ (IRIS, 2009). It is equivalent to an RfD of $66 \mu\text{g}/\text{kg}$ body weight/day. A safety factor of 100 was incorporated to account for sensitive individuals, for the use of a lowest observed adverse effect level (LOAEL) rather than a no observed adverse effects level (NOAEL) and a safety factor of 3 was incorporated due to an absence of reproductive and chronic respiratory data. This RfD was also used for the assessment of oral exposures.

1.4.3 Hydrogen Sulphide

Hydrogen sulphide is a poisonous, colourless gas with a characteristic odour of rotten eggs. It naturally occurs in the gases of volcanoes, sulphur springs, undersea vents, swamps and stagnant bodies of water and in crude petroleum and natural gas. Additionally, bacteria, fungi, and actinomycetes release hydrogen sulphide during the decomposition of sulphur containing proteins and by the direct reduction of sulphate.

Hydrogen sulphide is frequently encountered in various industries and may be released to the environment as a result of their operations. Some of these industries include natural gas production, municipal sewage pumping and treatment plants, landfilling, swine containment and manure handling, pulp and paper production, construction in wetlands, asphalt roofing, pelt processing, animal slaughter facilities, tanneries, petroleum refining, petrochemical synthesis, coke production plants, viscose rayon manufacture, sulphur production, iron smelting, and food processing (ASTDR, 2006).

In a retrospective epidemiologic study using cancer registry data from 1981 to 1990 for residents of Rotorua, New Zealand, the authors of the study concluded that the lack of adequate exposure information did not permit findings of causal relationships between hydrogen sulphide and cancer incidence. No studies were located regarding carcinogenicity in humans after oral or dermal exposure to hydrogen sulphide (ATSDR, 2006).



1.5 Not Assessed

1.5.1 Carbon Disulphide

Carbon disulphide (ASTDR, 2009) is a colourless liquid with a pleasant odour, resembling the smell of Chloroform. It readily volatilizes at room temperature; the vapour is more than twice as heavy as air, and readily combusts. Carbon disulphide is both man-made and naturally occurring. It is synthesized through high temperature combination of carbon and sulphur for uses as an industrial solvent. It occurs naturally in gases released from marshes. Carbon disulphide does not readily remain dissolved in water and is highly mobile in soils. It does not appear to bioconcentrate or bioaccumulate, particularly in aquatic organisms.

At high levels, carbon disulphide has been reported to have effects on the nervous system. Additional effects that have been reported include changes in breathing rhythms, induction of chest pain and skin burns. There is no definitive data as to the carcinogenicity of carbon disulphide. An RfD of 0.10 mg/kg-d and a RfC of 0.7 mg/m³ have been developed for carbon disulphide (IRIS, 2009).

1.5.2 Carbonyl Sulphide

Carbonyl sulfide is a colorless, flammable gas. It is odourless when pure but may have a sulfur odour when it contains impurities. It occurs naturally in petroleum crude oil, in salt marshes, in soil, and in volcanic gases. Worldwide, about 4 billion pounds are released each year from these natural sources. Carbonyl sulfide is produced as a by-product when carbon disulfide is made. Three companies currently make carbon disulfide in the United States. The US EPA has no information on current amounts of carbonyl sulfide made or used in the US. Companies that make pesticides are thought to be the largest users of carbonyl sulphide (US EPA, 1994).

Carbonyl sulfide dissolves when mixed with water. Some of it reacts with water to produce hydrogen sulfide. Most direct releases of carbonyl sulfide to the environment are to air. Carbonyl sulfide can also escape from water and soil exposed to air. Once in air, it can remain for several years before breaking down to other chemicals. Because of its ability to mix with water and its inability to bind well to soil, carbonyl sulfide that makes its way into the ground can move through the ground and enter groundwater.

Exposure to carbonyl sulfide can occur in the workplace or in the environment following releases to air, water, land, or groundwater. Carbonyl sulfide enters the body when breathed in with contaminated air or when consumed with contaminated food or water. It can also be absorbed through skin contact. It is not likely to be stored in the body because of its breakdown and removal (US EPA, 1994). Carbonyl sulphide has not undergone a complete evaluation and determination under US EPA's IRIS program for evidence of human carcinogenic potential (IRIS, 2009).

1.5.3 Chlorine

Chlorine is a highly reactive gas. It is a naturally occurring element. Chlorine is produced in very large amounts (23 billion pounds in 1992) by eighteen companies in the United States. US demand for chlorine is expected to increase slightly over the next several years and then decline. The expected decline in US demand is due to environmental concerns for chlorinated organic chemicals. The largest users of chlorine are companies that make ethylene dichloride and other chlorinated solvents, polyvinyl chloride (PVC) resins, chlorofluorocarbons, and propylene oxide. Paper companies use chlorine to bleach paper. Water and wastewater treatment plants use chlorine to reduce water levels of microorganisms that can spread disease to humans (US EPA, 1994).

Chlorine dissolves when mixed with water. It can also escape from water and enter air under certain conditions. Most direct releases of chlorine to the environment are to air and to surface water. Once in air or in water, chlorine reacts with other chemicals. It combines with inorganic material in water to form chloride salts. It combines with organic material in water to form chlorinated organic chemicals. Because of its reactivity chlorine is not likely to move through the ground and enter groundwater.

Exposure to chlorine can occur in the workplace or in the environment following releases to air, water, or land. People who use laundry bleach and swimming pool chemicals containing chlorine products are usually not exposed to chlorine itself. Chlorine is generally found only in industrial settings. Chlorine enters the body breathed in with contaminated air or when consumed with contaminated food or water. It does not remain in the body due to its reactivity (US EPA, 1994).

Breathing small amounts of chlorine for short periods of time adversely affects the human respiratory system. Effects range from coughing and chest pain to water retention in the lungs. Chlorine irritates the skin, the eyes, and the respiratory system. These effects are not likely to occur at levels of chlorine that are normally found in the environment. A carcinogenicity assessment of chlorine is not available at this time (IRIS, 2009).

1.6 Not Listed

1.6.1 Butane

Butane is an aliphatic hydrocarbon. It is a colourless gas with a natural gas or gasoline-like odour.

Butane is found in aerosols, lighter fuel and refills, small blow torches and camping stoves. It is used in organic synthesis. Pure grades are used in calibrating instruments and as a food additive. It is widely available. Compounds sold as 'butane' often contain mixtures of methane, ethane, propane, iso-butane and n-butane (International Programme on Chemical Safety [IPCS], 1998a).



Butane is a simple asphyxiant (that is, depriving victim of oxygen) with explosive and flammable potential. It is also widely used substance of abuse. The main target organs are in the central nervous and cardiovascular system.

No studies were located regarding carcinogenicity in humans after inhalation, oral or dermal exposure to butane (ICPS, 1998a).

1.6.2 Decane

Decane is a colourless liquid with a characteristic odour (IPCS, 1998b).

Decane is used in the paint manufacture industry and as a wood varnish. Decane can be found in the following products: scatter rugs, bathmats, and sets (rugs 2 by 2.5 m and smaller); wood office furniture, chairs, and work surfaces (modular systems); and, other rubber floor and wall coverings including cove base, wainscoting, etc. (US Environmental Defence Fund [EDF] Scorecard, 2009).

No studies were located regarding carcinogenicity in humans after inhalation, oral or dermal exposure to butane (ICPS, 1998b).

1.6.3 Ethylene

Ethylene is a flammable gas. It is used as a refrigerant and in welding and in cutting metals.

Ethylene is used in the manufacture of agricultural and pesticide products. For example, ethylene is used to manufacture ethylene oxide which is used to accelerate the ripening of fruit.

Skin contact with ethylene can cause frostbite. Exposure to ethylene can cause headaches, dizziness, fatigue, light-headedness, confusion, and unconsciousness. No studies were located regarding carcinogenicity in humans after inhalation, oral or dermal exposure to butane (New Jersey Department of Health and Senior Services, 2002).

1.6.4 Ethylene Glycol

Ethylene glycol (ATSDR, 2009) is a colourless, odourless liquid that is soluble in water. It is released into the environment primarily through industrial emissions and through the use and disposal of ethylene glycol-based automobile antifreeze and airport de-icing formulations. Ethylene glycol that is released into the environment does not persist since it is degraded within days to a few weeks in air, water, and soil. Available monitoring data indicate that ethylene glycol is only found near areas of release. Background concentrations of ethylene glycol in the environment are not available.

Since ethylene glycol is not expected to be present away from areas where it is released, background exposure of the general population to this substance is not expected to be important. The most common route of exposure to ethylene glycol for the general population is through dermal contact with ethylene glycol-containing antifreeze. However, accidental or intentional ingestion of antifreeze is the most serious route of exposure, resulting in thousands of poisoning reported each year in the United States. Occupational exposure through dermal contact and inhalation of ethylene glycol vapour or mist is expected for individuals involved in airport de-icing spray operations (ATSDR, 2007d).

An epidemiologic study on renal cancer mortality examined the work and health histories of 1,666 chemical plant employees and found no evaluation in the odds ratio for workers exposed to ethylene glycol, although the sample size was small. Exposure was presumed to be by inhalation. No studies were located regarding carcinogenicity in humans after oral or dermal exposure to ethylene glycol (ATSDR, 2007d).

1.6.5 Mercaptans

Mercaptan is a sulphur containing organic compound with the general formulas of RSH, where R is any radical, such as methyl or ethyl. Mercaptans are odorous substances offensive at low concentrations and toxic at higher levels. They are emitted from geothermal sources, industrial processes, and food processing facilities (American Society for Testing and Materials [ASTM], 2007).

Mercaptan, which has an odour of rotten eggs, is added to natural gas to impart an odour to natural gas so that leaks can be detected. There are other uses for mercaptans in industry, including jet fuel, pharmaceuticals and livestock feed additives. They are used in many chemical plants.

Methyl mercaptan, from the mercaptan group, has been evaluated by the ATSDR (1992b). Thus, the following discussion regarding the carcinogenicity of mercaptans focuses on methyl mercaptan. No studies were located regarding the cancerous effects of methyl mercaptans on humans through chronic inhalation, oral or dermal exposure to methyl mercaptans.

1.6.6 Methylcyclopentane

Methylcyclopentane is a colourless liquid with a gasoline-like odour. It is flammable and insoluble in water.

Methylcyclopentane is used as a wood stains and varnishes. The following products contain methylcyclopentane: aerosol paint concentrates, automobile body polish and cleaners, general performance sealants (PVAC, butyl, vinyl, etc.), laundry starch preparations, lubricating greases and oils, paint and varnish removers and thinners, solvent thinned interior clear finishes and stains, synthetic resin and rubber adhesives, and waterproofing compounds (Scorecard, 2009). The carcinogenicity of methylcyclopentane has not been rated in IRIS (2009).



1.6.7 Nonane

Nonane is colourless liquid with a characteristic odour (IPCS, 1995). Nonane is used in the manufacture of wood office work surfaces (i.e., modular systems) (Scorecard, 2009).

Nonane can be absorbed into the body by inhalation of its vapour and by ingestion. Effects of short-term exposure may include irritation of the eyes, the skin and the respiratory tract. Swallowing the liquid may cause aspiration into the lungs with the risk of chemical pneumonitis. The substance may cause effects on the central nervous system. Exposure to the vapour could cause lowering of consciousness (IPCS, 1995). No studies have documented the cancerous effects in humans due to inhalation, oral or dermal exposure to nonane (IRIS, 2009).

1.6.8 Octane

Octane is a colourless liquid with a characteristic odour. The vapour is heavier than air and may travel along the ground; thus, distant ignition possible. As a result of flow, agitation, etc., electrostatic charges can be generated (IPCS, 1997).

Octane is used in the manufacture of wood stains and varnishes. It may be found in the following products: aerosol paint concentrates; eye preparations (mascara, eye shadow, eye liners, eye creams etc.); furniture polish and cleaners; laundry starch preparations; lubricating oils; other automotive chemicals; paint and varnish removers and paint thinners; solvent thinned exterior undercoaters and primers, interior clear finishes, and solvent thinned interior stains; synthetic resin and rubber adhesives; wood office furniture; and, wood office work surfaces (modular systems) (Scorecard, 2009).

The substance is irritating to the eyes the skin and the respiratory tract. Swallowing the liquid may cause aspiration into the lungs with the risk of chemical pneumonitis. Exposure to high concentrations of vapour could cause lowering of consciousness (IPCS, 1997). No studies have documented the cancerous effects in humans due to inhalation, oral or dermal exposure to octane (IRIS, 2009).

1.6.9 Particulate Matter

Particulate matter (PM) consists of minute solid or liquid particles that remain suspended in the air and can be inhaled into the respiratory system. The particles vary in size, shape and chemical composition and are a vehicle for a number of compounds that adsorb onto the surface of particulates. The fine particulate fraction (less than 2.5 microns) is mainly composed of particles such as sulphates that are formed from gases, while the coarse fraction (greater than 10 microns) is formed from the break-up of larger particles originating from wind blown dust (HC, 1998).

PM originates from both natural sources and man-made sources. Natural sources include: volcanoes, wind erosion of soil and rock, forest fires and plants. The main sources associated with human activity

are industrial processes, fuel combustion, transportation and solid wastes. Industrial operations emitting very fine particles include: power stations, smelters, mills, refineries, factories, solid waste incinerators and construction activities. Other sources include agriculture, landfills and exhaust from motor vehicles, aircraft and marine vessels. Particulates can contain a variety of compounds such as acid mist, arsenic, beryllium, cadmium, lime, mercury and silica (HC, 1998).

Particle size affects removal rate and residence times in the atmosphere (Canadian Environmental Protection Act [CEPA], 2000). Smaller particles (i.e., less than $2.5\ \mu\text{m}$) can remain in air for weeks, while larger particles (i.e., greater than $2.5\ \mu\text{m}$) usually settle out in a few hours to a few days (USEPA, 1997). Effective scattering of light by smaller particles can contribute to reduced visibility (CEPA, 2000). Resident time is also dependent upon meteorological factors such as wind speed and temperature. The chemical constituents adsorbed on the surface of the particle determine its persistence (HC, 1998). As particles settle out they may deposit on water, plants, and soils. Contaminants adsorbed on the particles may then enter the food chain through direct absorption by plants, or via other pathways (HC, 1998). However, with particulate matter specifically, the pathway of concern is exposure to inhalable particles via the air pathway, particularly the finer fraction (i.e., less than $2.5\ \mu\text{m}$) which can penetrate deeper into the lungs.

Fine particulate matter (PM_{2.5}) can enter deep into the airways where there is the greatest potential for health effects; however, the chemical composition of the particle will also determine its effect on health. Some of the particles themselves may be toxic or they may have toxic elements adsorbed onto them.

The main health effects of concern with PM exposure are effects on pulmonary function, increased respiratory symptoms and aggravation of existing heart and lung disease as measured by increased physician visits, hospitalization and mortality. Particles in the lung may also impede the natural ability of the respiratory system to clear itself of foreign matter and may affect other body defence mechanisms. Studies indicate an association between premature mortality due to respiratory disease and airborne particulates (among other air pollutants).

The elderly, those with chronic pulmonary or heart disease and the very young seem to be the most vulnerable segments of the population to particulate air pollution, in addition to asthmatics, smokers and people with the flu or bronchitis (HC, 1998).

The acute exposure limit for PM_{2.5} of $30\ \mu\text{g}/\text{m}^3$ was based on the Canada-wide standard recommended for 24-hour exposure to PM_{2.5} by the Canadian Council of Ministers of the Environment (CCME, 1999). A draft reference level of $15\ \mu\text{g}/\text{m}^3$ has also been developed based on a regression of hospitalization rates versus PM_{2.5} concentrations in different cities (CEPA/Federal-Provincial Advisory Committee Working Group on Air Quality Objectives and Guidelines [CEPA/FPAC WGAQOG], 1999); however, this is not currently being proposed as a regulatory guideline.



The chronic exposure limit for PM_{2.5} of 15 µg/m³ was based on the National Ambient Air Quality guideline for annual exposure to PM_{2.5} developed by the Environmental Protection Agency (USEPA, 1997). Both these guidelines were developed based on health considerations.

1.6.10 Pentane

Pentane is a colourless liquid with a gasoline-like odour. The vapour is heavier than air and may travel along the ground; distant ignition possible, and may accumulate in low ceiling spaces causing deficiency of oxygen. Pentane reacts with strong oxidants (e.g., peroxides, nitrates and perchlorates), causing fire and explosion hazards. It will also attack some forms of plastics, rubber and coatings (IPCS, 1999).

Pentane is used as an additive in automotive, aviation, and farm fuels, and in making ice and low-manufactured for use in laboratories (e.g., for liquid chromatography). It may also be found in the following products: aerosol paint concentrates; loose mineral wool fiber (blowing and pouring); lubricating oils; synthetic resin and rubber adhesives (Scorecard, 2009).

Swallowing the liquid may cause aspiration into the lungs with the risk of chemical pneumonitis. The substance may cause effects on the central nervous system. Repeated or prolonged contact with skin may cause dermatitis (IPCS, 1999). No studies have documented the cancerous effects in humans due to inhalation, oral or dermal exposure to pentane (IRIS, 2009).

1.6.11 Propane

Propane is a colourless gas or liquid which often has a foul smelling odorant added. The gas is heavier than air and may travel along the ground; distant ignition possible, and may accumulate in low ceiling spaces causing deficiency of oxygen. As a result of flow, agitation, etc., electrostatic charges can be generated (Scorecard, 2009).

Propane is the principal component to Liquefied Petroleum Gas (LPG). It is used as a household, industrial and vehicle fuel, as a refrigerant and aerosol, and in manufacturing other chemicals.

Exposure to high concentrations of propane may cause dizziness, lightheadedness, and unconsciousness. Extremely high concentrations may cause death by suffocation from lack of oxygen (New Jersey Department of Health and Senior Services, 2004a). On loss of containment, propane evaporates very quickly displacing the air and causing a serious risk of suffocation when in confined areas. Rapid evaporation of the liquid may cause frostbite. The substance may cause effects on the central nervous system (IPCS, 2003). No studies have documented the cancerous effects in humans due to inhalation, oral or dermal exposure to propane (IRIS, 2009).

1.6.12 Propylene

Propylene is a colourless gas with a slight odour, or is a liquid under pressure. The gas is heavier than air and may travel along the ground; distant ignition possible and may accumulate in low ceiling spaces causing deficiency of oxygen. As a result of flow, agitation, etc., electrostatic charges can be generated (Scorecard, 2009).

Propylene is used in the production of many organic chemicals including resins, plastics, synthetic rubber and gasoline.

On loss of containment this gas can cause suffocation by lowering the oxygen content of the air in confined areas. Rapid evaporation of the liquid may cause frostbite. The substance may cause effects on the central nervous system. Exposure could cause lowering of consciousness (Scorecard, 2009). No studies have documented the cancerous effects in humans due to inhalation, oral or dermal exposure to propylene (IRIS, 2009).

1.6.13 Straight-Chain Alkane Hydrocarbons (n-C₁₁ through n-C₁₅)

Straight-chain alkanes contain only single carbon-carbon bonds, where carbons are attached to no more than two other carbons in a continuous chain. Straight-chain hydrocarbons in the range of n-C₁₁ to n-C₁₅ are liquids at room temperature and form the major part of diesel and aviation fuel (Potter and Simmons, 1998).

Data is typically unavailable for many of the individual components of petroleum hydrocarbons; however, it is available for fractions of hydrocarbons. The Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG) divided hydrocarbon fractions into aliphatics and aromatics. For the aliphatics, hydrocarbons were grouped into C_{>10} to C₁₂ and C_{>12} to C₁₆, which encompasses the alkane hydrocarbons n-C₁₁ to n-C₁₅ (Edwards et al., 1997). There is minimal toxicity data available on individual components within the C₉ to C₁₆ aliphatic range. Data which have been used to develop oral and inhalation criteria for this fraction were studies on JP-8 (C₉ to C₁₆) and studies on dearomatized petroleum streams which together cover the entire range of the fraction. The RfC developed from these studies was 1.0 mg/m³ and the RfD was 0.1 mg/kg-d (Edwards et al., 1997).

1.6.14 Thiophene

Thiophene is a colourless liquid with a slight aromatic odour. Thiophene is used in organic synthesis, as an intermediate for pharmaceuticals, and to make resins and dyes.

Exposure to thiophene may be through inhalation or dermal contact. Inhalation can cause irritation of the nose, throat and lungs and cause coughing, wheezing, and/or shortness of breath. Dermal contact can cause skin and eye irritation and may cause burns to the eye. Exposure to high levels can cause nausea,



vomiting and headaches (New Jersey Department of Health and Senior Services, 2000b). No studies have documented the cancerous effects in humans due to inhalation, oral or dermal exposure to thiophene (IRIS, 2009).

1.6.15 1,2,4-Trimethylbenzene

1,2,4-Trimethylbenzene (also known as pseudocumene) is a colourless liquid with a distinctive, sweet odour. It is primarily used as a gasoline additive, and is also used to make pharmaceuticals, dyes and other chemicals, and is found in many solvents (New Jersey Department of Health and Senior Services, 2008). It may be found in the following products: building and construction plastic foam insulation, including pipe and block; flat water thinned interior paints and tinting bases; mineral wool building batts, blankets and rolls; miscellaneous paint-related products; non-wood upholstered office side and arm chairs; other rubber floor and wall coverings incl cove base, wainscoting, etc.; paint thinners; scatter rugs, bathmats, and sets (rugs 2 x 2.5 m and smaller); sheet vinyl flooring; wood office furniture; wood office secretarial chairs; wood office work surfaces (modular systems) (Scorecard, 2009).

1,2,4-Trimethylbenzene is irritating to the eyes the skin and the respiratory tract. If it is swallowed, aspiration into the lungs may result in chemical pneumonitis. The substance may cause effects on the central nervous system, such as fatigue, dizziness, lack of coordination, anxiety, and confusion. Effects of long term exposure may include that lungs may be affected by repeated or prolonged exposure, resulting in chronic bronchitis. 1,2,4-Trimethylbenzene may have effects on the central nervous system and blood (IPCS, 2002). No studies have documented the cancerous effects in humans due to inhalation, oral or dermal exposure to 1,2,4-trimethylbenzene (IRIS, 2009).

1.7 Other

1.7.1 Total Reduced Sulphur (TRS) Compounds

TRS is a gaseous mixture of compounds consisting mainly of hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide. TRS compounds produce offensive odours similar to rotten eggs or cabbage. Industrial sources of TRS include the steel industry, pulp and paper mills, refineries and sewage treatment facilities. Natural sources include swamps, bogs and marshes. TRS compounds are not normally considered a health hazard, although each component has its own characteristics and effects. The most commonly reported health concerns related to TRS substances are nausea and headaches. TSR are, however, a primary cause of odours. Once released into the atmosphere, oxidation products of TRS compounds, such as sulphuric acid, contribute to the acidity of the environment (Ontario Ministry of the Environment, 2007).

TRS Compounds include the following PCOCs: carbon disulphide, carbonyl sulphide, and hydrogen sulphide. Please refer to the appropriate sections above for toxicological profiles.

1.7.2 Volatile Organic Compounds (VOCs)

A VOC is any organic compound that participates in atmospheric photochemical reactions, except those designated by the US EPA as having negligible photochemical reactivity. Many VOCs are found in emissions from burning coal, oil and gasoline and in evaporation at gasoline service stations. These and other sources, such as solvents, cleaners and paints, all contribute to the baseline level of VOCs found in outdoor air. Some VOCs are also released from tobacco smoke. VOCs are of special concern because they photo-chemically react (in sunlight) to cause ozone or smog (US EPA, 2007b).

Certain VOCs, such as benzene, 1,3-butadiene, and others are known carcinogens. Many others are either probable or possible carcinogens. Refer to individual toxicity profiles (e.g., ATSDR or IRIS) for complete information regarding known, possible, or probable cancerous effects of VOCs.

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Appendix 2 Questionnaire

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EXAMPLE OF THE QUESTIONNAIRE

1. BACKGROUND

Environment Canada intends to regulate emissions of volatile organic compounds (VOCs), benzene, and methane from the oil and gas sector and oil sands in particular. Environment Canada is also interested in exploring potential mitigation measures that currently exist or are in the process of development for reducing or preventing emissions of total hydrocarbons, VOC, benzene and methane from tailings ponds (and mine face if possible).

WorleyParsons was awarded a contract by Environment Canada to review and summarize emission factors for mine faces and tailings ponds as well as other sources of VOCs, benzene and methane associated with oil sands facilities. Additionally, a portion of the scope was to identify control technologies for these emissions from oil sands facilities.

The following questionnaire has been compiled to assist WorleyParsons in gathering data from oil sands operators if they are willing to assist with this project. WorleyParsons would like to compile data on total hydrocarbon, VOC, benzene and methane emissions from tailings ponds and mine faces of the oil sands mining facilities, and the current mitigation options used to reduce these emissions on the basis of practical experience and real data. WorleyParsons requests the support of oil sands operators to assist with this project.

It should be noted that WorleyParsons recognizes that oil sands operators may have concerns with the provision of data as a result of confidentiality. For this reason, WorleyParsons is committed to the following:

1. Data will not be disclosed in a manner that could identify the facility or operator. Data will be presented in statistical form with no reference given to the operator without their express consent.
2. Confidential or proprietary information will not be disclosed with the exception of generalizations if required.
3. WorleyParsons staff are willing to sign a confidentiality agreement with any operator that agrees to provide data and will remain subject to their terms and conditions.

*****Note that the confidentiality agreement is currently under internal review and may be amended prior to sending the questionnaire.*****



WorleyParsons

resources & energy

2. QUESTIONNAIRE

1. Company Name:

2. Facility Name:

3. Facility Location:

4. Is the facility operational or in construction?

5. What is the daily production capacity (actual or proposed; barrels per day)?

6. What is the annual production capacity (actual or proposed; barrels per annum)?

7. Please specify the mining method (in situ vs. surface):

8. What is the total area of mine?

9. How many tailings ponds are on Site?

10. What is the total area of tailings pond(s)?

11. What is the area of each tailings pond?

12. Please provide a summary and a schematic diagram describing the current oil sands production process.

13. Are air emissions monitored on site?

14. If yes, what parameters do you monitor? VOC's, Benzene, Total Hydrocarbons, Methane?

15. Please provide a summary of air monitoring data.



16. Were air emissions predicted prior to monitoring? If yes, how were they predicted?
17. How do the predicted versus measured air emissions compare (please provide relative percent difference (RPD) or predicted values)?
18. If emission factors were used, please provide the basis of the calculation for the following compounds:
- a. Volatile organic compounds
 - b. Methane
 - c. Benzene
 - d. Total Hydrocarbons
 - e. Other compounds

ENVIRONMENT CANADA

**REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
AND OPTIONS FOR REDUCING EMISSIONS**

19. If emissions factors were not used please provide model or assumptions for predicting air emissions from mine faces and tailings ponds, as well as the reference of the method used.

20. Please describe the technologies used on-site to control/reduce air emissions from mine faces and tailings ponds and their estimated removal efficiency.

21. Please describe advantages and difficulties encountered from using the technologies reported in question 20.

Syncrude Answers to Questionnaire

1. BACKGROUND

Environment Canada intends to regulate emissions of volatile organic compounds (VOCs), benzene, and methane from the oil and gas sector and oil sands in particular. Environment Canada is also interested in exploring potential mitigation measures that currently exist or are in the process of development for reducing or preventing emissions of total hydrocarbons, VOC, benzene and methane from tailings ponds (and mine face if possible).

WorleyParsons was awarded a contract by Environment Canada to review and summarize emission factors for mine faces and tailings ponds as well as other sources of VOCs, benzene and methane associated with oil sands facilities. Additionally, a portion of the scope was to identify control technologies for these emissions from oil sands facilities.

The following questionnaire has been compiled to assist WorleyParsons in gathering data from oil sands operators if they are willing to assist with this project. WorleyParsons would like to compile data on total hydrocarbon, VOC, benzene and methane emissions from tailings ponds and mine faces of the oil sands mining facilities, and the current mitigation options used to reduce these emissions on the basis of practical experience and real data. WorleyParsons requests the support of oil sands operators to assist with this project.

2. QUESTIONNAIRE

1. Company Name:

Syncrude Canada Ltd.

2. Facility Name:

Mildred Lake and Aurora North

3. Facility Location:

Syncrude's **Mildred Lake Plant Site** is a large, integrated oil sands mine, bitumen extraction plant, utilities plant and upgrading facility located approximately 40 km north of Ft. McMurray at Mildred Lake. The Mildred Lake Oil Sands Plant is situated on Oil Sands Leases 17 and 22 located on portions of Townships 92 and 93, Ranges 10 and 11, west of the 4th Meridian. The Main Stack, the tallest structure at the Mildred Lake Plant Site, is located at 57° 2' 27" North latitude and 110° 36' 57" West longitude (UTM 6322111N, 462632E).

Syncrude's **Aurora North Mine**, an integrated oil sands mining, utilities, and extraction operation, is located 35 km northeast of the Mildred Lake Plant Site, across the Athabasca River on Oil Sands Leases 10, 12 and 34 in Township 96, within Ranges 9, 10 and 11, West of the 4th Meridian. The PSV Vent stack for Aurora Train 1, one of the tallest structures within the Extraction/Utilities Plant at the Aurora North Mine Site, is located at 57° 17' 56" North latitude and 111° 30' 12" West longitude (UTM N6350774, E469674). The Syncrude Mildred Lake Plant Site is connected to the Aurora North Mine Site via a service corridor which contains power connections to the Alberta grid, natural gas pipelines, bitumen froth product pipelines from Aurora to Mildred Lake site, water transport lines from Mildred Lake site to the Aurora mine site and road connections to Hwy 63. The service corridor is located on portions of Township 93, Ranges 10 and 11, west of the 4th Meridian.

4. Is the facility operational, in construction, or under approval?

Operational.

5. What is the daily production capacity (actual or proposed; barrels per day)?

More than 17.8 million cubic meters of Syncrude Sweet Blend in 2007.

6. What is the total surface area of the active mine face?

A definition of "active mine face" is needed in order to respond. The mine is in a constant state of flux and the surface area of exposed benches, overburden, and oilsand feed faces varies constantly.

7. How many tailings ponds are on site, and what is the surface area of each pond?

The following process water ponds are located at Syncrude:

Aurora Settling Basin (6 square kilometres)

Mildred Lake Settling Basin (10 square kilometres)

East Inpit (1.5 square kilometres)

West Inpit (6 square kilometres)

South West Sand Storage (6 square kilometres)

South West Inpit (1square kilometre)

8. If air emissions are monitored on site, what parameters do you monitor? VOC's, Benzene, Total Hydrocarbons (THC), Methane?

For Syncrude Fugitive Emission measurement programs the target air pollutants are methane, volatile organic compounds (which includes benzene), reduced sulphur compounds, and inerts (which includes CO₂).

9. Please provide a summary of air monitoring data.

The following table provides a summary of annual fugitive emissions from the active mining areas and the tailings ponds. The VOC and benzene emission data is consistent with the Syncrude Section 71 submission (based on 2006 fugitive emission estimates):

	VOC	Benzene	Methane	RSC
	tpy	tpy	tpy	tpy
Mildred Lake mine	3,004	0.7	*See below	21
Aurora mine	15,291	.03		63
Mine total	18,295	.73		84
Mildred Lake ponds	5994	39		62
Aurora ponds	461	.16		9
Ponds total	6,455	39.2		71

*Methane reported as the total of mine face plus tailings fugitive emissions in 2007:

Mildred Lake (23,975 tonnes/year)

Aurora (1,852 tonnes/year)

10. Were air emissions from tailings ponds and mine faces predicted prior to monitoring? If yes, how were they predicted?

Syncrude has conducted extensive fugitive emission monitoring programs at the Mildred Lake site and at the Aurora site since 1998. The emission data generated from these monitoring programs is utilized in preparing annual emission estimates from the process ponds and mining areas.

11. What are the estimated annual emissions of VOC, CH₄, Benzene, and THC that originate from tailings ponds and mine faces, and how were these estimates generated?

Refer to response to question 9.

12. How do the predicted versus measured air emissions compare for tailings ponds and mine faces (please provide relative percent difference (RPD) or predicted values)?

Not applicable. Emission estimates are based on measured values obtained from fugitive emission measurement programs.

13. If emission factors were used, how were they used to calculate the following emissions from the mine faces and tailings ponds?

At the Mildred Lake site and at the Aurora site, as part of fugitive emission measurement programs, isolation flux measurements were performed on the surface of tailings ponds and on the surface of exposed oilsands material (i.e. bench top, mine face, overburden, conveyors) in mining areas to develop emission factors and speciation profiles that may be used to better estimate emissions from the subject sources. The target analytes were methane, volatile organic compounds (including benzene), reduced sulphur compounds and carbon dioxide. An overview of the methodology utilized is provided in Appendix 1 of this document.

- a. Volatile organic compounds
- b. Methane
- c. Benzene
- d. THC

14. If emissions factors were not used please provide model or assumptions for predicting air emissions from mine faces and tailings ponds, as well as the reference of the method used.

Not applicable.

15. Please describe the technologies or measures used on-site to control/reduce air emissions from mine faces and tailings ponds and their estimated removal efficiency.

The Syncrude Naphtha Recovery Units recovers naphtha from the extraction froth treatment units streams so as to minimize the discharge of naphtha to the Mildred Lake Settling Basin (MLSB). This technology reduces air emissions from the ponds. Naphtha recovery by the on-line NRU's averaged 87 % during the 2005-2007-time period.

Syncrude processes wastewater streams from the Froth Treatment Units (inclined plate separators and centrifuges) through an NRU to minimize naphtha discharge to the ponds when the NRU is operating.

The Energy Utilities Board (EUB) regulates naphtha loss at Syncrude to less than 0.0043 barrels per barrel of bitumen processed.

16. Please describe advantages and difficulties encountered from using the technologies or measures reported in question 15.

The system performs as expected and helps Syncrude to achieve industry –leading performance while meeting the tight regulatory requirement.

17. Which additional control technologies or measures are currently under consideration? Please describe any related pilot testing or research.

Not applicable.

Appendix 1

Measurement of Emissions from Syncrude Canada's Mildred Lake Settling Basin: Fall 2006

Prepared By Clearstone Engineering, Mar 31, 2007

Section 2 Methodology

2.1. Flux Monitoring

The flux measurements were performed using the U.S. EPA (Kienbusch, 1986) isolation flux chamber design shown in Figure 1. Furthermore, the U.S. EPA protocol for performing flux measurements on surface impoundments was followed (Gholson et al., 1989). This method involves purging the chamber with a known flow rate of purified air until a peak or steady-state pollutant concentration is achieved in the exhaust stream, and then collecting a sample of the chamber exhaust for detailed analysis. A simple mass balance is performed to determine the flux rate. This is done using the following relation:

$$E_i = C_i Q / A$$

where,

E_i = emission flux rate of the target species,

C_i = concentration of the target species,

Q = purified air sweep rate, and

A = surface area enclosed.

The parameters recorded for each flux measurement included the following: water temperature, ambient temperature, barometric pressure, time and date, temperature inside the chamber, purified air sweep rate or exhaust gas flow rate (depending on the type of measurement), and THC concentrations in the chamber exhaust. The THC concentrations were monitored using a TVA 1000 organic vapour analyser calibrated to methane and equipped with both a flame ionisation detector (FID) and a photo ionisation detector (PID).

Several key assumptions inherent in use of the flux chamber technique are:

- good mixing occurs in the chamber,
- a representative gas sample is collected for analysis,
- no physical or chemical reactions occur between the inside surfaces of the chamber and the emissions (e.g., condensation), and
- the natural emission process is not disrupted or significantly altered by the presence of the chamber.

The first three assumptions were addressed through appropriate design and quality assurance(QA)/quality control (QC) measures (i.e., a standard chamber design was used, a method blank was run, and the selected protocol as well as previous unpublished data showed good recovery efficiencies for the target pollutants). The validity of the last assumption is dependent on the nature of the emission process. Flux chambers do not attempt to replicate natural wind effects at the measurement surface, may cause some change in surface temperatures and, in the case of liquids, may alter small scale surface currents (Gholson et al., 1989). Accordingly, disruptions caused by the flux chamber may only be insignificant in situations where resistances at the air-surface interface are small compared to those below the surface, or where the emission rate is kinetically controlled and not mass-transfer controlled. Moreover, pollutant concentrations in the chamber must not be allowed to build up to greater than 10 percent of the equilibrium vapour-phase concentration (this would tend to suppress the emission rate). This was assured through careful real-time monitoring of conditions in the chamber. The sensitivity of the method depends on the detection limit of the selected analytical technique. The results are generally within 50 to 124 percent of the true emission rate (Kienbusch, 1986). Thus, the results of isolation flux chamber measurements may tend to understate actual emissions.

2.2. Vapour/Air Sampling

All vapour or air samples were collected in evacuated SilcoCanTM canisters due to their superior resistance to sample degradation. The special Silcosteel-treated lining is fairly inert to reactive sulphur compounds such as H₂S and methyl mercaptan and polar compounds such as alcohols, oxygenates and aldehydes. SilcoCanTM canisters were also used for the SF₆ tracer measurements as they offered a convenient and reliable means of collecting 15-minute integrated samples.

2.3. Analytical

All chemical analyses were performed by Alberta Research Council (ARC) at their main laboratory in Vegreville. A brief summary of the quality control/quality assurance procedure and different analytical procedures that were applied is provided in the subsections below.

2.3.1. Quality-Control/Quality-Assurance (QA/QC) Procedures

QA/QC measures included, but were not be limited to, adherence to established sampling and analytical protocols, regular calibrations, use of method and travel blanks, and use of data-collection and sample-tracking sheets. The isolation flux chambers (IFCs) were cleaned regularly and periodic method blanks were performed to confirm that the systems were free of any contamination. In addition, the flux measurements were performed in the general order of increasing source strengths.

2.3.2. Inerts

The analysis for inerts determined concentrations of N₂, O₂, CO₂ and CO in the gas samples. The analyses were performed by gas chromatography with thermal conductivity detection (GC/TCD). The minimum detection limit for this method was 50 ppm for CO₂ and 100 ppm for the other inerts.

2.3.3. Reduced Sulphur Compounds (RSCs)

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

Table 1. Listing of the target reduced sulphur compounds (RSCs).

CAS Number Substance Name

638-02-8	2,5-Dimethyl Thiophene	
872-55-9	2-Ethyl Thiophene	
554-14-3	2-Methyl Thiophene	
616-44-4	3-Methyl Thiophene	
592-88-1	Allyl Sulphide	
109-79-5	Butyl Mercaptan	
544-40-1	Butyl Sulphide	
75-15-0	Carbon Disulphide	
463-58-1	Carbonyl Sulphide	
624-92-0	Dimethyl Disulphide	
75-18-3	Dimethyl Sulphide	
3658-80-8	Dimethyl Trisulphide	
75-08-1	Ethyl Mercaptan	
352-93-2	Ethyl Sulphide	
111-31-9	Hexyl Mercaptan	
7783-06-4	Hydrogen Sulphide	
75-33-2	Isopropyl Mercaptan	
74-93-1	Methyl Mercaptan	
107-03-9	Propyl Mercaptan	
7446-09-5	Sulphur Dioxide	
110-02-1/513-44-0 and 513-53-1	Thiophene/ <i>iso</i> and <i>sec</i> Butyl Mercaptan	110-66-7 <i>n</i>
	Amyl Mercaptan	
1679—09-0	<i>tert</i> Amyl Mercaptan	
75-66-1	<i>tert</i> Butyl Mercaptan	

2.3.4. C₁ through C₄ Gases

The analyses for lighter VOCs were done by gas chromatography with flame ionization detection (GC/FID). The minimum detection limit for individual compounds was 50 ppb. The target compounds are summarized in Table 2.

2.3.5. C₅ through C₁₂₊ Gases

Analyses for the heavier VOCs in gas samples were done by mass spectroscopy (GC/MS) with cryogenic focusing to provide a minimum detection limit of 10 µg/m³. For liquid samples, a purge and trap GC/MS analysis was performed for compounds in the C₅ to C₁₂ range and a

solvent extraction GC/MS analysis was done for compounds heavier than C₁₂. The GC/MS was operated in full scan (or total ion) mode. In this operating mode the substance type denoted by each chromatographic peak is determined based on the best match quality achieved with the available entries in the instrument's mass spectral library. Additionally, the instrument was calibrated using a calibration standard of selected target compounds (see Table 3), and therefore provided exact matches where these substances occurred in the collected samples.

2.4. Data Management

All analytical results were maintained electronically in a computer database for efficient management and processing. Microsoft's Access data management system was used for this purpose. An electronic copy of the database is provided with this report. The database comprises the following tables:

Air Impurities – Presents the net composition profile of the impurities in each supply cylinder of purge air used during the flux measurements.

Flux Measurements - Presents the following data for each isolation flux chamber (IFC) emission measurement: field measured total organic vapour concentration in the chamber exhaust at the end of the measurement, sample identification code if a sample of the IFC exhaust was collected, identification code of the sweep air cylinder, final temperature inside the IFC (°C), local barometric pressure (kPa), air sweep/purge rate (L/min) (after any rotameter specific corrections), temperature of the liquid surface (°C), ambient temperature (°C), and name of the emission zone and emission source for which the measurement applies.

Table 2. Listing of the target substances in the C₁ to C₄ range.

CAS Number	Substance Name
106-99-0	1,3-Butadiene
106-98-9	1-Butene
74-86-2	Acetylene
106-97-8	Butane
74-84-0	Ethane
107-00-6	Ethylacetylene
74-85-1	Ethylene
75-28-5	Isobutane
115-11-7	Isobutylene
74-82-8	Methane
74-98-6	Propane
115-07-1	Propylene
74-99-7	Propyne
590-18-1	Cis-2-Butene
624-64-6	Trans-2-Butene

Table 3. Listing of the target substances in the C₅ to C₁₂₊ range.

CAS Number	Substance Name
630-20-6	1,1,1,2-Tetrachloroethane
71-55-6	1,1,1-Trichloroethane
79-34-5	1,1,2,2-Tetrachloroethane
79-00-5	1,1,2-Trichloroethane
75-34-3	1,1-Dichloroethane
75-35-4	1,1-Dichloroethylene
563-58-6	1,1-Dichloropropylene
87-61-6	1,2,3-Trichlorobenzene
96-18-4	1,2,3-Trichloropropane
120-82-1	1,2,4-Trichlorobenzene
95-63-6	1,2,4-Trimethylbenzene
96-12-8	1,2-Dibromo-3-chloropropane
106-93-4	1,2-Dibromoethane
95-50-1	1,2-Dichlorobenzene
107-06-2	1,2-Dichloroethane
78-87-5	1,2-Dichloropropane
108-67-8	1,3,5-Trimethylbenzene
541-73-1	1,3-Dichlorobenzene
142-28-9	1,3-Dichloropropane
106-46-7	1,4-Dichlorobenzene
594-20-7	2,2-Dichloropropane
110-75-8	2-Chloroethoxyethylene
95-49-8	2-Chlorotoluene
106-43-4	4-Chlorotoluene
71-43-2	Benzene
108-86-1	Bromobenzene
75-27-4	Bromodichloromethane
75-25-2	Bromoform
74-83-9	Bromomethane
56-23-5	Carbon tetrachloride
108-90-7	Chlorobenzene
75-00-3	Chloroethane
67-66-3	Chloroform
124-48-1	Dibromochloromethane
74-95-3	Dibromomethane
100-41-4	Ethyl benzene
87-68-3	Hexachlorobutadiene
98-82-8	Isopropylbenzene (Cumene)
1634-04-4	MTBE
75-09-2	Methylene chloride
91-20-3	Naphthalene
100-42-5	Styrene
127-18-4	Tetrachloroethylene
108-88-3	Toluene

79-01-6	Trichloroethylene
75-69-4	Trichlorofluoromethane
75-01-4	Vinyl chloride
156-59-2	cis-1,2-Dichloroethylene
10061-01-5	cis-1,3-Dichloropropylene
108-38-3 / 106-42-3	m,p-Xylene
104-51-8	n-Butylbenzene
103-65-1	n-Propylbenzene
95-47-6	o-Xylene
99-87-6	p-Isopropyltoluene
135-98-8	sec-Butylbenzene
98-06-6	tert-Butylbenzene
156-60-5	trans-1,2-Dichloroethylene
10061-02-6	trans-1,3-Dichloropropylene

Site Emission Factors - Lists the emission factor(s) applied to each listed source.

Site Speciation Profiles - Lists the speciation profiles applied to the emission estimates for each listed source.

SYN – Raw analytical results provided by ARC. The table is provided by ARC in a Paradox format and is then converted to an Access format. The table is proofed before being used to ensure that each record has a proper molecular weight, CAS number, and chemical formula. Where a range of compounds comes through the chromatograph as a single hump, the hump is treated as a single substance and is assigned an average molecular weight and chemical formula, as well as a unique CAS number. All humps with similar retention times are assumed to be the same blend of compounds. The molecular weight of unknown peaks and unresolved humps are estimated based on the values of known peaks with similar retention times.

Point Vapour Profile - Net composition of the vapour fraction of each flux chamber sample (i.e., after correcting for trace impurities in the sweep air).

Zone Emission Factors - Average emission factors determined for each zone on each source.

Zone Vapour Profiles - Average net speciation profiles for the emissions from each zone on each pond. These profiles are determined based on the speciated emissions from each measurement point in the corresponding zones.

2.5. Data Processing

Where reduced sulphur compounds are reported as equivalent sulphur, the values denote the total amount of sulphur contained in the substance. Where hydrocarbons are reported as equivalent CH₄ values, the value is calculated as the amount of methane that would be required to provide the same amount of carbon as is contained in the actual sample. Analytical results (concentrations) are reported in ppm and µg/m³. Speciation profiles are reported in mole percent and weight percent.

2.3.2. Inerts

The analysis for inerts determined concentrations of N₂, O₂, CO₂ and CO in the gas samples. The analyses were performed by gas chromatography with thermal conductivity detection (GC/TCD). The minimum detection limit for this method was 50 ppm for CO₂ and 100 ppm for the other inerts.

2.3.3. Reduced Sulphur Compounds (RSCs)

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

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75-33-2	Isopropyl Mercaptan
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107-03-9	Propyl Mercaptan
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2.3.4. C₁ through C₄ Gases

The analyses for lighter VOCs were done by gas chromatography with flame ionization detection (GC/FID). The minimum detection limit for individual compounds was 50 ppb. The target compounds are summarized in Table 2.

2.3.5. C₅ through C₁₂+ Gases

Analyses for the heavier VOCs in gas samples were done by mass spectroscopy (GC/MS) with cryogenic focusing to provide a minimum detection limit of 10 µg/m³. For liquid samples, a purge and trap GC/MS analysis was performed for compounds in the C₅ to C₁₂ range and a solvent extraction GC/MS analysis was done for compounds heavier than C₁₂. The GC/MS was operated in full scan (or total ion) mode. In this operating mode the substance type denoted by each chromatographic peak is determined based on the best match quality achieved with the available entries in the instrument's mass spectral library. Additionally, the instrument was calibrated using a calibration standard of selected target compounds (see Table 3), and therefore provided exact matches where these substances occurred in the collected samples.

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74-85-1	Ethylene
75-28-5	Isobutane
115-11-7	Isobutylene
74-82-8	Methane
74-98-6	Propane
115-07-1	Propylene
74-99-7	Propyne

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79-00-5	1,1,2-Trichloroethane
75-34-3	1,1-Dichloroethane
75-35-4	1,1-Dichloroethylene
563-58-6	1,1-Dichloropropylene
87-61-6	1,2,3-Trichlorobenzene
96-18-4	1,2,3-Trichloropropane
120-82-1	1,2,4-Trichlorobenzene
95-63-6	1,2,4-Trimethylbenzene
96-12-8	1,2-Dibromo-3-chloropropane
106-93-4	1,2-Dibromoethane
95-50-1	1,2-Dichlorobenzene
107-06-2	1,2-Dichloroethane
78-87-5	1,2-Dichloropropane
108-67-8	1,3,5-Trimethylbenzene
541-73-1	1,3-Dichlorobenzene
142-28-9	1,3-Dichloropropane
106-46-7	1,4-Dichlorobenzene
594-20-7	2,2-Dichloropropane
110-75-8	2-Chloroethoxyethylene
95-49-8	2-Chlorotoluene
106-43-4	4-Chlorotoluene
71-43-2	Benzene
108-86-1	Bromobenzene
75-27-4	Bromodichloromethane
75-25-2	Bromoform
74-83-9	Bromomethane
56-23-5	Carbon tetrachloride
108-90-7	Chlorobenzene
75-00-3	Chloroethane
67-66-3	Chloroform
124-48-1	Dibromochloromethane
74-95-3	Dibromomethane
100-41-4	Ethyl benzene
87-68-3	Hexachlorobutadiene
98-82-8	Isopropylbenzene (Cumene)
1634-04-4	MTBE
75-09-2	Methylene chloride
91-20-3	Naphthalene

100-42-5	Styrene
127-18-4	Tetrachloroethylene
108-88-3	Toluene
79-01-6	Trichloroethylene
75-69-4	Trichlorofluoromethane
75-01-4	Vinyl chloride
156-59-2	cis-1,2-Dichloroethylene
10061-01-5	cis-1,3-Dichloropropylene
108-38-3 / 106-42-3	m,p-Xylene
104-51-8	n-Butylbenzene
103-65-1	n-Propylbenzene
95-47-6	o-Xylene
99-87-6	p-Isopropyltoluene
135-98-8	sec-Butylbenzene
98-06-6	tert-Butylbenzene
156-60-5	trans-1,2-Dichloroethylene
10061-02-6	trans-1,3-Dichloropropylene

Site Emission Factors - Lists the emission factor(s) applied to each listed source.

Site Speciation Profiles - Lists the speciation profiles applied to the emission estimates for each listed source.

SYN – Raw analytical results provided by ARC. The table is provided by ARC in a Paradox format and is then converted to an Access format. The table is proofed before being used to ensure that each record has a proper molecular weight, CAS number, and chemical formula. Where a range of compounds comes through the chromatograph as a single hump, the hump is treated as a single substance and is assigned an average molecular weight and chemical formula, as well as a unique CAS number. All humps with similar retention times are assumed to be the same blend of compounds. The molecular weight of unknown peaks and unresolved humps are estimated based on the values of known peaks with similar retention times.

Point Vapour Profile - Net composition of the vapour fraction of each flux chamber sample (i.e., after correcting for trace impurities in the sweep air).

Zone Emission Factors - Average emission factors determined for each zone on each source.

Zone Vapour Profiles - Average net speciation profiles for the emissions from each zone on each pond. These profiles are determined based on the speciated emissions from each measurement point in the corresponding zones.

2.5. Data Processing

Where reduced sulphur compounds are reported as equivalent sulphur, the values denote the total amount of sulphur contained in the substance. Where hydrocarbons are reported as equivalent CH₄ values, the value is calculated as the amount of methane that would be required to provide

the same amount of carbon as is contained in the actual sample. Analytical results (concentrations) are reported in ppm and $\mu\text{g}/\text{m}^3$. Speciation profiles are reported in mole percent and weight perc

Suncor Answers to Questionnaire

QUESTIONNAIRE

Company Name:

- Suncor Energy Inc.

2. Facility Name:

- Suncor Energy Inc. Oil Sands

3. Facility Location:

- 22 km NE of Fort McMurray

4. Is the facility operational, in construction, or under approval?

- In operation

5. What is the daily production capacity (actual or proposed; barrels per day)?

- Current Capacity: 350,000 BPD of Synthetic Crude Oil

6. What is the total surface area of the active mine face?

- Total surface area of the active mine face is 1,621,256 m² (Based on 2008 data).

7. How many tailings ponds are on site, and what is the surface area of each pond?

Pond	Surface Area (km2)
1A	0.506
1	1.304
2/3	2.944
5	2.616
6	3.293
7	3.288
8A	2.004
8B	6.966
STP	8.829

8. If air emissions are monitored on site, what parameters do you monitor? VOC's, Benzene, Total Hydrocarbons (THC), Methane?

- Methane (CH₄), volatile organic compounds (VOCs), Benzene, Toluene, THC, RCS, H₂S, and SO₂.

9. Please provide a summary of air monitoring data.

Results from an on-site air quality monitoring program consisting of a mobile air monitoring system is summarized in the Table A below. Note that the program was only done for the tailing ponds and no testing was conducted on the mine surfaces. Another form of air monitoring was done using detailed laboratory analyses of the air grab samples which are provided in Table B. The air samples were collected at 3.9 meters above ground, while the grab samples were collected at ground level.

Table A:

<i>Summary of the onsite air monitoring conducted by AIR Monitors</i>										
Monitoring Point	Description	H2S			SO2			THC		
		Max (ppb)	Min (ppb)	Avg (ppb)	Max (ppb)	Min (ppb)	Avg (ppb)	Max (ppb)	Min (ppb)	Avg (ppb)
1	Cross wind from Pond 2/3 (east side)	2.3	1.1	1.8	2.1	0.7	1.3	3.43	3.15	3.34
2	Cross wind from Pond 2/3 (west side)	11.5	2.1	9.2	2.1	0.7	1.2	3.66	2.81	3.25
3	Partiallt downwind from Pond 2/3	25.6	11.7	17.6	2.9	1.3	2	5.24	2.44	3.98
4	Near outfall to Pond 1A	82	3.8	22.2	2.2	1.1	1.7	15.64	4.02	6.68
5	Between Ponds 1 and 1A (1A partially upwind)	4.7	2.9	5.5	3.5	1.8	2.4	29.07	4.48	11.49
6	Partially downwind of Pond 1 (along dike road)	2.1	1.5	1.8	7.9	6.6	7.3	4.65	2.99	3.8
7	Downwind of Pond 5	2.3	1	1.78	0.6	0.1	0.3	2.33	2.19	2.25
8	Upwind of Pond 5	0.4	0.1	0.2	0.3	0.2	0.3	2.23	2.2	2.22
9	Downwind of Pond 6	2.9	0.2	1.1	2.2	0.2	0.9	13.95	2.34	3.81
10	Partially downwind of Pond 6	0.9	0.3	0.7	0.9	0.6	0.8	3.66	2.45	2.7
11	Downwind of VRU and Ponds 2/3 and 5	15.1	6.2	10.3	3.4	0.6	2.6	25.12	2.78	9.84
12	Upwind of VRU but downwind of Ponds 2/3 and 5	13.9	6.5	9.8	2.9	0.5	1.2	5.62	2.81	3.67
13	Downwind of VRU, baseplant and Pond 5	6.9	4	5	140	1.3	33.1	3.53	2.49	2.87
14	Partially crosswind from North Tank Farm	16	2.3	7.4	1.7	0.3	0.7	4.89	3.18	3.85
15	Downwind of North Tank Farm	165.4	5.7	47.9	1	0.5	0.9	6.12	4.77	5.45
16	Downwind of Mannix Staion No. 5	1.4	0.5	1	0.8	0.3	0.5	2.94	2.08	2.21
17	Downwind of Williams Extraction Plant and Enbridge Tank Farm	1.6	0.4	1.1	0.8	0.1	0.4	5.78	2.17	2.6

Table B:

<i>Summary of Detailed Analysis results of air grab samples collected in parallel with the onsite ambient air monitoring program</i>									
Monitoring Point	Sample No.	Description	H ₂ S (ppb)	RCS (ppb)	CH ₄ (ppb)	VOC (ppb)	RCS per (RSC+VOC) (mol %)		
1	T06-3593	Crosswind from Pond 2/3 (east side)	0	1.2	2.9	5	19.4		
2	T06-3594, T06-3595	Crosswind from Pond 2/3 (west side)	0, 0	6.3, 6.9	3.1, 4.5	27, 43	18.9, 13.8		
3	T06-3596	Partially downwind from Pond 2/3	0	16	3.8	41	28.1		
4	T06-3597	Near outfall to Pond 1A	0.2	18.4	12.2	388	4.5		
5	T06-3598	Between Ponds 1 and 1A (1A partially upwind)	0	7.9	22.4	189	4		
6	T06-3599	Partially downwind from Pond 1 (along dike road)	22	31.3	3.4	18	63.5		
7	T06-3600	Downwind of Pond 5	0	0.7	3	3	18.9		
8	T06-3601	Upwind of Pond 5	0	0.6	4.2	2	23.1		
9	T06-3602	Downwind of Pond 6	0	26.9	2.7	64	29.6		
10	T06-3603	Partially downwind of Pond 6	3.1	4.8	2.6	14	25.5		
11	T06-3604	Downwind of VRU and Ponds 2/3 and 5	0	37.7	4.3	1871	2		
12	T06-3605	Downwind of VRU and Ponds 2/3 and 5	0.1	154.1	5	5516	2.7		
13	T06-3606	Upwind of VRU but downwind of Ponds 2/3 and 5	0.6	4.7	2.7	106	4.2		
14	-	Downwind of VRU, baseplant and Pond 5	-	-	-	-	-		
15	T06-3607	Partially crosswind from North Tank Farm	10	13.4	2.4	394	3.4		
16	-	Downwind of North Tank Farm	-	-	-	-	-		
17	-	Downwind of Mannix Station No. 5	-	-	-	-	-		
18	-	Downwind of Williams Extraction Plant and Enbridge Tank Farm	-	-	-	-	-		

10. Were air emissions from tailings ponds and mine faces predicted prior to monitoring? If yes, how were they predicted?

- Unknown on historical basis. Monitoring results were included in the inventory as of 2002 after field measurement done to derive emission factors.

11. What are the estimated annual emissions of VOC, CH₄, Benzene, and THC that originate from tailings ponds and mine faces, and how were these estimates generated?

Here is a brief summary of the results from the isolation flux testing done for various ponds on-site conducted in the fall of 2007. Note that there were no estimations done on our mine surfaces.

Emission Source	Emission Zone	Methane (ug/m2/s)	Benzene (ug/m2/s)	Toluene (ug/m2/s)	Ethyl-Benzene (ug/m2/s)	Xylene (ug/m2/s)	THC (ug/m2/s)	H2S (ug/m2/s)	TRS (as S) (ug/m2/s)	TRS (ug/m2/s)
Pond 1	1/3 from Outfall (Bubble Zone)	1.9	0.01	0.04	0	0.29	4.88	0	0.36	1.2
Pond 1	2/3 from Outfall	2.8	0.01	0.05	0	0.3	5.83	0	0.43	1.44
Pond 1	Outfall	88.83	0.01	0.04	0.04	0.3	96.4	0	0.02	0.05
Pond 1A	Centre of Pond	3.94	0.04	0.79	0.17	0.94	13.24	0	1.79	6.08
Pond 1A	Near Outfall from Pond 1	4.98	0.05	1	0.21	1.18	16.9	0	2.39	8.07
Pond 1A	Near Outfall from Pond 2/3	9.55	0.11	2.2	0.47	2.61	33.53	0	4.55	15.43
Pond 2/3	1/3 from Outfall (Bubble Zone)	72.93	0.05	1.05	0.29	1.64	90.58	0	2.42	8.31
Pond 2/3	2/3 from Outfall	26.66	0.06	0.99	0.23	1.21	38.89	7.36	8.99	14.42
Pond 2/3	Outfall	7.4	0.06	1.6	0.48	3.22	36.48	0	2.96	9.97
Pond 5	1/3 from Outfall	0.05	0.03	0.03	0.03	0.12	1.96	0	0.16	0.69
Pond 5	Outfall	2.14	0.02	0.06	0.1	0.3	5.86	0	0.44	1.49
Pond 6	1/3 from East Outfall	57.96	0	0.01	0.01	0.07	60.01	0	0.1	0.33
Pond 6	Near East Outfall	2.27	0.01	0.07	0.2	0.62	12.09	0	0.84	2.92
Pond 6	West Side	12.9	0	0.01	0	0.05	13.74	0	0.1	0.35

There were several measurements taken throughout the year (i.e. spring, summer and fall). The results are recorded as a flux rate. In order to obtain an annual emission, the rates in the table provided above can be converted to annual rates.

a. Volatile organic compounds – This is shown in the table in above. The emission flux rates were obtained at different locations of the tailing ponds. On each pond, isolation flux measurements were typically performed at the outfall, and then 1/3 and 2/3 of the distance across the pond from the outfall.

b. Methane

- Annual estimated emissions of CH₄ in Tailing Ponds = 14087 Tonnes
- Annual estimated emissions of CH₄ in Mine Surfaces = 531 Tonnes
- The estimates are generated based on the surface areas of the pond and mine faces multiplied by the average CH₄ emission factors of pond and mine areas. Emissions were calculated and based on a flux survey that was done in the forth quarter in 2001. ("Hydrogen and Reduced Sulfur Compound (RSC) Emission From Tailing Ponds at Suncor's Tar Island Site – Project J2001-41 – Conducted by AirZOne Inc).

c. Benzene – This is shown in the table above. The emission flux rates were performed at different locations of the tailing ponds. On each pond, isolation flux measurements were typically performed at the outfall, and then 1/3 and 2/3 of the distance across the pond from the outfall.

d. THC - This is shown in the table above. The emission flux rates were performed at different locations of the tailing ponds. On each pond, isolation flux measurements were typically performed at the outfall, and then 1/3 and 2/3 of the distance across the pond from the outfall.

12. How do the predicted versus measured air emissions compare for tailings ponds and mine faces (please provide relative percent difference (RPD) or predicted values)?

- Suncor does not predict the emissions. Reported emissions are based on the actual pond or mine surface areas and corresponding emission factors derive from flux emissions measurement.

13. If emission factors were used, how were they used to calculate the following emissions from the mine faces and tailings ponds?

Volatile organic compounds, Benzene, THC

- Emission factors are results from the emission flux measurements from current and previous surveys using the U.S.EPA isolation flux chamber, and the U.S. EPA protocol for performing flux measurements on surface impoundments.

All sampling and field measurements were performed by Clearstone Engineering Ltd and sample analyses were performed by Alberta Research Council at their laboratory in Vegerville.

Methane

- Average pond CH₄ emission factors are calculated from the zonal % for different areas of the pond multiplied by the emission factor for each area of pond (ug/m²/s).

Estimation of CH₄ emission from Tailing Ponds is based on the results of survey: "Hydrocarbon (HC) and Reduced Sulfur Compound (RSC) Emission From Tailings Ponds at Suncor's Tar Island site – Project J2001-41" Conducted by AirZOne, Inc. analysis in 4th quarter of 2001.

Pond surface emissions were measured with flux chamber. Zonal % data was taken from the report "Hydrocarbon (HC) and Reduced Sulfur Compound (RSC) Emission From Tailings Ponds at Suncor's Tar Island site – Project J2001-41" – Conducted by AirZOne Inc. analysis in 4th quarter of 2001.

- Emission factors of the different mine areas were determined by the flux chamber survey; "Mine Surface Emissions of Hydrocarbon (HC) and Reduced Sulfur Compound (RSC) Emission at Suncor's Tar Island Site – Project J2012" conducted by AirZOne Inc. in the 4th quarter of 2001, similar to that used for measurement of pond surface emissions.

14. If emissions factors were not used please provide model or assumptions for predicting air emissions from mine faces and tailings ponds, as well as the reference of the method used.

- N/A

15. Please describe the technologies or measures used on-site to control/reduce air emissions from mine faces and tailings ponds and their estimated removal efficiency.

- No measures or technologies are utilized to control or reduced air emissions from mine faces. Emissions of CH₄ from mine faces and tailing ponds are attributed to the presence of naturally occurring microbiological organisms which react with hydrocarbon and emit CH₄. Suncor is required to control the amount of light (Naphtha) and heavy (bitumen) hydrocarbons to the tailing ponds.

16. Please describe advantages and difficulties encountered from using the technologies or measures reported in question 15.

- N/A

17. Which additional control technologies or measures are currently under consideration? Please describe any related pilot testing or research.

- N/A

Appendix 3 Air Quality Guidelines



Appendix 3-1

Summary - Provincial and Federal Ambient Air Quality Objectives and Standards

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

Substance	CAS	Averaging period	Alberta		British Columbia (µg/m ³)			Ontario	CCME CWS ⁵
			(µg/m ³)	(ppbv) ¹	BC Level A ²	BC Level B ³	BC Level C ⁴	(µg/m ³)	(µg/m ³)
Acenaphthene	83-32-9	---	---	---	---	---	---	---	---
Acenaphthylene	208-96-8	---	---	---	---	---	---	---	---
Benzene	71-43-2	1 hour	30	9	---	---	---	---	---
e-Benzene	---	---	---	---	---	---	---	---	---
1,2,4-MBenzene	---	---	---	---	---	---	---	---	---
Benzo(a)phenanthrene	218-01-9	---	---	---	---	---	---	---	---
1,3-Butadiene	106-99-0	---	---	---	---	---	---	---	---
i-Butane	---	---	---	---	---	---	---	---	---
n-Butane	---	---	---	---	---	---	---	---	---
2,2-Mbutane	---	---	---	---	---	---	---	---	---
n-C11	---	---	---	---	---	---	---	---	---
n-C12	---	---	---	---	---	---	---	---	---
n-C13	---	---	---	---	---	---	---	---	---
n-C14	---	---	---	---	---	---	---	---	---
n-C15	---	---	---	---	---	---	---	---	---
Carbon disulphide	75-15-0	1 hour	30	10	---	---	---	---	---
Chlorine	7782-50-5	24 hour	---	---	---	---	---	330	---
		10 min	---	---	---	---	---	230	---
		1 hour	15	5	---	---	---	---	---
		24 hour	---	---	---	---	---	10	---
COS (carbonyl sulphide)	463-58-1	---	---	---	---	---	---	---	---
Cumene (Isopropylbenzene)	98-82-8	1 hour	500	100	---	---	---	---	---
Cyclohexane	110-82-7	24 hour	---	---	---	---	---	6,100	---
n-Decane	---	1 hour	---	---	---	---	---	60,000	---
Ethylbenzene	100-41-4	1 hour	2,000	460	---	---	---	---	---
Ethylene	74-85-1	10 min	---	---	---	---	---	1,900	---
		1 hour	1,200	1,044	---	---	---	---	---
		3 day	45	40	---	---	---	---	---
		mean	30	26	---	---	---	---	---
		24 hour	---	---	---	---	---	1,000	---
Ethylene Glycol	107-21-1	24 hour	---	---	---	---	---	12,700	---
Fluorene	86-73-7	---	---	---	---	---	---	---	---
n-Heptane	---	24 hour	---	---	---	---	---	11,000	---
n-Hexane	110-54-3	1 hour	21,000	5,958	---	---	---	---	---
		24 hour	7,000	1,986	---	---	---	---	---
Hydrogen sulphide	7783-06-4	10 min	---	---	---	---	---	13	---
		1 hour	14	10	7.5 to 14	28 to 45	42 to 45	---	---
		24 hour	4	3	4	6 to 7.5	7.5 to 8	7	---
Mercaptans	---	10 min	---	---	---	---	---	13	---
Methyl-cyclopentane	---	---	---	---	---	---	---	---	---
Naphthalene	---	10 min	---	---	---	---	---	22.5	---
		24 hour	---	---	---	---	---	50	---
n-Nonane	---	---	---	---	---	---	---	---	---
n-Octane	---	10 min	---	---	---	---	---	61,800	---
i-Pentane	---	---	---	---	---	---	---	---	---
n-Pentane	---	---	---	---	---	---	---	---	---
Phenanthrene	85-01-8	---	---	---	---	---	---	---	---
PM	NA - M08	---	---	---	---	---	---	---	---
PM10	NA - M09	24 hour	---	---	---	50	---	50	25
PM2.5	NA - M10	1 hour	80	---	---	---	---	---	---
		24 hour	30	---	---	---	---	30	15
Propane	---	---	---	---	---	---	---	---	---
Propylene	115-07-1	24 hour	---	---	---	---	---	4,000	---
Pyrene	129-00-0	---	---	---	---	---	---	---	---
Thiophenes	---	---	---	---	---	---	---	---	---
Toluene	108-88-3	1 hour	1,880	499	---	---	---	---	---
		24 hour	400	106	---	---	---	2,000	---



Appendix 3-1

Summary - Provincial and Federal Ambient Air Quality Objectives and Standards

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

Substance	CAS	Averaging period	Alberta		British Columbia (µg/m ³)			Ontario	CCME CWS ⁵
			(µg/m ³)	(ppbv) ¹	BC Level A ²	BC Level B ³	BC Level C ⁴	(µg/m ³)	(µg/m ³)
Total Reduced Sulphur	NA - M14	10 min	---	---	---	---	---	13	---
		1 hour	---	---	7	28	---	---	---
		24 hour	---	---	3	6	---	14	---
1,2,4-Trimethylbenzene	95-63-6	24 hour	---	---	---	---	---	220	---
VOCs	NA - M16	---	---	---	---	---	---	---	---
Xylenes	1330-20-7	10 min	---	---	---	---	---	3,000	---
		1 hour	2,300	529	---	---	---	---	---
		24 hour	700	161	---	---	---	730	---

SOURCES:

Alberta Environment, 2008. Alberta Ambient Air Quality Objectives and Guidelines.

Air Policy Branch. environment.gov.ab.ca/info/library/5726.pdf.

British Columbia Ministry of Environment, 2004. Air Quality Objectives and Standards. Environmental Quality Branch.
<http://www.env.gov.bc.ca/air/airquality/pdfs/aaqtable.pdf>.

Canadian Council of Ministers of the Environment, 2000. Canada Wide-Standards for Particulate Matter (PM) and Ozone.

NOTES:

1. ppbv = parts per billion volume
2. Provide long term protection.
3. Provide adequate protection, but may affect personal comfort.
4. Appropriate action required to protect human health.
5. CCME CWS = Canadian Council of Ministers of the Environment Canada-Wide Standards
6. --- = No applicable objective or standard



Appendix 3-2

Summary - State and International Ambient Air Quality Objectives, Guidelines, Limit Values and Standards

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

Potential Contaminant of Concern (PCOC)	CAS	Averaging period	California Standards		Colorado Standards	US EPA Standards				European Union Limit Values ($\mu\text{g}/\text{m}^3$)	United Kingdom Objectives ($\mu\text{g}/\text{m}^3$)
			($\mu\text{g}/\text{m}^3$)	(ppm) ¹		Primary Standards ($\mu\text{g}/\text{m}^3$)	(ppm)	Secondary Standards ($\mu\text{g}/\text{m}^3$)	(ppm)		
Acenaphthene	83-32-9	---	---	---	---	---	---	---	---	---	---
Acenaphthylene	208-96-8	---	---	---	---	---	---	---	---	---	---
Benzene	71-43-2	Annual mean	---	---	---	---	---	---	---	5 ²	5 ³
e-Benzene		---	---	---	---	---	---	---	---	---	---
1,2,4-MBenzene		---	---	---	---	---	---	---	---	---	---
Benzo(a)phenanthrene	218-01-9	---	---	---	---	---	---	---	---	---	---
1,3-Butadiene	106-99-0	Running Annual Mean	---	---	---	---	---	---	---	---	2.25
i-Butane		---	---	---	---	---	---	---	---	---	---
n-Butane		---	---	---	---	---	---	---	---	---	---
2,2-Mbutane		---	---	---	---	---	---	---	---	---	---
n-C11		---	---	---	---	---	---	---	---	---	---
n-C12		---	---	---	---	---	---	---	---	---	---
n-C13		---	---	---	---	---	---	---	---	---	---
n-C14		---	---	---	---	---	---	---	---	---	---
n-C15		---	---	---	---	---	---	---	---	---	---
Carbon disulphide	75-15-0	---	---	---	---	---	---	---	---	---	---
Chlorine	7782-50-5	---	---	---	---	---	---	---	---	---	---
COS (carbonyl sulphide)	463-58-1	---	---	---	---	---	---	---	---	---	---
Cumene (Isopropylbenzene)	98-82-8	---	---	---	---	---	---	---	---	---	---
Cyclohexane	110-82-7	---	---	---	---	---	---	---	---	---	---
n-Decane		---	---	---	---	---	---	---	---	---	---
Ethylbenzene	100-41-4	---	---	---	---	---	---	---	---	---	---
Ethylene	74-85-1	---	---	---	---	---	---	---	---	---	---
Ethylene Glycol	107-21-1	---	---	---	---	---	---	---	---	---	---
Fluorene	86-73-7	---	---	---	---	---	---	---	---	---	---
n-Heptane		---	---	---	---	---	---	---	---	---	---
n-Hexane	110-54-3	---	---	---	---	---	---	---	---	---	---
Hydrogen sulphide	7783-06-4	1 hour	42	0.03	---	---	---	---	---	---	---
Mercaptans		---	---	---	---	---	---	---	---	---	---
Methyl-cyclopentane		---	---	---	---	---	---	---	---	---	---
Naphthalene		---	---	---	---	---	---	---	---	---	---



Appendix 3-2

Summary - State and International Ambient Air Quality Objectives, Guidelines, Limit Values and Standards

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

n-Nonane		---	---	---	---	---	---	---	---	---	---
n-Octane		---	---	---	---	---	---	---	---	---	---
i-Pentane		---	---	---	---	---	---	---	---	---	---
n-Pentane		---	---	---	---	---	---	---	---	---	---
Phenanthrene	85-01-8	---	---	---	---	---	---	---	---	---	---
PM	NA - M08	---	---	---	---	---	---	---	---	---	---
PM10	NA - M09	24 hour	50	---	150	150		Same as Primary	50 ⁴	50 ⁵	
		Annual Arithmetic Mean	20	---	50	---	---	---	40 ⁶	40	
PM2.5	NA - M10	24 hour	---	---	---	35	---	Same as Primary	---	---	
		Annual Arithmetic Mean	12	---	---	15	---	Same as Primary	Stage 1 = 25 Stage 2 = 20 ⁷	25	
Propane		---	---	---	---	---	---	---	---	---	---
Propylene	115-07-1	---	---	---	---	---	---	---	---	---	---
Pyrene	129-00-0	---	---	---	---	---	---	---	---	---	---
Thiophenes		---	---	---	---	---	---	---	---	---	---
Toluene	108-88-3	---	---	---	---	---	---	---	---	---	---
Total Reduced Sulphur	NA - M14	---	---	---	---	---	---	---	---	---	---
1,2,4-Trimethylbenzene	95-63-6	---	---	---	---	---	---	---	---	---	---
VOCs (vinyl chloride)	NA - M16	24 hour	26	0.01	---	---	---	---	---	---	---
Xylenes	1330-20-7	---	---	---	---	---	---	---	---	---	---

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NOTES:

1. ppm = parts per million
2. Margin of tolerance: 5 µg/m³ (100%) on December 13, 2000, decreasing on January 1, 2006 and every 12 months thereafter by 1 µg/m³ to reach 0% by January 1, 2010.
3. Applies to England and Wales.
4. Not to be exceeded more than 35 times a calendar year. Margin of tolerance: 50%.
5. Not to be exceeded more than 35 times a calendar year.
6. Stage 1 Margin of tolerance: 20% on June 11, 2008/, decreasing o the next January 1 and every 12 months thereafter by equal annual percentages to reach 0% by January 1, 2015.
Stage 2 limit value to be reviewed by the Commission in 2013.
7. Margin of tolerance: 20%.
8. --- = objective, guideline, limit value, or standard not developed
9. State of Texas has adopted the US EPA National Ambient Air Quality Standards.

Appendix 4 Prediction of Emissions Methodology

Methodology for Predicting Emissions from Mine Faces of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

Table 4-I Predicted Emissions from Mine Faces of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects by Year

Year	1967	1978	2002	2006	2007	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2021	2022
Capacity (bbbl/d)	294000	290700	155000	116300	4000	64111	236361	229111	184111	64111	364111	64111	64111	64111	300000	200000	200000
Area (km ²)	61	12	5	12	8	1	9	9	31	1	31	1	1	1	29	47	7
Total hydrocarbon (C ₁₊)	73996	11745	5433	14489	9640	977	10799	10636	37573	977	37678	977	977	977	34566	56923	7957
Methane (C ₁)	50866	5331	3735	9960	6627	672	7423	7312	25829	672	25901	672	672	672	23761	39130	5470
C ₂₊	23129	78	1698	4529	3013	305	3375	3325	11744	305	11777	305	305	305	10804	17793	2487
C ₂ to C ₄ alkanes and alkenes	795	72	58	154	102	10	115	113	399	10	400	10	10	10	367	604	84
C ₅ to C ₆ Alkanes and alkenes	443	5121	33	87	58	6	65	64	225	6	226	6	6	6	207	341	48
C ₉ to C ₁₂ alkanes and alkenes	21631	3	1588	4235	2818	286	3157	3109	10983	286	11014	286	286	286	10104	16640	2326
Cyclohexane	17	0	1	3	2	0	3	3	9	0	9	0	0	0	9	13	2
Benzene	1	4	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
C ₉ to C ₁₂ non-benzene aromatics	17	0	1	3	2	0	3	3	9	0	9	0	0	0	8	13	2
Total aldehydes	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total ketones	0	22	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total RS	148	11745	11	29	19	2	22	21	75	2	75	2	2	2	69	114	16
Methane (C ₁)	50866	52	3735	9960	6627	672	7423	7312	25829	672	25901	672	672	672	23761	39130	5470
Ethane (C ₂)	593	14	44	116	77	8	87	85	301	8	302	8	8	8	277	456	64
C ₃ to C ₄ alkanes	159	4872	12	31	21	2	23	23	81	2	81	2	2	2	74	122	17
C ₅ to C ₆ alkanes	20624	194	1514	4038	2687	272	3010	2965	10472	272	10501	272	272	272	9634	15865	2218
C ₉ to C ₁₂ alkanes	897	44	66	176	117	12	131	129	455	12	457	12	12	12	419	690	96
C ₁₃₊ alkanes	188	0	14	37	25	2	27	27	96	2	96	2	2	2	88	145	20
Ethylene (C ₂)	0	3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₅ to C ₆ alkenes	34	28	2	7	4	0	5	5	17	0	17	0	0	0	16	26	4
C ₉ to C ₁₂ alkenes	125	98	9	24	16	2	18	18	63	2	63	2	2	2	58	96	13
C ₉ to C ₁₂ aromatics	445	11	33	87	58	6	65	64	226	6	227	6	6	6	208	342	48
C ₁₃₊ alkenes	50	0	4	10	6	1	7	7	25	1	25	1	1	1	23	38	5
Benzene (C ₆)	1	4	0	0	0	0	0	0	0	0	0	0	0	0	0	1	0
C ₉ to C ₁₂ non-benzene aromatics	17	2	1	3	2	0	3	3	9	0	9	0	0	0	8	13	2
C ₉ to C ₁₂ aromatics	9	0	1	2	1	0	1	1	4	0	4	0	0	0	4	7	1

Table 4-II Calculating Cumulative Predicted Emissions from Mine Faces of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects

Year	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022
Capacity (bbbl/d)	312,440,000	313,900,000	313,900,000	337,300,556	423,572,361	507,197,917	574,388,472	597,799,028	623,389,583	#####	#####	800,901,250	910,401,250	#####	#####	983,401,250	1,056,401,250
Area (km ²)	90	98	98	98	107	116	147	148	180	180	180	181	210	210	210	257	264
Total hydrocarbon (C ₁₊)	105,663	115,302	115,302	116,279	127,078	137,714	175,287	176,264	214,919	214,919	215,896	216,873	251,438	251,438	251,438	308,361	316,318
Methane (C ₁)	69,892	76,519	76,519	77,191	84,614	91,826	117,754	118,426	144,998	144,998	145,669	146,341	170,102	170,102	170,102	209,232	214,702
C ₂₊	29,435	32,448	32,448	36,128	39,453	51,197	51,503	63,585	63,585	63,585	63,891	64,196	75,000	75,000	75,000	92,793	95,280
C ₂ to C ₄ alkanes and alkenes	1,068	1,171	1,171	1,181	1,296	1,409	1,807	1,818	2,228	2,228	2,238	2,248	2,615	2,615	2,615	3,219	3,304
C ₅ to C ₆ Alkanes and alkenes	5,683	5,741	5,741	5,747	5,811	5,875	6,106	6,106	6,337	6,337	6,343	6,349	6,556	6,556	6,556	6,897	6,944
C ₉ to C ₁₂ alkanes and alkenes	27,457	30,275	30,275	30,560	33,717	36,826	47,810	48,095	59,395	59,395	59,680	59,966	70,070	70,070	70,070	86,710	89,036
Cyclohexane	22	25	25	25	27	30	39	39	48	48	48	48	57	57	57	70	72
Benzene	5	5	5	5	5	5	5	5	6	6	6	6	6	6	6	6	7
C ₉ to C ₁₂ non-benzene aromatics	22	24	24	25	27	30	39	39	48	48	48	48	57	57	57	70	72
Total aldehydes	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total ketones	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22
Total RS	11,932	11,951	11,951	11,953	11,975	11,996	12,071	12,073	12,150	12,150	12,152	12,154	12,223	12,223	12,223	12,336	12,352
Methane (C ₁)	64,624	71,251	71,251	71,922	79,345	86,657	112,496	113,157	139,729	139,729	140,401	141,075	164,834	164,834	164,834	203,964	209,434
Ethane (C ₂)	767	844	844	852	938	1,023	1,324	1,332	1,642	1,642	1,650	1,658	1,934	1,934	1,934	2,390	2,454
C ₃ to C ₄ alkanes	5,074	5,094	5,094	5,096	5,120	5,142	5,223	5,225	5,308	5,308	5,310	5,312	5,387	5,387	5,387	5,509	5,526
C ₅ to C ₆ alkanes	26,371	29,058	29,058	29,330	32,340	35,304	45,777	46,049	56,823	56,823	57,095	57,367	67,001	67,001	67,001	82,867	85,084
C ₉ to C ₁₂ alkanes	1,182	1,299	1,299	1,311	1,442	1,571	2,026	2,038	2,507	2,507	2,518	2,530	2,949	2,949	2,949	3,639	3,736
C ₁₃₊ alkanes	239	264	264	266	294	321	416	419	517	517	520	522	610	610	610	755	775
Ethylene (C ₂)	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
C ₅ to C ₆ alkenes	71	75	75	76	81	85	102	103	120	120	121	121	137	137	137	163	166
C ₉ to C ₁₂ alkenes	256	272	272	274	292	310	373	375	440	440	441	443	501	501	501	597	610
C ₉ to C ₁₂ aromatics	576	634	634	640	705	769	995	1,001	1,233	1,233	1,239	1,245	1,453	1,453	1,453	1,795	1,843
C ₁₃₊ alkenes	64	70	70	71	78	85	110	111	137	137	138	139	162	162	162	200	206
Benzene (C ₆)	5	5	5	5	5	5	5	5	6	6	6	6	6	6	6	7	7
C ₉ to C ₁₂ non-benzene aromatics	24	27	27	27	29	32	41	41	50	50	50	51	59	59	59	72	74
C ₉ to C ₁₂ aromatics	11	12	12	12	14	15	19	19	24	24	24	24	28	28	28	35	36
PAHs	35	39	39	39	43	47	60	60	74	74	74	75	87	87	87	107	110
VOC	34,602	37,613	37,613	37,918	41,291	44,614	56,350	56,565	68,730	68,730	69,035	69,340	80,138	80,138	80,138	97,919	100,404
Mines starting operation	Suncor Millennium	Suncor North Steep		CNRL-Horizon	CNRL-Horizon	CNRL-Horizon	CNRL-Horizon	CNRL-Horizon	CNRL-Horizon	CNRL-Horizon	CNRL-Horizon	CNRL-Horizon	Imperial Oil Keart			Shell Pierre River	Total E&P- Joslyn
	Mine	Bank Extension		Mine	Mine	Mine	Mine	Mine	Mine	Horizon Mine	Horizon Mine	Mine	Mine			Mine	Mine
	Synchrude Mildred				Synenco Northem	Mine Petro Canada-		Shell Jack Pine									
	Lake-North Mine				Lights Mine	Fort Hills		Mine Area 2	Mine Area 3								
	Synchrude Mildred				Albian Sand-			Suncor Voyageur									
	Lake West Base				Muskog River												
	Mine				Area 2												
	Synchrude Aurora				Shell Jack Pine												
	North Mine				Mine Area 1												
	Synchrude Aurora																
	South Mine																

Methodology for Predicting Emissions from Tailings Ponds of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects

CLIENT: Environment Canada

PROJECT NO.: B2179 0000

PROJECT NAME: Review and Summary of Emission Factors for Oil Sands Tailings Ponds and Mining Faces and Options for Reducing Emissions

Table 4-III Predicted Emissions from Tailings Ponds of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects arranged by Year

Year	1967	1978	2002	2006	2007	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2021	2022
Capacity (tbbld)	294000	290700	155000	116300	4000	64111	236361	229111	184111	64111	364111	64111	64111	64111	300000	200000	200000
Area (km ²)	2	72	0	7	13	2	6	2	2	2	5	2	2	2	19	0	3
Total hydrocarbon (C ₁₊)	18367	39432	285	15946	18367	4141	14278	4693	22508	4141	11375	4141	4141	4141	42317	386	7569
Methane (C ₁)	2869	31318	233	13063	2869	3392	11697	3845	6261	3392	9318	3392	3392	3392	34666	317	6201
C ₂₊	15498	8114	52	2883	15498	749	2582	849	16247	749	2057	749	749	749	7651	70	1389
C ₆ to C ₉ alkanes and alkenes	4	0	0	0	0	0	0	0	4	0	0	0	0	0	0	0	0
C ₆ to C ₉ Alkanes and alkenes	8674	339	3	192	8874	50	172	57	8923	50	137	50	50	50	511	5	91
C ₆ to C ₁₂ alkanes and alkenes	3225	7436	45	2521	3225	655	2258	742	3879	655	1798	655	655	655	6691	61	1197
Cyclohexane	2181	8	0	5	2181	1	5	2	2182	1	4	1	1	1	14	0	3
Benzene	0	19	0	10	0	3	9	3	3	7	3	3	3	3	28	0	5
C ₆ to C ₉ non-benzene aromatics	1034	193	2	101	1034	26	90	30	1060	26	72	26	26	26	267	2	48
Total aldehydes	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total ketones	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total RS	184	146	0	14	184	4	12	4	188	4	10	4	4	4	37	0	7
Methane (C ₁)	2869	31318	233	13063	2869	3392	11697	3845	6262	3392	9318	3392	3392	3392	34666	317	6201
Ethane (C ₂)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₃ to C ₄ alkanes	4	0	0	0	4	0	0	0	4	0	0	0	0	0	0	0	0
C ₆ to C ₉ alkanes	8111	7501	46	2575	8111	669	2306	758	8779	669	1837	669	669	669	6833	62	1222
C ₆ to C ₁₂ alkanes	2133	218	2	103	2133	27	92	30	2160	27	74	27	27	27	274	3	49
C ₁₃₊ alkanes	358	17	0	8	358	2	7	2	360	2	6	2	2	2	21	0	4
Ethylene (C ₂)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₃ to C ₄ alkenes	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C ₆ to C ₉ alkenes	2712	49	1	30	2712	8	27	9	2720	8	22	8	8	8	80	1	14
C ₉ to C ₁₂ alkenes	965	10	0	6	965	2	5	2	967	2	4	2	2	2	15	0	3
C ₁₃₊ alkenes	0	1	0	0	0	0	0	0	0	0	0	0	0	0	1	0	0
Benzene (C ₆)	33	19	0	10	33	3	9	3	36	3	7	3	3	3	28	0	5
C ₆ to C ₉ non-benzene aromatics	1538	193	2	101	1538	26	90	30	1564	26	72	26	26	26	267	2	48
C ₉ to C ₁₂ aromatics	364	110	1	49	364	13	44	14	377	13	35	13	13	13	131	1	23

Table 4-IV Calculating Cumulative Predicted Emissions from Tailings Ponds of Operating, Approved and Publicly Disclosed Oil Sands Mining Projects

Year	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	
Capacity (tbbld)	312,440,000	313,900,000	313,900,000	313,900,000	376,771,250	436,996,250	480,796,250	480,796,250	590,296,250	590,296,250	590,296,250	800,901,250	910,401,250	910,401,250	910,401,250	983,401,250	1,056,401,250	
Area (km2)	2	72	72	72	96	102	104	106	108	113	115	117	119	138	138	138	142	
Total hydrocarbon (C ₁₊)	2	72	72	72	96538	110816	115509	138017	142158	153533	157674	161815	165956	208274	208274	208660	216229	
Methane (C ₁)	2	72	72	72	53744	65441	69286	75547	78939	88258	91650	95042	98435	133101	133101	133417	139618	
C ₂₊	2	72	72	72	42793	45374	46223	62470	63218	65275	66024	66772	67521	75172	75172	75242	76611	
C ₂ to C ₆ alkanes and alkenes	2	72	72	72	8	8	8	12	12	12	12	12	12	12	12	12	12	
C ₂ to C ₆ Alkanes and alkenes	2	72	72	72	18332	18504	18560	27484	27534	27671	27721	27771	27821	28332	28332	28336	28428	
C ₆ to C ₁₂ alkanes and alkenes	2	72	72	72	17106	19364	20106	23985	24640	26439	27093	27748	28403	35094	35094	35155	36352	
Cyclohexane	2	72	72	72	4377	4382	4383	6566	6567	6571	6572	6574	6575	6589	6589	6589	6592	
Benzene	2	72	72	72	32	41	44	47	50	57	60	63	65	93	93	93	98	
C ₆ to C ₉ non-benzene aromatics	2	72	72	72	2389	2479	2509	3568	3594	3666	3692	3718	3745	4012	4012	4012	4062	
Total aldehydes	2	72	72	72	0	0	0	0	0	0	0	0	0	0	0	0	0	
Total ketones	2	72	72	72	0	0	0	0	0	0	0	0	0	0	0	0	0	
Total RS	2	72	72	72	532	545	549	737	740	750	754	757	761	798	798	798	805	
Methane (C ₁)	2	72	72	72	53745	65442	69286	75548	78940	88258	91651	95043	98435	133102	133102	133102	139619	
Ethane (C ₂)	2	72	72	72	0	0	0	0	0	0	0	0	0	0	0	0	0	
C ₃ to C ₄ alkanes	2	72	72	72	8	8	8	12	12	12	12	12	12	12	12	12	12	
C ₆ to C ₉ alkanes	2	72	72	72	27012	29317	30075	38854	39523	41360	42028	42697	43366	50199	50199	50199	51484	
C ₉ to C ₁₂ alkanes	2	72	72	72	4616	4708	4739	6899	6926	6999	7026	7053	7080	7354	7354	7354	7405	
C ₁₃₊ alkanes	2	72	72	72	744	751	753	1113	1115	1121	1123	1125	1127	1148	1148	1148	1152	
Ethylene (C ₂)	2	72	72	72	0	0	0	0	0	0	0	0	0	0	0	0	0	
C ₃ to C ₄ alkenes	2	72	72	72	0	0	0	0	0	0	0	0	0	0	0	0	0	
C ₆ to C ₉ alkenes	2	72	72	72	5512	5539	5547	8267	8275	8297	8305	8312	8320	8400	8400	8401	8415	
C ₉ to C ₁₂ alkenes	2	72	72	72	1948	1953	1955	2922	2923	2927	2929	2930	2932	2947	2947	2947	2950	
C ₁₃₊ alkenes	2	72	72	72	1	2	2	2	2	3	3	3	3	4	4	4	4	
Benzene (C ₆)	2	72	72	72	98	108	111	147	150	157	160	162	165	193	193	193	198	
C ₆ to C ₉ non-benzene aromatics	2	72	72	72	3397	3487	3517	5081	5107	5179	5205	5231	5257	5525	5525	5527	5575	
C ₉ to C ₁₂ aromatics	2	72	72	72	901	945	960	1336	1349	1384	1397	1410	1423	1553	1553	1555	1578	
PAHs	3	143	143	4298	4433	4477	6417	6456	6563	6602	6641	6680	7078	7078	7078	7082	7153	
VOCs	16	715	715	39840	42278	43080	58070	58777	60719	61426	62133	62840	70065	70065	70065	70131	71424	
Mines starting operation	Suncor Millennium Mine Syncrude Mildred Lake-North Mine Syncrude Mildred Lake West Base Mine Syncrude Aurora North Mine Syncrude Aurora South Mine	Suncor North Steep Bank Extension		CNRL-Horizon Mine	CNRL-Horizon Mine Synenco Northern Lights Mine Albian Sand- Muskeg River Area 2 Shell Jack Pine Mine Area 1	Mine Petro Canada- Fort Hills	CNRL-Horizon Mine Shell Jack Pine	CNRL-Horizon Mine Shell Jack Pine	CNRL-Horizon Mine Shell Jack Pine	CNRL-Horizon Mine Shell Jack Pine	CNRL-Horizon Mine Shell Jack Pine	CNRL-Horizon Mine Shell Jack Pine	CNRL-Horizon Mine Shell Jack Pine	Imperial Oil Keart Mine			Shell Piere River Mine	Total E&P- Jostyn Mine

Notes:

Table 4-I

Emissions from mine faces were obtained from Table 4.

Emissions from mine faces during the same year were summed.

CNRL bitumen productions and emissions is assumed to increase 229111 bbl/year between 2009 and 2017, when the mine reaches full capacity.

CNRL emissions from mine faces and surface areas of mine faces are assumed to increase linearly between 2009 and 2017.

Table4-II

Cumulative emissions from mine faces for a certain year were calculated by summing emissions from previous years until that year.

Table 4-III

Emissions from tailings ponds were obtained from Table 6.

Emissions from tailings ponds during the same year were summed.

CNRL bitumen productions and emissions is assumed to increase 229111 bbl/year between 2009 and 2017, when the mine reaches full capacity.

CNRL emissions from tailings ponds and tailings ponds surface area are assumed to increase linearly between 2009 and 2017.

Table4-IV

Cumulative emissions from tailings ponds for a certain year were calculated by summing emissions from previous years until that year.

Appendix 5 Wastewater Treatment Technologies

APPENDIX 5

Wastewater Treatment Technologies

1. INTRODUCTION

Water treatment technologies can be categorized into primary, secondary, and tertiary processes. Primary treatment comprises the physical processes of solid-liquid, liquid-liquid, and or gas-liquid separation, and includes processes such as sedimentation, flotation, filtration, and aeration. These separation processes are often facilitated by chemical treatments such as coagulation and flocculation particularly where suspensions are stable and resistant to sedimentation. Secondary treatment processes refer to biological treatment, or methods involving the use of microorganisms to stabilize wastewater water through the removal of nutrients and organic compounds. Biological treatment technologies include aerated lagoons, activated sludge, and fixed-film bioreactors. These processes are designed to reduce BOD but do not effectively remove dissolved inorganic species and recalcitrant organic compounds. Tertiary treatment, also referred to as advanced treatment, encompasses a wide range of processes that target dissolved and particulate species that are not effectively removed by primary and secondary methods. Advanced treatment technologies include chemical precipitation, advanced oxidation, membranes, and ion exchange, adsorption, and treatment wetlands.

Depending on the treatment objectives, a treatment train may be established comprising of primary, second and tertiary process. In the oil industry, wastewater treatment begins with oil and suspended solids, removal followed by further clarification with coagulants and flocculants, biological treatment to remove organic compounds and use of tertiary processes to demineral and further detoxify the effluent (Mujeriego and Asano, 1999).

There are numerous references and technical handbooks reviewing wastewater treatment theory and system design. It is not the intention of this chapter to discuss the basic theory of wastewater treatment, but rather to discuss the treatment processes, development and applications of the technologies in the oil industry.

2. SEDIMENTATION

Sedimentation is one of the earliest water treatment processes. Sedimentation, also known as clarification, refers to the downward settling of particles through the water column to clarify a surface layer of water. Sedimentation is most commonly used as a pretreatment technology to remove suspended solids and precipitates, flocs, and other aggregates generated by other treatment processes. The accumulated sludge is subsequently processed via biological or non-biological means using thickening, digestion, dewatering, filtration, centrifugation, incineration, and/or drying beds (Mujeriego and Asano, 1999).



The three main categories of clarifiers used in sedimentation are horizontal flow, solids contact, and inclined surface (Allen, 2006). Horizontal flow tanks are either rectangular or circular, and are designed to allow for consistent flow with low turbulence. Circular flow patterns can be used to generate centrifugal forces that increase the settling velocities of particles or the coalescence of oil. Centrifugal-action desanders and coalescers are currently used in the oil sands industry (Allen, 2006). Settled solids are subsequently scraped from the tank bottom by sludge removal mechanisms. In solids-contact clarifiers, influent solids are trapped by a sludge blanket in the tank, which is scraped and undergoes further treatment before discarding. Inclined surface clarifiers contain angled plates or tubes which increase settling rates by reducing the distance that the particles have to travel. The latter is a preferred technology, since it reduces the settling time, and process time.

3. AERATION AND STRIPPING

Aeration refers to the addition of a gas for chemical treatment (e.g., disinfection or oxidation), or to promote the loss of VOCs to the atmosphere through air stripping. The main types of aeration systems are diffused-air, surface aerator, spray, and packed-tower systems (Allen, 2006). Diffused aerators inject air bubbles into the water column, whereas surface aerators use rotating drums or brushes to increase contact between the water surface and the air. Spray aerators spray water droplets into the air, thus VOCs partition from the droplets to the air via volatilization and the water droplets are allowed to settle. In a packed tower design liquid is injected at the top of a column filled with packing material and flows counter-current to air injected at the bottom. The packed tower system has proven to have a higher stripping efficiency, removal of less volatile compounds and resistance to fouling compared to other aeration systems.

Air stripping is a proven treatment technology for VOCs in oil-field produced water. Fang and Lin (1998) reported a rapid decrease in benzene concentrations from 1,000 part per million (ppm) to <5 ppm after air stripping off-shore produced waters. Aliphatic hydrocarbons can also be removed successfully from produced water with air stripping. Soluble organic compounds such as methanol and formic acid cannot be effectively removed by air stripping because they dissociate in aqueous solutions (Fang and Lin, 1998). Air stripping is also unsuitable when the volatility of the compound is pH dependent.

4. COAGULATION AND FLOCCULATION

Coagulation and flocculation are chemical processes that facilitate sedimentation, flotation and/or filtration of suspended solids, oil, colloids, and/or trace metals (Nenov, 1995; Ebeling et al. 2003). Coagulation refers to the destabilization of colloidal or particulate suspensions. Flocculation refers to bridging between groups of particulates or added polymers to form larger aggregates.

A wide range of coagulants and flocculants are used in the removal of free and dispersed oil droplets in oily wastewaters. Removal of oil with inorganic coagulants occurs by charge neutralization of oil droplets or coprecipitation on metal hydroxides. Inorganic salts also act as de-emulsifiers by forming insoluble

salts with emulsifying agents. Organic coagulants (polyamines, polyacrylates) have been shown to be more effective than inorganic salts, producing lower effluent oil residuals and less sludge, and have largely replaced inorganic coagulants in the treatment of refinery and petrochemical effluent. Hydrolyzed polyacrylamide (HPAM) has been shown to coalesce small oil droplets (3-5 μm diameters) and improve oil-water separation in polymer-flood produced water (Deng et al., 2002). Non-ionic polymers (polyethylene oxide-b-propylene oxide and polyvinyl alcohol) used in combination with flotation can achieve up to 92% oil removal. However this depends on oil inflow, flocculant hydrophilicity, and molecular weight.

Electrocoagulation has also shown potential as a treatment for produced water. Rubach and Saur (1997) tested electrocoagulation (or electroflocculation) with aluminium cathodes on North Sea produced water and reported separation efficiencies of 99% for saturated hydrocarbons, 98% for aromatics, and 96% for polar compounds. Electrocoagulation has also been shown to separate clay particles from water (Holt et al., 2005), and thus could have potential in oil sands tailings treatment. Coagulation and flocculation processes are in use in the oil sands industry and have been extensively researched, particularly where the settling of fine tailings is concerned (Allen, 2006). The addition of alum to tailings can result in the rapid separation of a clear surface water layer, and a large reduction in sludge volume; however this method of coagulation is applied in pilot scale water treatment and has not yet been adopted for large-scale treatment of tailings (Allen, 2006).

5. FLOTATION

Flotation processes rely on air bubbles to separate low density solids or liquids from wastewater. The mining industry was the first industry to apply this technology to solids from ore slurries; flotation has since been applied in wastewater and drinking water treatment. Standard applications of flotation include the separation of oil and grease, floc, metal ions, and algal blooms from aqueous streams (Bennett, 1988). Flotation processes can remove 60-95% of suspended solids and 65-98% of oil and grease (Allen, 2006).

Flotation is a key process for the deoiling of produced water. In addition to the aided flotation processes described above, oil may be separated by natural flotation in settling tanks, or artificial gravity generated by rotational forces. Widespread technologies include the American Petroleum Institute (API) separator, corrugated plate interceptors (CPI), hydrocyclones, and centrifugation, induced gas flotation (IGF), and dissolved air flotation (DAF), dissolved air precipitation (DAP), and electrolytic flotation. Chemical aids (flocculants, de-emulsifiers) are often used to improve the deoiling performance of these processes. Other deoiling technologies such as granular bed media filtration, diatomaceous earth, cartridge filtration, micro- and ultrafiltration, and biological treatment will be discussed in subsequent sections.

Separation of solids or liquids with flotation is dependent on particle/liquid bubble interactions, bubble size, rise velocity, water density, and temperature. There are three principal mechanisms for particle-bubble attachment: (i) precipitation of a bubble on a particle; (ii) collision of a bubble on a particle; and (iii)



entrapment of arising bubble in floc (Allen, 2006). Solid/liquid-bubble interactions are in turn dependent on surface charge and hydrophobicity of floc particles, feedwater chemistry, the size of the floc, and turbulence in the flotation vessel. Recent research has focused on chemical techniques for improving the efficiency of flotation such as the addition of coagulants and flocculants to promote interaction between bubbles and target pollutants. Jameson (1999) tested chemical pre-treatments followed by flotation for treatment of a clay suspension and an oil-in-water emulsion. The addition of a cationic polymer to the clay suspension improved the performance of the flotation unit by reversing the negative surface charge on the clay particles, which in turn attracted negatively-charged hydrophobic molecules and increased particle hydrophobicity. Separation of the oil-in water emulsion was improved by adding a flocculant that promoted the coalescence of oil into larger drops and facilitated attachment of air bubbles. The addition of surfactants to increase hydrophobicity and floatability of particles/droplets can also be beneficial (Zamboulis et al, 2004). Feedwater pH can affect flotation processes through its influence over zeta potentials and the behaviour of coagulants, flocculants, and surfactants.

5.1 API Separators

API separators are simple settling basins designed to allow the natural flotation of free oil to the surface, where it can be removed by skimming. Residence times are long and chemical flocculants may be introduced to improve removal rates. Since small oil droplets (e.g. smaller than 20-50 μ m diameter) are not removed by API separators, removal rates can vary depending on the size distribution of oil in the solution (Allen, 2006). API separators can reduce oil concentrations in produced water to residual levels of approximately 100 mg/L. Pollutant removal efficiencies of the API separator for suspended solids and oil can be between 10 and 50% and 60 and 99%, respectively (Allen, 2006).

5.2 Corrugated/Parallel Plate Interceptors

Plate interceptors also have a simple design, consisting of tanks with corrugated or flat inclined plates which capture oil droplets and promote coagulation. Similarly to API separators, plate separators are only effective at removing large oil droplets (20-30 μ m), and produce effluents of 100 mg/L residual oil content for typical produced waters. However, plate interceptors occupy 15-20% less space than API separators. Deng et al. (2002) have modified the plate interceptors, by adding coalescence and separation sections in which feed water is directed through a series of hexagonal cells, resulting. resulted in 95% removal of oil from oilfield produced water.

5.3 Hydrocyclones

Hydrocyclones rely on a tangential inflow to generate a vortex that pushes oil to the center and water to the outside of the circular flow. Hydrocyclones are capable of removing oil droplets as small as 5 μ m, and typically achieves 90% removal of free oil down to residual concentrations of <10 ppm. Allen (2006) reported that air-sparged hydrocyclones can effectively remove emulsified oil and can produce relatively low oil residuals (e.g., 21 ppm). Residuals from the treatment process are not described.

5.4 Centrifugation

Centrifuges are most often used for low volume operations or viscous fluids, and are effective at removing oil droplets in the 1.5-3 μm size range. Separation of oil from water using centrifugation is similar to principles applied for hydrocyclones, except that centrifuges rely on a motor to generate the centripetal force. System residuals were not described for the oil industry by the authors.

5.5 DAF

In DAF, bubbles are produced by forcing supersaturated water through a needle. The subsequent depressurization of the water when it exits the needle produces a stream of tiny bubbles (50-100 μm). DAF bubbles are produced with minimal turbulence and thus are more suitable to the clarification of light floc and precipitates that may breakup or redissolve in turbulent conditions. System residual of the process were not mentioned.

5.6 IGF

IGF units for produced water treatment comprise four separate cells in which bubbles of methane or nitrogen gas are introduced to the cells (Allen, 2006). Oil residuals in IGF effluent range from 20-30 mg/L, and oil droplets as small as 25 μm can be removed. Total oil reductions of greater than 95% have been reported (Allen, 2006). The effectiveness of IGF is dependent on three groups of chemical reagents known as collectors, froth-forming agents and modifiers. Collectors increase the hydrophobicity of oil droplets; froth-forming agents reduce the surface tension between oil and water and promote the formation of gas bubbles. Modifiers influence the effects of collectors and froth-forming agents (e.g., shift in pH). Induced gas flotation is preferable over dissolved air flotation (DAF) for boiler feed water treatment because oxygen added by DAF increases the corrosivity of the water, thus affecting the material and equipment used (Allen, 2006). For this reason produced water recycling at heavy oil installations rely on IGF units for de-oiling. Residuals from the treatment system were not described.

5.7 Dissolved Air Precipitation

Dissolved air precipitation (DAP) is another flotation method in which air is introduced to a column under pressure, forming microbubbles (diameter less than 100 μm) when pressure in the vessel is released. Thoma et al. (1999) tested DAP on oilfield produced water and reported 95% removal of dissolved octane, 75% removal of micro-dispersed decane, and 40-70% removal of ethylbenzene and toluene.

5.8 Electrolytic Flotation

Electrolytic flotation is capable of separating oil-in-water emulsions and is widely applied in manufacturing industries (e.g., food processing). Electrolytic flotation units are versatile and competitive to settling tank



technologies which require a large area. The electrolytic flotation units are small and compact and require less maintenance and running (Hosny, 1996). Gas bubbles are formed on the surface of iron or aluminium electrodes, and then rise up to the surface where the oil is removed by skimming. However the extent to which it is used for produced water treatment is unclear (Allen, 2006). Early studies on the treatment of in situ oil sands produced water with electrolytic flotation yielded positive results, however it was concluded that considerable technological advances were required before the process could be applied commercially (Allen, 2006). Hosny et al. (1996) reported 60% removal of emulsified oil using an electro-flotation cell with a lead anode and stainless steel cathode. Oil removal rates were increased by 10-20% with the addition of salt and a flocculant. Residuals from the treatment system were not described.

6. FILTRATION

Filtration refers to the use of a water-permeable barrier that restricts the passage of solids or liquids. Non-membrane filtration processes can be broadly classified into granular media, and precoat, cartridge filtration. In addition to multi-layer granular media filters, a wide range of materials have been used in single-layer filters for oily water treatment, including hay, polyurethane foam, glass fibre, slag fibre, pitch coke, ligneous materials, and peat. Filters are formed from these materials by encapsulating them in wire or synthetic polymer mesh. In filtration-coalescence filters, emulsified oil droplets adsorb to filter media that promote coalescence, which is followed in turn by desorption of larger oil droplets. Adsorbents such as activated carbon, fly ash, and synthetic polymers have also been incorporated into deoiling filters.

Granular media filters typically consist of packed sand and anthracite columns, though other filter media such as magnetite (iron oxide) and garnet (silicate mineral) may be included in mixed-media filters (Allen, 2006). Solids are retained as feed water passes through the filter media. Retention of the solids can occur on the surface or within the granular materials of the filter. Retention on the surface of the granular layer is termed cake filtration, whereas retention of solids within the material is termed depth filtration. Granular bed filtration systems can be designed as upflow filters (pressure-driven) or deep downflow filters (gravity-driven). In upflow filters, feed water enters at the bottom of the vessel and passes upwards through the granular layer, trapping solids in eddies that form behind particles. In deep downflow filtration, the primary removal mechanism is adsorption, which is promoted by chemical or electrostatic forces of attraction between the target particle and filter medium (Allen, 2006).

In precoat filtration, the filter medium is a thin layer of diatomaceous earth set on permeable materials that is supported by a rigid filter element. As filtration proceeds, the diatomaceous earth sloughs off and is replaced by dosing the feed water with the filter media. Precoat filtration can remove particles as small as 0.5 μm and is typically used as a polishing step to remove small particles, microbes and oil, although filtration of the latter can lead to fouling problems (Allen, 2006). Cartridge filters consist of polypropylene, glass fibre, or woven metal meshes and are easily interchanged for cleaning or disposal.

Filtration is an integral component in produced water treatment trains either as an intermediate step between primary and secondary oil removal processes or as a final polishing step prior to tertiary

treatment processes (Allen, 2006). Deep bed filters are not recommended for influent oil concentrations exceeding 100 mg/L (Allen, 2006). Granular media filtration combined with flocculants can reduce oil residuals to 5-10 mg/L but will not remove soluble oil (Allen, 2006).

6.1 Micro-and Ultrafiltration

Micro- and ultrafiltration are pressure driven membrane processes that reject particles as small as 0.1 μm and 0.01 μm , respectively (Allen, 2008). Over the last two decades, synthetic polymer and ceramic membranes have been studied by the oil industry for their potential to remove oil, suspended solids and other pollutants produced from the produced water. Lab- and pilot scale studies on membrane treatment of produced waters have demonstrated over 90% oil rejection with concentrations or less than 20 ppm. However wide scale acceptance of membranes has been hindered by concerns over fouling and membrane durability.

6.2 Nanofiltration

Nanofiltration is a process that has a molecular weight cutoff as low as 300-400 Dalton (Da). Da is a unit of mass used to express atomic and molecular masses. The nanofiltration membranes can be an alternative for partial demineralization, softening, and removal of soluble organic compounds from produced water (Allen, 2008). The process has been demonstrated to successfully remove NA, which are precursors to methane generation in the tailings ponds.

Among volatile and aromatic compounds, molecular diameter may be a greater predictor of rejection than molecular weight. Molecular diameter is dependent on the chemical structure, properties and conformity of atoms within the compounds. A study has shown that there was a positive relationship between molecular width of aromatic compounds and rejection, while there was no correlation between molecular weight and rejection of aromatic compounds (Kiso et al., 2001). Nanofiltration also removed 90% of semi-volatile organic compounds and resulted in lower rejection for VOCs. Although nanofiltration has higher associated removal efficiencies, costs associated with this technology currently exceed conventional technologies (Allen, 2008).

7. ADSORPTION

Adsorption is defined as the accumulation of one substance on the surface of another substance and is an important retention mechanism in many water treatment processes, including coagulation, chemical precipitation, filtration, and ion exchange. As a water treatment process, adsorption involves the addition of an adsorbent material (e.g., activated carbon) to a reaction vessel to bind specific pollutants, followed by separation from the aqueous phase by filtration. Adsorbents are used in a wide array of treatment processes, but are particularly suited to the removal of organic carbon compounds, dyes, and heavy metals.



Both organic and inorganic adsorbents are used in water treatment. The most common organic adsorbent is activated carbon, which is produced from a range of materials including anthracite and bituminous coal, lignite, pine, peat, and coconut shells (Pollard et al., 1992). Activated carbon is prepared in a two-step process involving carbonization, in which all non-carbon elements are removed from the base material, and activation, whereby a catalyst is used to clear away tarry substances and produce a porous structure with a large surface area (100-1,500 m²/L).

There are two main forms of activated carbon used in wastewater treatment; granular activated carbon (GAC), which is often used in filter beds, and powdered activated carbon (PAC), which is added to reaction vessels as a free-floating adsorbent. A third type, cloth or fibrous activated carbon (FAC), has been shown to outperform granular activated carbon in certain applications, however, treatment units have to be redesigned to accommodate FAC, which increases the costs of using the system. (Ahsan et al., 2001). Activated carbon can be reused, but must be regenerated via thermal, chemical, or biological processes.

Natural and waste materials (both organic and inorganic) offer low cost alternatives to activated carbon. These materials include bark, lignin, charcoal, cement, zeolite, bentonite, fly ash, peat, steel plant slag, soil organic matter, and alumina. Ahsan et al. (2001) examined the use of natural and waste materials as sorbents for removal of suspended solids, phosphate, nitrate, ammonium, and COD from municipal wastewater. Charcoal was the most effective at removing suspended solids and COD. Cement and waste paper had the highest removal rates for phosphate, and nitrolite removed the most ammonium. Fly ash has been shown to effectively adsorb copper and zinc in solution (Allen, 2006), and calcium and magnesium oxides (from decomposed bentonite) have been shown to be an effective treatment alternative for oily wastewater compared to sand filtration/coagulation/ultrafiltration (Allen, 2006). Peat is a porous, inexpensive material with excellent adsorption and ion exchange capabilities. In a review on the use of peat in water treatment Couillard (1994) reported 90-99% removal of emulsified oil, 53-97% removal of benzene, toluene, and m-xylene, 99% removal of copper, and 93-96% removal of zinc.

Activated carbon is capable of removing many of the soluble organic compounds associated with the petroleum industry. Activated carbon treatment of produced water was reported to remove 95-100% of naphthenates, 75-100% of dispersed oil, 25% of production chemicals, and 15% of aliphatics with (Allen, 2006). Naphthenic acid concentrations can be reduced by 75% in oil sands process water after acidification and treatment with GAC, and 80-100% reduction after acidification and PAC treatment. Activated carbon was shown to remove 73% of TOC from oil sands water. Activated carbon has also been shown to detoxify process water from Utah oil sands (McTernan et al., 1986). However, activated carbon is an expensive option for treatment of produced waters for its relatively low adsorption capacities for soluble organics. Total cost estimates for the activated carbon treatment were \$2.29 US dollars (USD) /m³; (1994 base year), were over 2-fold higher than other technologies used in the oil industry (Allen, 2006). Activated carbon treatment of oil sands process water had a much lower estimated cost (\$0.197 USD/m³; [1996 base year]) (Allen, 2006).

ENVIRONMENT CANADA

**REVIEW AND SUMMARY OF EMISSION FACTORS FOR OIL SANDS TAILINGS PONDS AND MINING FACES
AND OPTIONS FOR REDUCING EMISSIONS**

Modified inorganic adsorbents can offer an alternative to activated carbon for produced water treatment. Gallup et al. 1996 compared GAC to anthracite, organically modified clay, and synthetic polymeric adsorbents on the basis of oil and BTEX removal from oilfield produced water. The organic-modified clays demonstrated the highest removal rates for emulsified crude oil (50%), but were ineffective at removing benzene (21%) and toluene (24%). Neither GAC nor carbonaceous adsorbents removed emulsified oil, but the carbonaceous adsorbents had the highest removal rates for benzene and toluene (93%). GAC had comparatively poor removal rates for benzene and toluene (23% each). In pilot studies it was determined that fouling from oil severely reduced the adsorptive capacity of the carbonaceous adsorbents, and an influent oil and grease concentration of 1 to 5 mg/L was recommended. Cost estimates indicated that carbonaceous adsorbents would be 4- to 7- fold less expensive than GAC to treat BTEX compounds in produced water.

A wide variety of sorbents are used in the petroleum industry to remove oil and soluble organic compounds (Table A). Natural organic adsorbents such as walnut shell media are widely used for oil removal (Allen, 2006) although synthetic adsorbents have also proven effective. In a comparison between walnut shell media and a synthetic adsorbent (surface-treated polyethylene terephthalate; PET), Yang et al. (2002) reported slightly higher oil removal rates for the PET adsorbent (83-99%), and noted that it was easier to clean than the walnut media.

Table A Adsorbents used on Oilfield Produced Water for PPCs in the Oil Industry (Allen, 2006)

Sorbent	Wastewater type	Major findings
Activated carbon	Offshore produced water (North Sea)	95-100% removal of naphthalenes 75-100% removal of dispersed oil 15% removal of aliphatic hydrocarbons 73% removal of total organic carbon
	Alberta oil tailings pond water	
	Utah oil sands process water	Process water detoxification
GAC ⁽¹⁾	Oilfield produced water	23% removal benzene and toluene ineffective on emulsified oil
Activated carbon w/ tetrabutyl ammonium and copper	Industrial wastewater	1.7- to 2-fold greater removal of phthalate than for unmodified activated carbon
Activated carbon + acidification	Alberta oil sands process water	75% removal of naphthenic acids w/ GAC 80-100% removal of naphthenic acids w/PAC ⁽²⁾
Inorganic and modified inorganic adsorbents		
Polymer-modified bentonite + granular activated carbon	Oilfield produced water	TPH reduced from 150 ppm to n.d O+G ⁽³⁾ reduced to non detection BTEX reduced to < 1 µg/L
Hydrophobic zeolite	Offshore produced water	60-70% removal of BTEX from produced water
Organoclay	Oilfield produced water	50% removal of emulsified oil 21% removal of benzene 24% removal of toluene



Sorbent	Wastewater type	Major findings
Carbonaceous adsorbent	Oilfield produced water	93% removal of benzene and toluene Ineffective on emulsified oil
Natural organic adsorbents		
Peat	Various	90-99% removal of emulsified oil 53-97% removal of benzene, toluene, and xylene; 99% removal of copper, 93-96% removal of zinc
Walnut media	Oilfield produced water	40% removal of oil and grease, residual concentration of 100 ppm
	Oilfield produced water	39% removal of oil and grease
	Heavy oil produced water	62-81% removal of oil, residual
Synthetic organic adsorbents		
Polymeric adsorbent	Oilfield produced water	31-42% removal of benzene and toluene
PET ⁽³⁾	Heavy oil produced	83-99% rejection of oil, residual
Macroreticular resin (polystyrene polymer water compounds cross-linked with divinylbenzene)	Oilfield produced	60-78% removal of soluble organic

⁽¹⁾ Granular activated carbon

⁽²⁾ Powdered activated carbon

⁽³⁾ Polyethylene terephthalate

8. BIOLOGICAL TREATMENT

Biological treatment refers to the use of microorganisms to stabilize BOD through nutrient absorption and oxidation of organic pollutants. In aerobic systems, the by-products of microbial oxidation are carbon dioxide, inorganic species (e.g., chloride), water, and energy. The energy released from the oxidation of organic compounds is used by the microorganisms for growth. Where dissolved oxygen concentrations are low sulphate or nitrate may be used as oxygen sources. In anaerobic systems organic compounds are broken down via hydrolysis and/or methanogenesis reactions (Allen, 2006).

Application of conventional biological treatment to more complex industrial effluents has been hindered to some degree by the relative sensitivity of microorganisms to feed water salinity and toxic organic chemicals. Improvements on suspended growth design have come in the form of fixed growth or fixed biofilm systems, fluidized bed reactors, and sequential batch biofilm reactors (Allen, 2008). In fixed growth systems, microbial cultures are plated on a substrate or bed that is subsequently immersed in the feed water stream (Allen, 2008). Fluidized bed reactors (FBR) consist of biofilm coated particles contained within a column. This typically yields a 10-fold increase in efficiency from the activated sludge system (Allen, 2008). Fluidized bed reactors exhibit greater resistance to toxic wastewaters than

conventional biological treatment, and can incorporate specialized microbes to digest toxic compounds including aromatic compounds, chlorinated organic compounds, and other recalcitrant contaminants (Allen, 2008).

Biological treatment has been tested extensively in the oil industry for application in the removal of organic carbon and nitrogen compounds (Table B). In order for the compound to be biodegraded it has to be solubilised for availability to the microorganism to metabolize. Some studies reported that biodegradation of hydrophobic compounds is facilitated by specialized microbial cultures, which solubilise hydrocarbons for transport across cellular membranes (Tellez et al., 2002). However, other studies have reported poor treatment performance due to toxic effects of produced water (Allen, 2008).

Recent advances in bioreactor technology have addressed the problem of microbial toxicity through combining GAC/PAC with FBR. The combination of activated carbon and microbial biofilm improves the removal of toxic organic compounds, mitigating their toxic effects (Allen, 2008). The addition of GAC/PAC FBR, reported a 99% removal of BTEX (Allen, 2008). Total costs for a single stage system using GAC/PAC combined with FBR were estimated at \$0.428 USD /m³, (2004 base year) (Allen, 2008).

Membrane bioreactors are another potential option for biological treatment of oilfield produced wastes. Biological solids from the activated sludge process are filtered by a membrane unit and returned to the bioreactor, eliminating the need for activated sludge treatment (Allen, 2008). Membrane bioreactors offer several advantages over conventional biological treatment, including higher biomass concentration, lower nutrient requirements, decreased sludge production, greater pollutant removal rates and smaller environmental footprint (Melin et al., 2006). Removal of organic micropollutants is also enhanced in membrane bioreactors relative to conventional systems or membranes alone, as result of effective pore size, and/or molecular weight cutoff (Melin et al., 2006).

For the oil sands industry, advances in biological treatment may lead to new alternatives for removal of naphthenic acids. Newer designs may consume 25% of the operational energy used in activated sludge systems while producing 55-75% less waste sludge. Consequently, costs for high rate processes may be lower than conventional biological treatment technologies. Estimated total costs for a GAC-FBR is \$0.62 USD/m³, (1997 base year), whereas energy costs alone for a small scale activated sludge treatment systems are estimated at \$0.62 USD /m³(2002 base year) (Allen, 2008).

Table B Biological Treatment Studies on Oilfield Produced Water (Allen, 2008)

Process	Wastewater	Findings
Activated sludge	Oilfield produced water	98-99% removal of total petroleum hydrocarbons initially affected by salinity
Activated sludge and powdered activated carbon	Oilfield brine	Microbes affected by high salinity; addition of powdered activated carbon improved degradation rates



Process	Wastewater	Findings
Biological treatment w/ polystyrene particles	Oilfield wastewater	65% removal of COD 80% removal of TOC 65% removal of phenols 40% removal of ammonium
Biological treatment	North Sea produced water	14-30% removal of phenols; poor removal
Fixed film membrane bioreactor	Oil refinery wastewater	85% removal of COD
FBR ⁽¹⁾ and PAC ⁽²⁾	Oil in water emulsion	TOC removal increased from 70% to 96% after addition of activated carbon
FBR	Gas well produced water	90% removal of soluble organics
FBR and GAC ⁽³⁾	Oilfield produced water	98% removal of BTEX
2-stage GAC and FBR-	Oilfield produced water	99% removal of BTEX 94% removal of oil
Membrane bioreactor	Oil contaminated water	99.9% removal of oil
Trickling filter	Oilfield produced water	15-25% removal of TOC microorganisms were negatively affected by toxicity from phenols

(1) Fluidized bead reactor

(2) Powdered activated carbon

(3) Granular activated carbon

9. ADVANCED OXIDATION

Chemical oxidation processes degrade pollutants through a series of ionic or radical reactions involving an oxidant compound that either accepts electrons or donates an electron-accepting group. The most frequently used oxidants in water and wastewater treatment include chloride (Cl^-), hydrogen peroxide (H_2O_2), ozone (O_3), and permanganate (MnO_4^-) or exposure to ultra violet light (UV) (Allen, 2008). Photocatalytic and sonochemical oxidation are the two primary chemical oxidation techniques that have demonstrated the potential to degrade chemical compounds associated with oilfield produced water. Chemical oxidation is most commonly used for compounds that are not amenable to biological treatment due to their toxicity or recalcitrant nature. Examples of these species include cyanide, formaldehyde and aromatic compounds (Gogate and Pandit, 2004).

9.1 Photocatalytic Oxidation

Photocatalytic oxidation is the process where organic compounds undergo oxidation as a result of chemical reaction by a radical produced through the photo-excitation of valence electrons on the surface of a catalyst (Allen, 2008). Photocatalyst particles can be immersed in the feed water as a slurry or fixed to a bed or the internal surface of the reactor. Fenton's reagent is the first photocatalytic oxidation technology, where solution of H_2O_2 and an iron catalyst is used to oxidize contaminants or wastewaters.

Fenton's reagent can be used to destroy organic compounds such as trichloroethylene (TCE) and tetrachloroethylene (PCE).

The most common photocatalysts are titanium dioxide (TiO_2) or associated aggregate particles comprising of TiO_2 immobilized on particular matter such as soil-gel or zeolite or derivitized TiO_2 compounds. Lab-scale experiments have demonstrated that photocatalytic reactions can degrade organic and inorganic compounds in oilfield produced water, including aliphatic and aromatic carboxylic acids, and NA (Maazarino and Paccinni, 1999). The biggest drawback of photocatalysis as it stands in the energy requirement. TiO_2 requires UV to be an active photocatalyst.

Advances in photocatalysis are focused on improving process efficiency. Photocatalytic degradation rates are dependent on efficient adsorption of pollutants onto the catalyst, which in turn may be affected by feed water pH or the presence of certain ionic species, which preferentially fill the adsorption sites in place of the target solutes (Allen, 2008). These issues have been resolved by surface modification of TiO_2 with chelating agents, reduction in the size of the photocatalysts to increase surface area, and increasing the photosensitivity and/or absorption wavelength of the photocatalysts (Allen, 2008).

The presence of salts in oilfield produced water can have a negative effect on radical production and photocatalytic reaction rates. High concentrations of radical scavengers such as chloride and bicarbonate can reduce reaction rates (Bessa et al., 2001), and high concentrations of electrolytes can affect the dispersal of nano-sized catalyst particles (Li et al., 2006). The problem of radical scavenging by chloride ions can be addressed by applying voltage across the photocatalytic cell, a process known as photoelectrocatalysis. Due to the electrolytic generation of chlorine and hypochlorite from chloride ions, the presence of chloride will enhance oxidation rates during photoelectrocatalysis (Santos et al., 2006).

Solar photocatalytic processes have also been developed and tested on soluble organic compounds, however only a few commercial applications are presently known (Allen, 2008). Cho et al. (2006) reported >70% reduction of BTEX with immobilized TiO_2 and solar light, and found degradation rates improved with the addition of hydrogen peroxide. A cellulose bleaching effluent from the pulp and paper manufacturing was degraded in batch conditions by photocatalysis using TiO_2 (Yebera et al., 2000). The effluent was completely decolourised and the total phenol content was reduced by 85%. Partial mineralization of the organic matter was confirmed by total organic carbon (TOC) reduction, approximately 50%.

9.2 Sonochemical oxidation

The application of ultrasonic energy is applied to a liquid, causes the formation and collapse of microbubbles. The collapse produces cavities of high temperature and pressure that can break apart or degrade particles and molecules. This also results in the sonolytic production of hydrogen and hydroxyl radicals from water molecules (Allen, 2008). Used in combination with an oxidant such as hydrogen



peroxide, ultrasonic cavitations becomes a sonochemical oxidation process, which effectively degrade organic compounds associated with produced water, including phenols, and PAHs (Allen, 2008).

To date ultrasonic irradiation has been implemented as a pre-oxidation step in tertiary treatment processes. However large-scale applications remain limited due to several limitations associated with the process. Treatment of large volumes of liquid is energy intensive. Additionally, the complete mineralization of high molecular weight compounds is generally unattainable (Gogate et al., 2004). Sonochemical oxidation is also relatively expensive compared to other technologies. Hybridization with other oxidation processes such as Fenton's process and photochemical processes is anticipated to improve energy efficiency of this technology and increase its potential as a water treatment technology.

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