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#### Assessment of the Significance of Emissions During *Ex-situ* Remedial Activities compared to Landfill Disposal 2012 Update

AUPRF Reference #09-9190-50

Meridian Project No. 11441.1

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November 26, 2012

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#### **Executive Summary**

Under the authorization of the Petroleum Technology Alliance Canada (PTAC), Meridian Environmental Inc. (Meridian) has conducted an assessment of the environmental significance of vapour emissions during *ex-situ* remediation activities. The work was conducted under the Alberta Upstream Petroleum Research Fund (AUPRF), under the direction of the Canadian Association of Petroleum Producers (CAPP) and the Small Explorers and Producers Association of Canada (SEPAC), as indicated in a letter of approval from PTAC dated August 24, 2010, and a subsequent letter of approval dated February 3, 2012. The following report documents the results of the assessment, and has been updated to reflect work conducted in 2012.

The purpose of this study was to conduct a life cycle analysis of emissions from *ex-situ* remediation as compared to landfill disposal for soils contaminated with volatile petroleum hydrocarbons (e.g. condensate). Specifically, the study involves the development of a modelling approach that can be used to evaluate potential health and environmental effects from toxic emissions, effects on air quality from criteria air contaminants, and greenhouse gas emissions. *Ex-situ* remediation and landfill disposal are compared using approaches as similar as possible in order to ensure the comparison is meaningful. The objective of the project is to be able to meaningfully assess the relative human health and environmental impacts of the two approaches in order to determine whether *ex-situ* remediation may be an appropriate approach at a specific site.

A literature review was conducted to identify relevant models to estimate emissions of volatile organic chemicals (VOCs), criteria air pollutants and particulates from both *ex situ* remediation and landfill disposal. The most appropriate available model for each process was selected based on scientific basis, defensibility, regulatory acceptance, applicability to Canadian conditions, and ability to meet project objectives.

The selected models were combined into a single recommended modelling approach capable of predicting life cycle emissions of all emissions evaluated, as well as short-term emissions of VOCs for the evaluation of human health and environmental effects using regulatory air dispersion models. A test of the modelling approach was conducted using data from an example site where ambient air monitoring had been conducted.

Work conducted in 2012 included:

- Further research into the use of biofilters with ex situ remediation, including evaluating the lifecycle emissions from ex situ remediation with and without biofilters, including consideration of the production and fate of the biofilters; and the effects of biofilters on ambient air quality.
- Collection of real-world emissions data from ex situ remediation to calibrate and confirm the modelling assumptions, in particular from highly contaminated soils.
- Development of a simple spreadsheet-based calculation tool for screening-level evaluations using the modelling approach described herein.

# **1** INTRODUCTION

## 1.1 General

Under the authorization of the Petroleum Technology Alliance Canada (PTAC), Meridian Environmental Inc. (Meridian) has conducted an assessment of the environmental significance of vapour emissions during *ex-situ* remediation activities. The work was conducted under the Alberta Upstream Petroleum Research Fund (AUPRF), under the direction of the Canadian Association of Petroleum Producers (CAPP) and the Small Explorers and Producers Association of Canada (SEPAC), as indicated in a letter of approval from PTAC dated August 24, 2010, and a subsequent letter of approval dated February 3, 2012. The following report documents the results of the assessment, and has been updated to reflect work conducted in 2012. The activities conducted in 2012 are also documented separately (Meridian, 2012).

## 1.2 Background

Onsite *ex-situ* soil remedial technologies involve the excavation of contaminated material and treatment onsite, potentially resulting in the release of volatile chemicals to ambient air. Volatile emissions resulting from remedial activities may contribute to greenhouse gas emissions through fugitive emissions (Valsaraj et al., 1994), as well as potentially impacting ambient air for humans or sensitive ecological receptors on or near remedial sites. Other potential chemicals of concern may also be emitted from soil as a result of biological processes during soil treatment. Fugitive emissions, whether from industrial processes or remedial efforts in the oil and gas industry are often subject to considerable uncertainty surrounding their quantity and composition, in part due to the inconsistent use of measurement systems, and the limitations therein. Additionally, fugitive emissions from remedial activities are often not considered at all due to measurement limitations, as well as the inconsistency of emissions and the deemed negligible permanent effects. Exposure to volatile contaminants that workers, nearby residents, or sensitive ecological receptors may receive during remedial soil processes had not been quantified. Currently, data gaps exist about the risks receptors may be receiving.

The United Nations Framework Convention on Climate Change (UNFCCC) is a binding international legal instrument directly dealing with climate change. Under this framework Canada, an Annex I Party, must report a national annual inventory of human-induced greenhouse gas emissions that are consistent with the intergovernmental panel on climatic change (IPCC) guidelines. Within the IPCC guidelines, fugitive emissions from remedial activities are not specifically addressed; however, fugitive emissions from the oil and natural gas industry as a whole are addressed (Section 4.2, Fugitive Emission, IPCC, 2006) and remedial emissions are grouped under venting 'disposal of waste associated gas at oil production facilities' (IPCC, 2006). Tier 3, the most comprehensive, bottom-up sum of emission estimates considers source type at the individual facility level including: venting, flaring, fugitive equipment leaks, evaporation losses and accidental leaks. Currently, there is no guidance given or methods recommended for use in quantifying emissions from remedial activities; furthermore vented volumes are considered highly suspect since these values are typically estimates and not based on actual measurements. Currently the IPCC guidelines state that audits and reviews should be conducted by industry representatives to determine if all vented and flared volumes are actually reported, that the reported volumes are actually vented or flared, or to develop appropriate apportioning of venting relative to flaring. Forthcoming ERCB directives are also expected to require reporting of these emissions.

As an Annex I Party member, Canada is required to continuously improve the quality of our national greenhouse gas inventory. Fugitive emissions from the energy industry accounted for approximately 10.6% of total emissions in 2007, not including any releases from *ex-situ* remediation (Environment Canada, 2007). Emissions from *ex-situ* remedial activities have been recognized as contributing significant impacts to ambient air, and accepted technologies to minimize volatile losses have been recommended for over a decade (US EPA, 1997). However, there are also emissions associated with other soil remediation processes, including landfill disposal.

There are three general approaches to estimating exposure concentrations in air: (1) ambient air monitoring, (2) emission measurements coupled with dispersion modelling, and (3) emission modelling coupled with dispersion modeling (USEPA, 2006). Mine surface emissions in oil sands exploration have been monitored by both Syncrude and Suncor using soil emission flux chamber measurements to calculate site-specific emission factors. This surface emission estimation accounts for area, time exposed, ambient temperature, and surface type; however, this estimation differs from remedial emissions as soil handling during remedial activities aims to increase the volatility of contaminants. The development of a scientifically defensible model to quantify remedial emissions during *ex-situ* activities will allow upstream oil and gas to more accurately estimate their emissions, and define the associated risks.

# 1.3 Purpose/Objectives

The purpose of this study was to conduct a life cycle analysis of emissions from *ex-situ* remediation as compared to landfill disposal for soils contaminated with volatile petroleum hydrocarbons (e.g. condensate). Specifically, the study involves the development of a modelling approach that can be used to evaluate potential health and environmental effects from toxic emissions, effects on air quality from criteria air contaminants, and greenhouse gas emissions. *Ex-situ* remediation and landfill disposal are compared using approaches as similar as possible in order to ensure the comparison is meaningful. The objective of the project is to be able to meaningfully assess the relative human health and environmental impacts of the two approaches in order to determine whether *ex-situ* remediation may be an appropriate approach at a specific site.

# 1.4 Scope of Work

The scope of work was based on a proposal submitted by Meridian on July 23, 2009, modified based on subsequent discussions with the 2010 CAPP project manager, Steve Kullman of Husky Energy Inc. and members of the AUPRF Steering Committee.

In general, the scope included the following components:

- Conduct a literature review to identify and assess existing models used to estimate emissions to ambient air from *ex-situ* remediation and landfill disposal, and to identify key factors that would influence contaminant volatility and modelling outcomes.
- Conduct a critical review of available models based on applicability, scientific defensibility and regulatory acceptance.
- Develop a modelling approach for evaluating volatile and particulate emissions and air concentrations from *ex-situ* remediation, and life-cycle emissions of volatile organic compounds (VOCs), criteria air contaminants and greenhouse gasses from *ex-situ* remediation and landfill disposal.
- Determine appropriate default model input parameters.

• Document the results of the project in a report.

The work scope was expanded in 2012 to include the collection of site data to calibrate the model, research into lifecycle emissions from biofilters, and development of a user spreadsheet for the model. This work is detailed in a separate report (Meridian, 2012); key results have been incorporated into this report.

## 2 METHODS

#### 2.1 General Approach to Life Cycle Assessment

Life cycle assessment is often applied as a technique to assess each and every impact associated with all the stages of a particular process. One key aspect in this application is that it compares potential environmental impacts of different options for providing the same service, in this case remediation of a site to meet guideline levels. Life cycle assessment is usually a comprehensive tool, covering a wide range of environmental impacts, which enables the estimation of direct as well as indirect environmental impacts related to the remediation activities being investigated. Its strengths are rooted in the basic engineering principles of material and energy balances, where some form or accounting is usually conducted. This can be achieved by compiling an inventory of relevant environmental releases, and evaluating the potential associated impacts.

Common categories of assessment in environmental life cycle assessment include greenhouse gases, acidification, smog, ozone layer depletion, eutrophication, energy use, toxicological pollutants, habitat destruction, desertification, land use, and depletion of mineral and fossil fuels. It is typical to categorize energy-environmental considerations in terms of various products of energy operations that flow into and potentially harm the environment. One way that energy systems interact with the environment is through the release of solid, liquid and gaseous phase by-products that are known to be hazardous to human health or to threaten ecosystems. Material by-products of energy consumption are often referred to as pollutants, hazardous emission, effluents and waste and are the focus of this life cycle assessment.

A life cycle assessment typically considers both primary and secondary impacts, where primary impacts are those local toxic impacts related to remedial activities, and secondary impacts are created due to the remediation process as well as upstream and downstream processes. Tertiary impacts refer to post-remediation phase impacts, such as site reuse restrictions, and will not be considered in this assessment due to a high level of associated uncertainty.

Often, to meet remedial objectives, and protect receptors from potential exposure, a volume of contaminated soil is disposed in a landfill disposal facility. Onsite *ex-situ* soil remedial technologies are alternative methods that involve the excavation of contaminated material and treatment onsite, resulting in the release of volatile chemicals and particulates to ambient air. These remedial emissions may affect ambient air quality in the vicinity of the site and contribute to overall emissions of greenhouse gases, total particulate emissions, and volatile organic compounds (VOCs). However, landfill disposal also generates and contributes to the emissions of greenhouse gases, total particulate, VOCs may also be released during excavation and transport.

A literature review of environmental life-cycle assessments related to remedial technologies indicates that landfill emissions are generally neglected as part of the assessment due to the

lack of data, or short time frame of the assessment; however, transport of equipment, material and soil to and from the site is generally considered (Lemming *et al.*, 2010). Often the focus of these *ex-situ* life assessments in the literature, although based on the life cycle principles, is to facilitate remedial comparisons and only considers energy use and impacts during the remediation project and related emissions. As the focus of this current report is the comparison, in a life cycle approach, of landfill and *ex-situ* remedial emissions the consideration of landfill emissions is required.

To complete this assessment a life cycle approach was used considering assessment damages that included the accounting of predicted pollutant emissions including greenhouse gases, and criteria air contaminants. To simplify the comparison, only aspects of the techniques that were quantifiable, comparable and specifically related to the remediation processes were considered. The assessment was considered a 'gate to grave' assessment and the environmental impacts of fuel production, equipment production, preceding site visits etc. were not considered, but rather the time scale began when remedial activities began on-site.

# 2.2 Contaminant Fate Modelling

Contaminant fate and transport models have historically been used in a variety of applications including risk assessment, analysis of remedial system performance, cost-benefit assessment and contaminant life cycle analysis (Benson et al., 1993; Poulsen et al., 2001). Models used in these applications attempt to simulate the chemical and physical processes affecting both the release and movement of multi-compound chemical mixtures. To enable a quantifiable comparison, kinetic or mass transfer equations are often applied because of their conceptual and mathematic simplicity. However, more complex modelling is often required to make estimations with defined timescales. The environmental effects associated with petroleum hydrocarbons are encountered at different length and times scales, so the various categories of human health and other adverse impacts are often divided into a more manageable length-time scale. For the purposes of this life cycle assessment, the time scale considered begins when remedial activities commence and concludes when the mass of contaminant is completely removed from the soil media. Environmental impacts assessment will benefit by disaggregating impacts of interest according to more defined processed of their impacts, as a single modelling platform would have little hope of reliably capturing all the effects (Lemming, 2010).

One approach is to solve the equations that govern the transport and transformation of pollutants to compute the contribution of a given source to the concentration of a pollutant at its impact location (Seinfeld and Pandis, 1998). Applying a chemical mass balance, which allocates a mass through the chemical analysis of pollutants measured at the source and can assume all or a portion of that mass is transferred to another media, is also frequently done in life cycle assessments (Tester, 2005). Greenhouse gas emissions models 'work' by solving the mathematic equations that express the laws of conservation of material and energy, and are therefore similar in theory to mass balance models where the mass in one media is assumed to be transferred to another media, but in the case of greenhouse gas and equipment emission modelling are the tools used to enable a quantifiable comparison in this life cycle approach of overall impacts from these two remedial scenarios.

While it is recognized that modelling also introduces uncertainty and that not every factor can be reduced to a number and inserted into a model, the use of modelling in this application is not

necessarily to provide a precise outcome value, but rather to allow for a relative comparison between the two scenarios. The application of mathematical models to comparative situations is often criticized, since studies can easily be swayed in favour of one product of process over another based on varying parameters, assumptions and differences in available data. To counter this, equivalent assumptions were made. The development of a modelling approach to enable a relative comparison is the basis of the work presented herein.

## 2.3 Atmospheric Fate of Petroleum Hydrocarbons

Contaminants found in the soil, representing a variety of compounds with varying carbon number, released into the atmosphere through volatilization will undergo additional transformation. Compounds released to air will have varying half-lives, and chemical specific transformation, often dependent on the availability of other compounds. To provide some context for the lifetimes of volatile compounds of main concern to human health a brief review of the atmospheric fate of key petroleum hydrocarbon compounds (benzene, ethylbenzene, toluene and xylenes) is provided.

Benzene released to the atmosphere will be found in the vapour phase, and reacts with photochemically produced hydroxyl radicals, with a predicted half-life of 13.4 days. However, in the presence of nitrogen oxides or sulphur dioxide, as would be expected at contaminated sites, this half-life is accelerated to 4-6 hours (US EPA, 2002b). The range of estimated half-lives for benzene is from 0.1 to 21 days, with photo-oxidation by-products including phenol, nitrophenol, nitrobenzene, formaldehyde, carbon dioxide and carbon monoxide, depending on the oxidant (Government of Canada, 1993a).

Ethylbenzene released to the atmosphere will exist predominately in the vapour phase, and also be broken down through photochemical degradation by reaction with hydroxyl radicals (US EPA, 1991). Ethylbenzene has also been found to undergo transformation reacting with NO<sub>3</sub> radicals and atomic oxygen (ATSDR, 2010). The predicted half-life ranges from 0.5 to 2 days through reaction with hydroxyl radicals (US EPA, 1991; ATSDR, 2010). Oxidation by-products from the reaction with hydroxyl radicals and nitrogen include ethylphenols, benzaldehyde acetophenone and nitro-ethylbenzenes (ATSDR, 2010), which are then themselves degraded further.

Toluene released to the atmosphere will also degrade by reacting with photo-chemically produced hydroxyl radicals yielding cresols, benzaldehyde, and a number of other products that are then themselves degraded further. The minimum half-life for toluene has been calculated to be 4.5 hours, but northern latitudes in winter are expected to result in longer half-lives (Government of Canada, 1992).

Xylenes in gas phase in the atmosphere will also photo-oxidize relatively quickly in a reaction with hydroxyl radicals yielding tolualdehydes, methyl glyoxal, methylbenzylnitrate, dimethyphenols and nitroxylenes, which over time are themselves degraded further. The range of lifetimes for xylenes has been estimated to be from 0.5 to 1.5 days (Government of Canada, 1993b).

The fate of these four contaminants, constituent components of residual condensate contamination, suggests that once released to air the predicted transformation times generally range from hours to days. Less data are available regarding the atmospheric fate and half-lives of other compounds found in volatile petroleum hydrocarbon mixtures. However, it is predicted

that photochemical oxidation and/or biological metabolism will play a role in the decomposition of such compounds as they have similar oxidative and enzymatic access points for cleavage; the time horizons for these activities are predicted to be similar. Overall, these volatile hydrocarbon compounds are not predicted to remain in the atmosphere longer than a few weeks before transformation to a breakdown product, which will also be further degraded. The resulting breakdown products either undergo additional atmospheric oxidation, or settle and undergo biological transformation. Either process will result in the eventual release of the constituent carbon as carbon dioxide or carbon monoxide; carbon monoxide eventually oxides atmospherically to carbon dioxide (Australian Government, 2009). Therefore, the carbon contained within contaminants released to the atmosphere is expected to eventually form carbon dioxide, and will be accounted for as such.

# 2.4 Processes Considered and Conceptual Models

For purposes of modelling, a conceptual model is required for each scenario to represent the processes and sources involved.

# 2.4.1 Ex-situ Remediation

Ex-situ remedial activities are varied but all include the physical disturbance of contaminated media for treatment. Soil disturbance will significantly increase the surface area of contaminated material to ambient air; often the aim of ex-situ remediation is aiding volatile contaminant partitioning from soil to air. Soil disturbance will also transform a significant portion of the contaminated media from anaerobic to aerobic conditions, affecting soil microbial carbon metabolism. Native microbial communities metabolize organic carbon sources, including hydrocarbons, often in cascade-type molecule breakdown. During these processes, substances that were previously non-volatile may be degraded to semi-volatile or volatile compounds and released to ambient air.

Ex-situ remediation aims to remove contaminant mass from soil media through the physical manipulation of the contaminated soil volume, encouraging partitioning from soil to air by exposing soil particle surfaces to air. Increasing soil exposure to air through physical manipulation, is the minimum requirement to be considered *ex-situ* remediation, however, this is often coupled with other techniques to encourage volatilization. The main techniques often used in combination with physical soil disturbance include biological treatment, chemical reduction or oxidation, and thermal desorption; for a more detailed overview of these techniques see Appendix A.

*Ex-situ* remediation is considered to involve the following processes:

- Mobilization/demobilization of equipment to the site.
- Excavation of contaminated soils.
- Onsite treatment of contaminated soils and replacement in the excavation.
- Long-term in situ degradation of residual contamination.

# 2.4.2 Landfill Disposal

As with the *ex-situ* remedial scenario, only residual contaminant mass contained within the soil media for the contaminant life-cycle will be reviewed, and the process and transport emissions will be considered using mathematic modelling and presented below.

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Hydrocarbon contaminants disposed in a landfill will undergo both aerobic and anaerobic biological transformation. The rate of gas production is a function of waste composition, age of waste (time since emplacement), climate, moisture content, particle size, compaction, nutrient availability, and buffering capacity (USEPA, 2005). Depending on these variables biochemical processes can produce a variety of volatile organic compounds in varying volume; it can therefore be difficult to predict the specific gas species that will be produced, or the volume generated especially for a class II or industrial landfill where little gas generation data is available. However, landfills will experience distinct phases in contaminant breakdown, as seen below.



Note: Phase duration time varies with landfill conditions Source: EPA 1997



Nitrous oxide, despite having a high greenhouse gas potential, is not an expected breakdown product of hydrocarbon degradation. Nitrous oxide is primarily produced from the bacterial breakdown of nitrogen in soils, and expected to be primarily released during the first phase as a result of soil spreading. Nitrous oxide, as a greenhouse gas, is not considered in the contaminant life-cycle.

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Under aerobic conditions most soil microbes can use oxygen as an electron acceptor and release carbon dioxide into the atmosphere, where denitrifiers released nitrous oxide under anaerobic conditions. Long-term anaerobic conditions will deplete major oxidants resulting in methanogen proliferation and the release of methane (Changsheng, 2007). Both nitrous oxide (298x) and methane (25x) have a higher global warming potential when compared to carbon dioxide (1x), the by-product of aerobic metabolism (IPCC, 2007).

Anaerobic degradation of petroleum hydrocarbons by microorganisms has been shown to occur at negligible rates in comparison to aerobic breakdown, however in the absence of oxygen studies have demonstrated the breakdown of saturated and aromatic hydrocarbon compounds, with methane as a by-product (Leahy and Colwell, 1990; Heider et al., 1999; Widdel and Rabus, 2001). This is relevant to landfill disposal, as the carbon mass contained in hydrocarbons disposed of in a landfill will most likely be transformed through biological processes and be released to the atmosphere, over the life-time of the contaminant, as methane.

Most hydrocarbons disposed in landfill are predicted to breakdown during the last phase, or the steady methanogenic phase, however it is unclear what proportion of the waste would be emitted as carbon dioxide or methane. Landfill disposal facilities monitored during the methanogenic phase, emit landfill gas that comprises roughly 45-60% methane (CH<sub>4</sub>) (IPCC, 2001; ESRD, 2008). Methane and carbon dioxide are the primary constituents of landfill gas but oxygen, nitrogen gas, and water vapour are also produced (US EPA, 2005). An overview of landfill gas composition during the methanogenic stage of the landfill can be seen in Table A.

Component	% Volume	Characteristic
CH <sub>4</sub>	45 to 60	Methane is a naturally occurring, colourless, and
		odourless gas. Its concentration in ambient air of
		~0.0002%. Landfills are the single largest source of
		man-made methane emissions
$CO_2$	40 to 60	Carbon dioxide is a colourless and slightly acidic gas
		that occurs naturally at a small concentration (0.03%)
		in the atmosphere
N <sub>2</sub>	2 to 5	Nitrogen gas comprises approximately 79% of the
		atmosphere. It is odourless, tasteless, and colourless.
O <sub>2</sub>	0.1 to 1	Oxygen gas comprises approximately 21% of the
		atmosphere. It is odourless, tasteless, and colourless.
Ammonia	0.1 to 1	Ammonia is colourless gas with a pungent odour.
		Atmospheric concentrations are less than 0.0001%
Non-methane	0.01-0.6	Non-methane organic compounds, excluding methane
organic		may occur naturally or be formed by synthetic chemical
compounds		processes.
Sulfides	0 to 1	Sulfides (e.g., hydrogen sulfide, dimethylsulfide,
		mercaptans) are naturally occurring gases that give the
		landfill gas mixture its rotten egg smell. Sulfides can
		cause unpleasant odours even at low concentrations.
		Ambient air concentrations are less than 0.001%
Hydrogen	0 to 0.2	Hydrogen gas is an odourless and colourless gas.
		Atmospheric concentrations are less than 0.001%.
CO	0 to 0.2	Carbon monoxide is an odourless and colourless gas.
		Atmospheric concentrations are less than 0.00001%.

 Table A. Typical Landfill Gases Production by Volume and Characteristics

US EPA, 2005

Overall, the fate of the carbon contained within the hydrocarbon mass disposed in a landfill will be emitted as either carbon dioxide or methane and therefore regarded as having a higher greenhouse gas potential than *ex-situ* emissions, which are not predicted to generate methane emissions. However, the appropriate fraction of emissions predicted as methane from hydrocarbon waste is unknown as most published information on the fraction of methane in landfill gas relates to waste with a large volume of degradable organic carbon like municipal and agricultural wastes. Industrial contaminants, including petroleum contaminants, differ in their susceptibility to biological decomposition; often taking decades to degrade through cascade type biochemical reactions involving numerous microbial species, and certain high molecular weight aromatics may not break down at all (Das and Chandran, 2010). Based on the time scale of degradation, it is expected that most, if not all, degradation will take place during landfill end-stage anaerobic methanogenic processes. Most predictions of roughly half the composition of the landfill gas comprising methane may underestimate methane emissions strictly from hydrocarbon contamination but in the absence of appropriate class 2 landfill data, or industrial landfill emission data, this value may be appropriate for adoption.

Landfill disposal is considered to include the following processes:

- Mobilization/demobilization of equipment to the site.
- Excavation of contaminated soils.
- Transport of contaminated soils to a landfill and placement in the landfill.
- Long-term degradation of contamination at the landfill.

## 2.5 Defining Pollutant Emissions

A review of life cycle assessments in the literature related to *ex-situ* remedial techniques reveals a difference in their fundamental approach and goals (Lemming, 2010). Some life cycle assessments appear to be a more detailed retrospective approach, while the approach taken in this report is to be more prospective, intending to serve as a decision-support in the choice between different remedial options and relies primarily on a modelling approach. The goals of a life cycle assessment are often defined by a functional unit, which in this case will be considered as the remedial volume of soil treated to effectively remove all contaminant mass. The removal of all contaminant mass may not be accomplished in *ex-situ* remediation, since only the achievement of applicable soil remediation guidelines is sought. However, remaining contaminant mass may continue to attenuate in soil after the remediation activities are completed. The impact categories considered include pollutants released to air including criteria air contaminants and greenhouse gases.

## 2.5.1 Volatile Organic Compounds

Volatile organic compounds (VOCs) are considered to include chemicals that contain carbon and hydrogen with boiling points roughly in the range of 50-250°C. This definition includes thousands of naturally occurring and synthetic chemicals. VOCs expected to be encountered during remedial activities at a site with residual natural gas condensate include primarily volatile aromatic and aliphatic hydrocarbons. These compounds are categorized in CCME (2008) as petroleum hydrocarbon sub-fractions 1 and 2 and consist of:

Fraction 1,  $C_6 - C_{10}$ :

- Benzene, toluene, ethylbenzene and xylenes (BTEX)
- Aromatics  $C_{>8}$ - $C_{10}$

• Aliphatics  $C_6$ - $C_8$ ,  $C_{>8}$ - $C_{10}$ 

Fraction 2,  $C_{>10} - C_{16}$ :

- Aromatics C<sub>>10</sub>-C<sub>12</sub>, C<sub>12</sub>-C<sub>16</sub>
- Aliphatics  $C_{>10}$ - $C_{12}$ ,  $C_{>12}$ - $C_{16}$

The present work focuses on natural gas condensate in soil. However, the same approach for quantifying the carbon in the contaminant mass can be applied to other volatile petroleum hydrocarbons. Only volatile compounds that can partition into air are considered; while it has been shown that *ex-situ* techniques encourage aerobic metabolism and breakdown of larger chain hydrocarbons influencing volatility (Leahy and Colwell, 1990), data gaps surrounding this process make it difficult to quantify and large chain compounds, which are non-volatile and are not considered herein.

# 2.5.2 Criteria Air Contaminants

Environment Canada defines criteria air contaminants as nitrogen (NO<sub>x</sub>), sulphur dioxide (SO<sub>2</sub>), carbon monoxide (CO), volatile organic compounds (VOCs – treated separately above), and particulate matter including total particulate matter (TPM), as well as particle matter less than 2.5 microns (PM<sub>2.5</sub>) and 10 microns (PM<sub>10</sub>) (Environment Canada, 2010). While ground level ozone and secondary particulate matter are also considered to be criteria air contaminants, they were not considered.

 $NO_x$  is the generic term for mono-nitrogen oxides NO and  $NO_2$ , which are produced during combustion and found in engine exhaust.  $SO_2$  is naturally occurring in petroleum products, and despite usually being removed to a large part in the refining process, the combustion of petroleum products releases measurable  $SO_2$ . Carbon monoxide is produced during the incomplete combustion of fossil fuels and biomass, including wildfires and controlled burns. Carbon monoxide is also produced indirectly from the photochemical oxidation of methane and other VOCs in the upper atmosphere (ATSDR, 2009).

# 2.5.3 Greenhouse Gasses

Greenhouse gases (GHG) included for consideration as part of this study will include methane and carbon dioxide. Methane, although not a volatile source onsite will be produced over the life cycle of the contaminant breakdown in the landfill (see Contaminant Life cycle below). The International Panel on Climate Change (IPCC) defines both of these compounds as greenhouse gases and can be seen below in Table B with their associated global warming potentials.

Table B. IPCC global warming Potentials for Relevant Greenhouse Gases					
Greenhouse Gas	Global Warming Potentials <sup>a</sup>				
Carbon dioxide	1				
Methane	25				

# Table B. IPCC global Warming Potentials for Relevant Greenhouse Gases

a – IPCC Fourth Assessment report, (2007), 100-year time horizon

# 2.6 Vapour Capture and Disposal

Any combination of hoods and/or ventilation systems that captures or contains organic vapours so they may be directed to an abatement or recovery device is known as a vapour capture system, also referred to as soil vapour recovery systems. The objectives of vapour recovery systems used in remedial work may be varied but are generally utilized to prevent harmful exposures to workers, prevent unacceptable emissions, or potentially captured volatiles for condensation, refinement and reuse. In many cases where vapours are captured to prevent ambient exposures the volatile compounds are bound to an active carbon filter. These filters are then disposed of, ending up in landfill disposal facilities. In such cases, the disposal of the carbon contained within the captured vapour will undergo the same processes as other carbon sources disposed in landfill facilities. A portion of this carbon will be metabolized though microbial catabolism emitted as carbon dioxide, and a portion of the carbon mass will be emitted as methane. As noted above the proportion of methane emitted from hydrocarbon sources is uncertain, this is also true for hydrocarbon bound in carbon filters, as well as the carbon represented in the filters. However, some mass of methane will be produced from this disposal otherwise not predicted to be produced in *ex-situ* remediation.

## 2.6.1 Biofilters

## Background

A typical biofilter uses a three-phase system, consisting of a gas phase transporting the target chemicals through the reactor, a liquid phase which contains an aqueous biofilm, and a solid phase substrate on which the microorganisms are present (Ikemoto *et al.* 2006).

The gas phase often consists of ambient air, with the typical open biofilter being exposed to the atmosphere and limited by the rate of ascending gas flow (Delhomenie and Heitz 2005). The speed of the biofiltration process is often limited by the rate of diffusion of contaminants inside the biofilm layer. A prototype biofilter using a convective flow biofilm to speed up this process was tested by Fang and Govind (2007) and found to be more effective than a diffusive flow biofilter; however, the majority of biofilters use diffusive flow.

Biofilms are populations of microorganisms attached to the solid biofilter substrate surfaces through polymeric substances, and the biofilm matrix will contain: water, microbial cells, polymers, absorbed nutrients, and metabolic byproducts (Singh *et al.* 2006). Establishment of a biofilm within a biofilter requires an initial microbial population and sufficient nutrient flow to maintain that population (Singh *et al.* 2006).

The solid substrate, or filter bed, is generally in the form of inert packing material, and is required to increase the available area for surface transfer between phases (Delhomenie and Heitz 2005). Microorganisms are immobilized on this surface, which is often also infused with a nutrient solution (Delhomenie and Heitz 2005). A filter bed should have: high surface area, high porosity to allow for gas transport, good water retention, nutrients to support microbes, and diverse indigenous microflora (Delhomenie and Heitz 2005). Options for filter bed material are peats, soils, or compost, which can also have additional material added for structural support, such as wood chips. Typical biofilter substrates have a porosity of 40 to 50%, a surface area of 1 to  $100 \text{ m}^2/\text{g}$ , and contain 1 to 5% organic matter (Nelson and Bohn 2011). Compost typically has a higher porosity (50 to 80%) and organic matter content (50 to 80%) along with greater microbial density (Nelson and Bohn 2011).

Use of other organisms besides bacteria, such has fungi, has also been attempted. A study by Harms *et al.* (2001) identified potential fungal species capable of degrading PHCs; however, there were not considered to be ideal for biofilters as they were less resilient and grew slower

than similar bacteria. Hasan and Sorial (2010) also looked at using fungi to enhance bioremediation in acidic environments, and found that adding fungi to a biofilter increased the available surface area, increasing the gas-phase uptake and elimination diffusion as a rate limiting step.

At this time most commercial biofilters operate using indigenous microbial populations.

#### **Relevant Parameters**

The parameters of greatest importance to biofilter operation are generally considered to be: air flow rate, temperature, pH, moisture, and substrate organic content (Delhomenie and Heitz 2005). The treatment rates are often limited by the mass transfer of target compounds to the biofilm phase, and mass transfer rates are most influenced by: target chemical properties, biofilter substrate properties, gas flow behavior, phase surface area, wettability of biofilter substrate, and environmental conditions (Kraakman *et al.* 2011).

During biofilter operation, moisture content often requires regular monitoring. The ideal moisture content is considered to be between 10 and 25% for soil substrate based biofilters, and between 20 and 20% for compost substrate based biofilters (Nelson and Bohn 2011). In order to maintain optimal humidity levels, active systems such as passing inlet air through a water column may be required depending on environmental conditions (Rani 2009).

## Treatment Rates

Removal efficiencies over 99% have been obtained for BTEX in lab tests (Mathur *et al.* 2007, Pandey *et al.* 2010) and complete removal of hexane in a compost biofilter (Zamir *et al.* 2011); however, lower removal efficiencies closer to 80% are often encountered in practice (Namkoong *et al.* 2003). Treatment rates are typically limited by the rate of mass transfer between phases in a biofilter, and are influenced by the initial concentration of microbes and the air flow rate through the biofilter (Delhomenie and Heitz 2005). Mass transport in biofilms is described by Fick's Law (Delhomenie and Heitz 2005), and soil water partitioning in biofilters is generally the limiting factor in treatment rates, whereas air-water partitioning tends to reach equilibrium at typical flow rates (Massabo *et al.* 2007).

Remediation rates are typically proportional to environmental temperature and are inversely proportional to the molecular weight of the target compounds (Sanscartier *et al.* 2011). Microbial activity is linked to ambient temperature, with an optimum between 20 and 40 °C; however, degradation processes can cause a temperature gradient to occur within the filter which can hinder maintenance of the filter (Delhomenie and Heitz 2005). Achieved treatment efficiency will vary depending on input concentrations of target compounds and the biofilters internal conditions; however, addition of silicon rubber pellets in a bioreactor or other compounds that can absorb/desorb gaseous components can be used to smooth out input concentrations, preventing possibly damaging high transient loadings of contaminants (Littlejohns and Daugulis 2008) and maintaining a more consistent treatment rate. Despite its relatively low molecular weight, removal rates of benzene are commonly the lowest among BTEX and other petroleum hydrocarbons (Namkoong *et al.* 2001) as it is easier to degrade water soluble compounds (Nelson and Bohn 2011).

Other chemical parameters of target compounds also influence the treatment rates of biofiltres. Degradation rates tend to increase with the presence of compounds with double bonds, and higher oxygen, nitrogen, and sulphur content (Nelson and Bohn 2011). The presence of certain contaminants can also interfere with the biodegradation of target compounds. For example, Hasan and Sorial (2009) found the degradation of n-hexane to be negatively impacted by the presence of benzene. Shim *et al.* (2006) determined that the presence of methyl tert-butyl ether (MTBE) decreased the elimination capacity for benzene, toluene and xylenes, with benzene degradation most strongly inhibited by MTBE. It was also found that MTBE could not be degraded alone, as it was co-metabolically degraded with benzene, toluene, or xylene.

The materials used in biofilter construction can also significantly treatment rates. The use of granulated activated carbon can be used to enhance gas adsorption (Mathur *et al.* 2007), and has been show to benefit treatment efficiency, depending on humidity (Nabatilan and Moe 2011). Use of higher porosity substrates can increase removal rates while reducing plugging issues (Nikakhtari and Hill 2008). When trying to remediate hydrophobic substances that will not readily dissolve into the biofilm phase, the use of surfactants has been found to enhance solubility and increase biofilter effectiveness (Hasan and Sorial 2010), this result has not been found to be significant in all cases involving PHCs (Lee *et al.* 2011).. The use of organic solvents has also been attempted to achieve this effect (Kraakman *et al.* 2011)

Operational and maintenance considerations are also important when trying to determine treatment rates. High conversion rates of target compounds can result in microbial growth rates high enough to result in filter clogging (Kraakman *et al.* 2011). Shim *et al.* (2006) found that the presence of specific pollutants, such as MTBE, can significantly alter the established bacteria communities and the expected treatment rates for other target compounds. Additionally, high inlet concentrations of target parameters may also damage the degrading biomass, Barona *et al.* (2007) found this to be the case with even low concentrations of toluene.

## Applicability to Emissions Model

Design of biofilters based on models or small-scale testing often runs in to difficulties due to uncertainties in determining the rate-limiting step in larger systems (Kraakman *et al.* 2011). While treatment rates can often be established based on easily measurable parameters, such as biofilter design or flow rate in lab scale tests, determining the actual treatment rate of a biofilter under field conditions would require some form of validation.

However, for all biofilters, there is a range of operational parameters over which biofiltration is effective, dependent on the filter design, microbial community, and contaminants of concern (Fang and Govind 2007). Therefore, it is possible that a standard removal efficiency credit could be applied to the emission model if a generic biofilter design was confirmed to be operating within the defined operational range. This credit would also be contingent on some basic site conditions, such as the absence of contaminants that may limit microbial growth, or adverse site conditions (such as extremes of temperature or humidity).

While overall removal efficiencies greater than 95% are possible and efficiencies of 80% or greater are expected to be achieved, actual removal efficiency will vary between contaminants and result in changes to the composition of volatile contaminants. Therefore application of an

overall removal credit should be based on the lowest expected removal efficiency, in order to account for difficult to degrade chemicals and the potential for inhibitory interactions between compounds. Based on a review of published literature on biofilter treatment of petroleum hydrocarbons, a minimum expected efficiency of 60% is considered reasonable for difficult to treat compounds such as toluene (Barona *et al.* 2007; Fang and Govind 2007; Zmir et al. 2011), n-hexane (Hasan and Sorial 2010; Zamir et al. 2011; Zmir et al. 2011), methyl tert-butyl ether (Mudliar et al. 2010), or benzene (Namkoong et al. 2001; Pandey et al. 2010). A 60% reduction factor has been applied to long-term air concentration exposure during ex-situ remediation, the biofilter reduction factor was not applied to the short-term air concentration.

A case-study, similar to the case used for the original emission model in Meridian (2011) was used to demonstrate the effect of the biofilter reduction factor on long term exposure concentrations. As discussed above, presence of a biofilter is assumed to reduce long term exposure concentrations by a factor directly proportional to the biofilter treatment efficiency. Use of a biofilter also increases engine combustion emissions of criteria air contaminants by a small factor due to transport of the biofilter to and from the site. Model inputs and outputs for the example site are included in Appendix E.

#### Lifecycle Emissions

Lifecycle emissions for biofilters can be considered similarly to how landfill emissions are handled in the Meridian (2011) model, which involves determining the mass of carbon entering the biofilter and then applying a standard conversion to  $CO_2$  factor. As biofilters will be operated aerobically, the calculation of emissions from ex-situ remediation does not change with the presence of a biofilter unit and it is assumed that 100% of contaminants will be converted to carbon dioxide.

Additional consideration for biofilters that require some active component, such as a fan to increase airflow or systems to maintain temperature or humidity has been incorporated into the 'hours of power generation' input ex-situ remediation.

The lifecycle emissions from construction and maintenance of biofilters are expected to be minimal, as soil or waste material is often used for the filter substrate, and indigenous microbes can be used under most conditions (Massabo *et al.* 2007), providing that an acclimatization period with the targeted contaminants is factored into the treatment rate (Delhomenie and Heitz 2005). For calculation purposes, it is assumed that the filter substrate is comprised of natural or waste materials and makes up the bulk of the biofilter mass. The remainder of the biofilter, consisting of the outer shell and and monitoring equipment, is assumed to be reused. Maintenance of the biofilter is necessary as bacteria have a tendency to accumulate at phase boundary interfaces (Hanzel *et al.* 2012); however, maintenance activities are not expected to represent a significant source of emissions. In order to account for additional transportation of the biofilter to the site and removal afterwards, if a biofilter is being used it is assumed by default that an additional truck is required to mobilize to the site twice based on the typical size of a biofilter.

#### 2.7 Review/Selection of Emissions Models

All processes thought to be directly involved in contributing emissions from *ex-situ* remedial activities, including criteria air contaminants and greenhouse gases, were considered. As discussed above, model selection considered multiple aspects of the model, its developmental purpose and potential application to estimating emissions from remediation. As no individual model was ideally suited to all aspects of the remediation scenarios, multiple models were utilized that were best suited to specific processes.

The basic approach for quantifying life-cycle emissions for both scenarios involved considering the emissions from contaminant breakdown, and the process and equipment emissions separately. Quantification of emissions from contaminant breakdown applied a mass balance approach, where the mass of carbon contained within the contaminants was calculated and assumed to completely volatilize over the course of the soil treatment. For the *ex situ* scenario the mass of the carbon is assumed to entirely transform to carbon dioxide, which was calculated. This approach was also conducted for the landfill disposal, however; a fraction of the emissions were assumed to be methane and calculated as such. Modelling was used to predict an emission concentration, or air concentration, as a function of time applicable to on-site worker exposure during an ex-situ remedial scenario, or for application in air dispersion modelling to potential near-by receptors.

Models with some form of regulatory acceptance, particularly federal regulatory acceptance that would be broadly applicable were preferred. The Environment Canada vehicular transport particulate emission model was taken from the NPRI toolbox and is currently a federally recommended model for the quantification of particulate emissions in industrial requirements. The CCME biosolids model is a national guidance tool with a certain level of regulatory recognition, and the GHGenius model was developed by scientists for Natural Resources Canada. The national acceptance, publication or endorsement of these models was considered in the model selection.

Models that specifically considered Canadian conditions, or were developed or endorsed by Canadian regulators, were also preferentially considered. For example, the GHGenius model applies Canadian fuel specifications, the Environment Canada NPRI toolbox model includes corrections for Canadian climatic conditions.

Another consideration was the ability of the model to quantify a variety of emissions using the same input assumptions. For instance, the GHGenius model was able to predict combustion product emissions for all criteria air contaminants, including particulates, as a function of emissions factors. The metrics of the emission were also important to the model selection; models that quantified an emission mass were preferred as this allowed a direct sum and comparison between processes. Another major consideration in the model selection was the data requirements of the model, models that require data inputs that would need to be based on scenario assumptions or site specific information as a major inputs were avoided.

Models were reviewed related to the partitioning and mixing of volatile contaminants to calculate air concentrations, equipment and process emissions of particulates, and separately calculated equipment and process emissions of criteria air contaminants. The reviewed models can be viewed in Appendix B.

## 2.8 Establishment of Input Parameters

Many model input parameters will vary on a site-specific basis (e.g. distance to landfill, chemical concentrations in soil). Others may vary on a site-specific basis but may not be routinely measured at contaminated sites (e.g. certain soil properties). A third group of model parameters either will not vary on a site-specific basis (e.g. some parameters related to landfills) or may not be readily known ahead of time (e.g. fuel efficiency of equipment and vehicles).

In order for the modelling approach to be manageable, model input parameters for the selected models are divided into three categories:

- Key site-specific parameters, which are always established on a site-specific basis. These variables are readily measured and have a significant effect on model results.
- Optional site-specific parameters, for which default values are provided but which may be adjusted on a site-specific basis where suitable data are available. These variables are less readily measured or have only minor effects on model results.
- General parameters, for which default values are provided and it is expected they would rarely, if ever, be adjusted on a site-specific basis. These variables are generally not readily measured.

For all except the key site-specific parameters, default values were selected based on values previously recommended by major regulatory agencies, recommendations of model authors, and scientific support.

## 3 RESULTS

## 3.1 Selected Modelling Approaches

A list of selected models for emission quantification requirements can be seen below in Table C. A summary of the relevant equations and model input parameters is provided in Appendix D.

Emission	Model
Ex-situ contaminant emission	Mass Transfer
Landfill gas emission	CCME Biosolids Emission Estimation
Combustion emissions (particulates, criteria air	GHGenius NRC Model
contaminants and greenhouse gases)	
Equipment process particulate emissions	US EPA Construction Particulate
	Emissions, 1993
Vehicular transport particulate emissions	Environment Canada NPRI Toolbox
	Estimating Road Dust Emissions

 Table C. Selected Models for Various Emissions Quantification Applications

The relevance of any modelling results is based on the accuracy of the data inputs. In order to ensure that the modelling results were as accurate as possible, recent data was applied for fuel usage and combustion emission analysis for emission factors, and internationally recognized uncertainties and assumptions often applied as correction factors. Both the CCME biosolids model and the GHGenius model have been published in the past year, and the NPRI toolbox vehicle particulate emission model was published or partially updated in 2009.

For some of the processes few models are available to quantify emissions, as in the case of the particulate process emissions. The US EPA particulate generation and emission equations are generally regarded as the definitive model for this application and many other regulatory agencies including those in Canada reference these models. In this case, the rational for the model selection became about current availability.

# 3.1.1 Estimating Volatile Organic Compound Emissions

VOC emissions occur from several different processes, some of which apply to both *ex situ* remediation and landfill disposal. In addition to the mass balance calculation used to estimate total potential emissions from the contaminants in the soil, the calculation of potential exposure to receptors either onsite, such as workers or nearby offsite receptors, may provide an additional consideration to augment the lifecycle analysis and is relevant to remedial decision making.

As detailed in Appendix B, the Jury model as implemented by US EPA or Ontario Ministry of Environment is suitable for estimating VOC emissions from excavations and from soil piles. The model calculates emission rates as a function of time. The highest emission rates (and hence the worst-case exposure) occur immediately after soil disturbance or handling, as the highest concentration of volatile contaminants will be present in soil and begin partitioning into the vapour filled pore space and moisture filled pore space before contaminant particles will move into the ambient air (Figure 2). As time passes, the contaminant mass in the soil will decrease, resulting in lower volatile emissions and ambient air exposure concentrations.

For estimation of risks from short-term exposure, calculations are conducted based on average emissions from initial exposure of the soil to the time used for the exposure limit. For example, for comparison with a 1-hour exposure limit or air quality guideline, emission rates are calculated from time = 0 to time = 1 hour. Total or long-term average emissions are evaluated based on the anticipated length of time a soil pile is present at the site.



Figure 2: Contaminant partitioning

Data on emissions during *ex situ* remediation were very limited and no existing models were identified; therefore a mass balance approach was used, in many respects similar to a US EPA (1992a) model for emissions from soil handling during a remedial excavation. For estimating potential short-term maximum exposures to workers, the maximum chemical concentration in soil is used. For estimating total emissions and long-term average exposures, average concentrations are more appropriate.

VOC emissions predicted for any of these processes are then used with regulatory air dispersion models to predict offsite air quality. For screening purposes, AERSCREEN is recommended as a screening-level air dispersion model with regulatory acceptance; for site-specific evaluations AERMOD or CALPUFF could also be used, as appropriate.

# 3.1.2 Estimating Particulate Matter Emissions

Particulate emissions, regardless of whether or not the emitted material is contaminated, are recognized as harmful to human health. Canada Wide Standards (CCME, 2000) have been published for particulate matter and recognize a fine fraction  $PM_{2.5}$  (airborne particles that are 2.5 microns or less), as well as larger particulates  $PM_{10}$  (airborne particles that are 10 micron or less in diameter); of which the fine particles are recognized as having the greatest effect on human health. The Canada Wide Standard for  $PM_{2.5}$  is 30 µg/m<sup>3</sup> over a 24-hour averaging time. Alberta Environment has also published objectives for total suspended particulates of 100 µg/m<sup>3</sup> over a 24-hour averaging period.

Contributions of total particulate emissions in both landfill and *ex-situ* remedial activities are a result of a variety of processes such as road traffic on paved and unpaved roads, equipment and vehicle exhaust, material transfer operations, mixing and tilling, soil spreading and is influenced by environmental factors like wind, soil moisture and particle size. Many of these processes and variables will fluctuate substantially over different phases of the remedial process and introduce significant uncertainty in trying to estimate particulate emissions over the course of the entire remedial process. To help address some of these uncertainties available guidance on estimating particulate emissions from heavy construction or soil moving operations recommends that emissions are to be estimated for each particular construction process (US EPA, 1995). Models reviewed to estimate particulate emissions related to these activities are presented in Appendix B; the final equations are presented in Appendix D.

# 3.1.3 Estimating Emissions of Criteria Air Contaminants

Few models are available to quantify emission of criteria air contaminants from fuel specifically used in Canada; fuel specifications vary regionally and emissions are related to the composition of the fuel used. Recently, Natural Resources Canada has published a spreadsheet tool referred to as the GHGenius model which was developed as a life cycle assessment tool that calculates greenhouse gases and criteria air contaminants generated from the time a fuel is extracted to the time that it is converted in a motive energy vehicle to produce power, considering internal combustion in various equipment sources. Due to the Canadian focus of this model and the regulatory acceptance, this model was deemed the most appropriate and used in the calculation of equipment engine emissions. This emission generation model is based on fuel use, and calculates the mass of pollutant emitted per GJ of fuel used by device. The amount of energy potential in GJ per L of petroleum diesel was adopted from the National Energy Board Energy (2010) conversion tables. Equipment fuels use was obtained from a recent comprehensive field study of fuel usage by equipment type (Frey et al., 2010), reflective of equipment utilized during both *ex-situ* remedial activities and landfill disposal.

# 3.1.4 Estimating Landfill Gas Generation

Models used to estimate landfill gas generation were reviewed and summarized in Appendix B. However, most available models are related to annual municipal landfill reporting requirements and calculate methane conversion as a function of time. For the purposes of this project, total emissions or conversion to methane over the life-cycle of the waste in the landfill are of more interest.

CCME has recently developed a biosolids emission estimation model which is intended to be used to calculate the greenhouse gas emissions from carbon contained in biosolids being disposed on in landfills. A modified version of this model was adopted, with adjustments made to the default assumptions related to methane generation, and uncertainty factors applied to the calculation of landfill methane generation from carbon inputs into a landfill.

## 3.2 Exposure Limits

Calculated concentrations in outdoor air (onsite or offsite) should be compared to appropriate limits. For worker exposure onsite, occupational exposure limits would apply. For offsite air quality impacts, ambient air quality guidelines/objectives and health-based limits apply. Suggested limits are summarized in Appendix C.

## 3.3 Recommended Approach Equations and Default Model Parameters

The modelling approach and equations recommended to complete the lifecycle analysis can be seen in Appendix D. Default model inputs used to complete the modelling are also documented within this appendix.

The modelling approach detailed in Appendix D is flexible enough to be adapted to a range of scenarios, since individual processes are modelled separately and the results combined. The approach yields both total lifecycle emissions of contaminants and predicted concentration in onsite and offsite ambient air.

## 3.4 Example Site Calculations

An example site scenario was created and calculations were completed based on site data provided by Husky Energy Inc. in order to test the modelling approach and compare results against site air quality measurements. The example calculations are detailed in Appendix E, the tables in this appendix detail the findings of these calculations, the inputs used, as well as the assumed site and chemical characteristics.

## 3.5 Model Sensitivity

Certain input parameters will have more of an impact on the outcome numbers than others. Modelling greenhouse gas emissions from landfill disposal is highly dependent on the fraction of methane assumed in landfill gas. This parameter is highly uncertain with respect to methane generation from petroleum hydrocarbons. The most sensitive variable input parameters in the calculation of contaminant flux from excavations and soil piles, and thus air concentrations include the fraction of organic carbon, bulk density, and soil porosity. The final calculation of air concentration is also highly influenced by the source length and wind speed. Concentrations predicted directly above a soil pile or within an excavation are inversely related to the wind speed; during a windy day air concentrations would be lower. Wind speed, allu bucket dimensions and allu bucket height are also sensitive parameters in the calculation of air concentrations during *ex-situ* allu soil treatment.

The calculation of particulate emission onsite from equipment processes is most influenced by soil moisture content, where higher soil moisture content results in lower particulate emissions. Wind speed is also and important factor for particulate emissions. In the calculation of particulates from vehicular traffic, the mass of the vehicle followed by the percent silt content are important to the calculation of a particulate emission factor. However, the distance travelled is the most influential factor on the overall particulate emissions from vehicular traffic. Emissions of volatiles from engine combustion are most influenced by the equipment specific fuel use and operational hours, as these emissions are based on fuel use and emission factors.

# 4 DISCUSSION

The modelling approach developed herein and summarized in Appendix D is intended to compare lifecycle emissions from alternative remediation scenarios, as well as evaluate potential human health and environmental impacts. There is considerable uncertainty in the overall lifecycle emissions; the modelling approach is intended primarily to enable a relative comparison between alternative scenarios. From this relative comparison, some broad conclusions can be made. Due to the anaerobic transformation in landfill disposal, a mass of methane will be emitted that will not be produced in the *ex-situ* remedial scenario, with a higher relative greenhouse gas potential. The transport/mobilisation distance and subsequent fuel used will influence the engine emissions of criteria air contaminants, which will be increased with increased distance to a landfill/site and could be an important consideration when making remedial decisions. Particulate emissions will be dependent on site characteristics including soil moisture, soil particle size and wind conditions.

The VOC emission models are believed to be conservative in most cases, and likely overpredict ambient air concentrations of VOCs.

#### 4.1 Uncertainty assessment

The results of this life-cycle assessment are subject to considerable uncertainty due to a variety of assumptions that have to be made to conduct the comparison. These assumptions have varying influences on the outcomes but some of the major assumptions and sources of uncertainty include the following.

Some contaminant mass will be volatilized to the atmosphere during transport and incorporation into the landfill cell; however, quantifying this loss is subject to considerable uncertainty and would assumed to be accounted for in the landfill transformation uncertainty factor. During phase 1, the aerobic phase, some volatile losses may also be expected; however, data quantifying volatile hydrocarbon losses during this phase are limited.

Information related to landfill gas generation from industrial and hazardous waste landfills is generally unavailable. The appropriateness of applying methane generation factors from municipal landfill gas generation to petroleum hydrocarbon wastes specifically is unknown. The model assumes landfill gas is not collected and the landfill environment transitions from an aerobic environment to an anaerobic environment. Both scenarios consider the complete breakdown and atmospheric emission of bound carbon as either methane or carbon dioxide, the appropriateness of this assumption over the life-time of the contaminant is unknown.

These more qualitative aspects, although important, are not always amenable to comparison. Consideration of landfill gas collection or other *ex-situ* remedial soil options was not explicitly considered as uncertainties associated with these techniques are difficult to account for.

## 4.2 Next Steps

While this project is considered to be substantially complete, the field data collected (Meridian, 2012) could not be used to reliably calibrate the model since the volatile hydrocarbon concentrations were relatively low and concentrations did not change significantly between preand post- treatment samples. Therefore, there may be value in collecting further field data from sites with high levels of volatile hydrocarbon (ideally condensate) contamination undergoing *ex situ* remediation.

## 5 CLOSURE

This report has been prepared under the Alberta Upstream Petroleum Research Fund (AUPRF), under the direction of the Canadian Association of Petroleum Producers (CAPP) and the Small Explorers and Producers Association of Canada (SEPAC), as indicated in a letter of approval from PTAC dated August 24, 2010, and a subsequent letter of approval dated February 3, 2012. Quantitative and qualitative environmental modelling and fate analysis involves a number of uncertainties and limitations. As a consequence, the use of the results presented herein to develop site management strategies may either be overly protective or may not necessarily provide complete protection of human and environmental receptors or prevent damage of property in all circumstances. The work presented herein was conducted in accordance with generally accepted protocols. Given the assumptions used herein, the modelling approach is believed to provide a conservative estimate of the risks involved. The services performed in the preparation of this report were conducted in a manner consistent with the level of skill and care ordinarily exercised by professional engineers and scientists practising under similar conditions.

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