# DEGRADATION AND MOBILITY OF PETROLEUM HYDROCARBONS IN OILSANDS WASTE AT THE AURORA FORT HILLS DISPOSAL AREA

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Saskatoon

By
TOMASZ KORBAS

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# Abstract

Surface mining in the Athabasca oil sands region of Northern Alberta, Canada, results in the disturbance of significant areas of boreal forest landscape. The Aurora Soil Capping Study is a reclamation research project that aims to find the optimal soil capping (cover) material and thickness to re-establish a boreal forest ecosystem above a lean oil sands (LOS) disposal area at Syncrude's Aurora North mine. The objectives of this laboratory and field-based study are to (1) characterize the in-situ hydrocarbon composition of the LOS material, (2) determine the effect of temperature on rates of gas flux and the biodegradation potential of petroleum hydrocarbons (PHC) as a result of microbial activity and (3) determine the potential for PHC to leach into the groundwater system. The results of the laboratory-study show that temperature has a significant effect on the rate of PHC degradation as indicated by the linear relationship observed between temperature and $CO_2$ gas flux rates. The respiratory results from the laboratory-based study were consistent and relatively comparable with data from the field study, which indicates that the column study could be useful in estimating in situ PHC degradation.

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# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Among rising global demand, increasing production of oil from the Athabasca oil sands in Northeastern Alberta has resulted from significant technological improvements in production, but has also been associated with increasing land disturbance in the region. Surface mining for oil sands extraction results in a significant disturbance of the boreal forest landscape. To mitigate the impact of surface mining to the environment, a land reclamation program has been enforced and monitored by The Alberta Environmental Protection and Enhancement Act (Canada's Oil Sands, 2000).

In practice, oil sands are excavated in an active mining zone and hauled to extraction facilities (depending on bitumen content). Oil sands with bitumen content economically feasible to extract the bitumen for upgrading to useable petroleum products usually exceeds approximately 6% (varies among oil companies). The remaining material, termed "lean oil sands" (LOS), with bitumen content usually below 6%, is not yet economical to process and is deposited in designated disposal areas. One such designated area is the Fort Hills disposal area at Syncrude's Aurora North mine.  Even though these disposed materials do not contain a high enough bitument content for extraction they can still contain a significant amount of bitument that will remain in the reclaimed landscape. There are concerns with the fate and transport of the bitumen resulting from the removal, disturbance and placement in different environmental conditions may pose an environmental risk in the reclaimed landscape.

A 36 hectare area within the Fort Hills disposal area has been reclaimed for the purpose of conducting reclamation research activities. The reclamation activities included surface landform grading of the deposited disposal material, soil placement of reclamation materials and revegetation planting.

This Aurora Soil Capping Study (ASCS) has several principle objectives, related to evaluation of the optimal soil capping (cover) material and thickness in order to quickly and successfully re-establish a self-sustaining native boreal forest ecosystem. Twelve various configurations of the reclamation material (peat mix, LFH - leaf litter, fibric and humic, and in situ oil sands mixture) with various thicknesses (0.3 to 1.5m) were placed in triplicates on one hectare plots. The main purpose of ASCS is to monitor and evaluate the efficiency of the capping materials and thicknesses as a medium for plant growth in order to determine which configuration is most effective and efficient for the reclamation of LOS material disposal areas. As part of that overall research effort, the study described in this paper focuses on the fluxes of gas arising from buried LOS and other overburden materials resulted from biodegradation of PHC, given the potential that such gas fluxes may have an effect on the performance of introduced vegetation planted in the test plots.

## 1.2 Objectives

The work presented in this thesis is a combination of field and laboratory studies focused on the following:

a) characterization of hydrocarbon composition in LOS material;

b) determination of the effect of temperature on gas flux rates;

c) biodegradation potential of petroleum hydrocarbons (PHCs) in the subsurface and near surface materials as a result of microbial activity; and

d) estimation of PHC leaching potential.

The results of this study will contribute to increasing our knowledge about Lean oil Sands and will help characterize the effects of these processes on the reclamation research being conducted at the Aurora Fort Hills disposal.

## 1.3 Thesis organization

In this work typical thesis format will be presented. Chapters 1, 2 and 3 consists of Introduction, Literature Review and the review of experimental Methods and Materials used in this study. The presentation of data is divided into two chapters. Chapter 4 represents data from the field study where surficial gas flux rates as well as soil gas compositions were investigated. Chapter 5 represents data from laboratory large scale mesocosm (Column Study) where LOS material was characterized in terms of bitumen content, biodegradation potential and mobility as leaching potential of PHC to groundwater system. In chapter 6 as final chapter, conclusions and recommendations are provided.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

This chapter presents a compilation of basic theoretical background information about genesis, characterization and subsurface processes such as degradation and mobility of the LOS material stored at the Fort Hills Dump at Syncrude Canada's Aurora North mine. Additionally, based on the available (though scarce) data on the LOS in the literature this chapter includes the description of relevant research done by the others. In addition and for the sake of completeness, information will be part of regarding the standard methodology that is used to characterize the LOS and similar material.

## 2.2 Location, genesis, characterization and reclamation of oil sand materials

Alberta's four major oil sands deposits (Figure 2.1) are estimated to hold 1350 billion barrels of oil, however only less than 10% of these reserves can be recovered by surface mining techniques. The remaining 90% of oil reserves are buried so deeply that a development of technologies capable of recovering bitumen in situ is required (Mossop 1980).

The Athabasca oil sand deposits were deposited during the early Cretaceous era. The bitumen was deposited within a single reservoir, the Lower Cretaceous McMurray - Wabasca interval (Figure 2.2). The origin of the oil is not well known but in general it is accepted that the formation of the oil sands came from Mississippian and Jurassic age sediments that traveled from

South East to the present location of deposits (Canada's oil sands, 2000). Through extensive study of geological distribution of oil it was observed that at the time the oil was pooled, it was less viscous and much lighter (mostly consisting of light HC) than at present (Mossop 1980). Continuous in situ biodegradation of light HC caused by microbes carried by oxygenated water over a long period of time turned trapped oil in into a black, sticky and highly viscous material called bitumen consisting mostly of complex, heavy molecules of PHC (Canada's oil sands, 2000). The characteristics of Bitumen in oil sands depend on the degree of biodegradation that took place in the past. So for example, the oil in the Athabasca and Cold Lake deposits traveled much longer and further than the deposits of Peace River thus these deposits were subjected to much greater degree of biodegradation (Figure 2.1).

Figure 2.1. Alberta major oil sand deposits

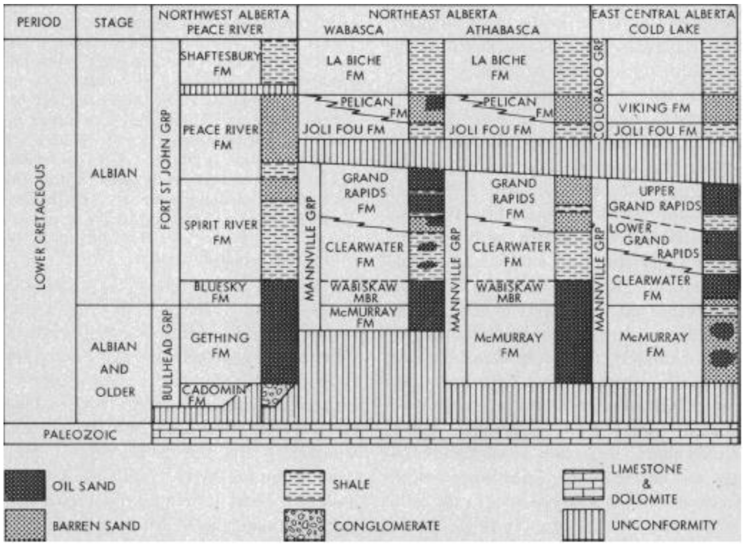


Figure 2.2 Formations in oil sands bearing regions of Alberta (Mossop 1980)

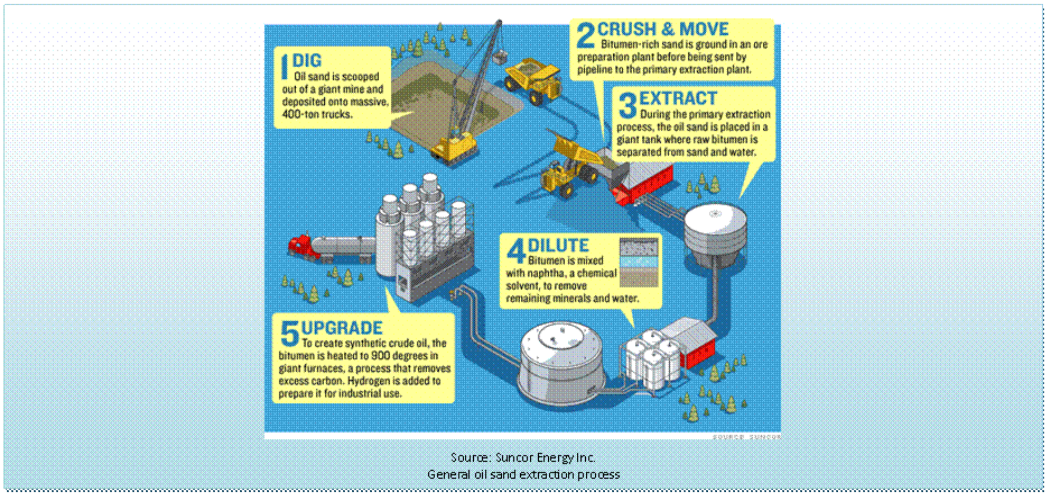
Characterization of oil sands from Athabasca deposits (Mossop/Canada's oil sands - outlook):

- composition: around 80% of Quartz sand, silt and clay, water and bitumen along with other minerals such as titanium, pyrite...
- grain size: High grade oil bearing sands in Athabasca are dominantly very fine to fine grained
- porosities: 25-35%
- microscopic habitat of bitumen: oil in the pores is not in direct contact with mineral grain which are surrounded by a thin film of water

The bitumen content of the oil sands may be used to characterize the material as very rich, moderate or lean:

- bitumen content: 0-18% by weight
  - rich oil sand - more than 10 % of bitumen
  - moderate oil sand - 6-10% of bitumen
  - lean oil sand - less than 6% of bitumen

The oil sands of economic interest occur mostly in the Cretaceous-aged McMurray Formation in the Athabasca oil sands. The Athabasca deposits contain approximately 870 billion barrels of oil but only 74 billion is feasibly surface-minable with the overburden less than 75m (Mossop 1980). In the process of oil recovery the overburden is scrapped off the surface and the ore body is mined and taken away for further processing (Figure 2.3).



Source: Suncor Energy Inc.
General oil sand extraction process

Figure 2.3. General oil sand extraction process

The ore body that averages about 50m in thickness is defined as oil sand with more than 6% of bitumen by weight (Mossop 1980). Whatever is left, oil sands with bitumen content less than 6% and overburden (a mixture of sand, gravel and earth) are primarily disposed in oil sand waste dumps.

One of these dumps is Fort Hills Dump at Aurora North, Syncrude (claimed to be one of the world's biggest). Some of the area in Fort Hills Dump (the area referred to as Aurora Capping Study, ACS) has been excluded from active waste dumping for the purpose of conducting research. The main objective of this reclamation research has been to find the optimal soil capping (cover) solutions for the Fort Hills Dump in order to re-establish self-sustaining native boreal forest ecosystem. Twelve various reclamation material types and configurations such as peat mix, LFH (leaf litter, fibric and humic) and native sand with and without surficial bitumen materials was placed as a cover in a series of triplicate plots within the Capping Study area.

An important aspect of overall Aurora capping study involved a full characterization and determination of degradation and mobility of the PHC stored in the subsurface at the Fort Hills Dump in terms of:

- natural (in situ) petroleum hydrocarbons (PHCs) concentrations
- PHC mobility – leaching to the groundwater system
- PHC biodegrability in the subsurface as a result of microbial activity
- gas flux production as an indicator and a factor controlling the subsurface microbial degradation of PHCs

The detailed results from this study are presented in this thesis. It is hoped that information collected in the course of this study will be useful in determining the right solutions for the soil reclamation covers.

## 2.3 Canada Wide Standard for Petroleum Hydrocarbons in soil

The Canadian Council of Ministers of the Environment (CCME) is a group that aims in protecting Canada's environment by developing national strategies, norms, and guidelines related to air, soil, water and waste management that could be used uniformly across the country as Canada-Wide Standards (CWS). CCME’s work related to soils has focused on the CWS for Petroleum Hydrocarbons (PHC) in soil, soil quality guidelines for the protection of environmental and human health, and contaminated sites (CCME 2008).

PHC contamination in soils varies with the petroleum source, soil type, the composition, degree of processing (crude, blended or refined) and the extent of weathering caused by exposure to the environment. Such factors have complicated the assessment of the human and environmental health risks associated with PHC contamination in soils. PHC in the environment are a concern for a number of reasons (CCME 2008):

- First, their reduced nature and volatility pose a fire/explosion hazard
- Second, most PHC constituents are toxic to some degree
- Third, lighter hydrocarbons are mobile and can be a problem even at considerable distances from their point of release due to transport in ground, water or air
- Fourth, larger and branched chain hydrocarbons are persistent in the environment, however, they are not as big of a concern as lighter fractions of hydrocarbons due to its physical-chemical properties describes below
- Fifth, PHC may create aesthetic problems such as offensive odour, taste or appearance in environmental media
- Finally, under some conditions PHC can degrade soil quality by interfering with water retention and transmission, and with nutrient supplies

The Canada-Wide Standard (CWS) for Petroleum Hydrocarbons (PHC) in soil and water is a standard which specifies consistent methods and outcomes for assessment and management of sites contaminated by PHC (CCME 2008).

Petroleum hydrocarbons (PHC) are described as mixture of organic compounds derived from geological substances such as oil, bitumen and coal. Typically Petroleum products contain hundreds to thousands of various compounds, composed mostly of carbon and hydrogen. Measuring that amount of separate PHC compounds is not feasible therefore, based on the physical-chemical properties and toxicological RfDs (reference doses) for the PHC, they were divided into four fractions (F1, F2, F3 and F4) according to the specified ranges of equivalent carbon number (ECN) (CCME 2008).

- Fraction F1 is composed of sub-fractions: aromatics and aliphatics HC in a carbon range (C6-C10). However, it was recommended that BTEX compounds (Benzene, Toluene, Ethylbenzene and Total xylenes) be analyzed separately in the PHC mixture and their concentration subtracted from F1 fraction. Due to its physio-chemical properties (volatility and relatively high solubility in water) the F1 fraction can reside in air and water therefore F1 concentration levels are formally developed in water,

- Fraction 2 is composed of aromatics and aliphatics HC in a carbon range ( C>10 to C16). Similarly to F1 fraction and F2 can be most likely be spotted in air and water but at lower concentrations than for F1. F2 concentration levels are formally regulated for water,

- Fraction 3 encompasses the range of ECN from C>16 to C34. Because of its low solubility in water and very low volatility F3 fraction concentration levels are developed specifically for soil. F3 is not regulated for water,

- Fraction 4 includes the range of ECN from C34 to C50. This fraction can represent a substantial and significant proportion of environmental PHC contamination, and of petroleum products and crude oils; Although the physical-chemical properties are less well defined in this fraction, the material is not volatile and is expected to have minimal environmental migration. F4 fraction contains heavy HCs of C>34 and it has extremely limited water solubility, subsurface mobility and volatilize insignificantly therefore F4 fraction is regulated for soil only.

Note, that in general, each carbon fraction contains all extractable hydrocarbon constituents which, on a gas chromatographic column, elute between and thus have a boiling point between the lower and higher indicated normal straight chain hydrocarbon (CCME 2008). However, it is known that certain molecules have carbon number exceeding C50 and then alternative method of PHC detections must be applied (CCME 2001b). High temperature chromatographic method (F4HTGC) (CCME 1993) is reported when more than 5% of the chromatogram elutes past C50. Then the results are reported as F4HTGC C34-C50+. The high temperature chromatography HTGC is capable of detecting carbon up to around C90 (Swyngedouw, 2010). The other method of analysing the PHC with C>50 is gravimetric method F4G (CCME 2001b). The results from gravimetric method provide the PHC concentrations in a range from F2 to the heaviest molecular weight hydrocarbons. In this method the heaviest hydrocarbons molecules can be detected even to over C100 (Peramanu, et al 1999).

Table 2.1 summarizes the Alberta Tier 1 guidelines for PHCs in coarse (more than 50 % of soil mass with particles >75μm mean diameter) and fine (more than 50 % of soil mass with particles <75μm mean diameter) grained surface soil (<1.5m depth) for natural land use purposes. Alberta Tier 1 guidelines are developed for growth media in soil.

Table 2.1 Alberta Tier 1 soil remediation guidelines for fine and course texture soils for natural land use

| PHC Fraction | Units | Coarse | Fine |
|---|---|---|---|
| **F1** | mg/kg | 210 | 210 |
| **F2** | mg/kg | 150 | 150 |
| **F3** | mg/kg | 300 | 1300 |
| **F4** | mg/kg | 2800 | 5600 |

## 2.4 Lean oil sand (LOS) and other similar materials in the literature

An important study related to LOS was described by Dr. S. Visser from the University of Calgary (Visser 2008a,b). Visser investigated the degradation of PHCs in LOS (fresh and weathered) and the effect of LOS on ecological receptors. This study was aimed to assess the impacts of LOS incorporated into reconstructed soil of the reclaimed site.

Prior to initiating the research, Visser used fresh LOS from Syncrude Canada to analyze for the PHC fractions according to CCME tier 1 method (CCME 2008a) and other physical/ chemical properties. Then after incorporation of LOS into peat/sand treatments, she monitored the respiration of $CO_2$ as an effect of microbial activity. Respiration of $CO_2$ production was monitored till stabilisation end point was achieved after 130 days. After that time the PHCs remained in the soil were mostly F3 and F4 fractions.

Through the initial characterisation of LOS material, the results of Visser study showed that LOS was comprised mostly of F3 (37.7%) and F4 (53.8%) of PHCs, heavy hydrocarbons. The rest contained small amounts of fractions F1 (0.15%) (excluding no detectable BTEX) and F2 (8.6%) of PHCs, which volatilize and biodegrade easily. Differences between the initial and final PHC fraction measurements were assumed to be a result of removal of PHC by volatilization, biodegradation and sorption during incubation process. Based on the final results obtained by Visser, approximately 25% of PHCs in LOS (including fractions F1, F2 and F3) were easily degraded and dissipated over short period of time due to volatilization and biodegradation in the rates of 100%, 75% and 31% respectively. Moreover, the study conducted on plants indicated that fresh LOS was considerably more toxic to plants than weathered LOS or PHC in surficial bitumen materials (Visser 2008 a,b).

The results from Visser's work presented in (Table 2.2) show that concentrations of F2-F4 PHC exceeded the Alberta tier 1 guidelines for PHC in surface soils.

Table 2.2. Extractable PHC in LOS used in PHC degradation and toxicity study (Visser, 2008a)

| **Analyte** | **Unit** | **Detection Limit** | **Mean +/- STDEV** |
|---|---|---|---|
| BTEX | mg/kg | 0.02 | <0.02 |
| F1 C6-C10 | mg/kg | 12 | 96.3 ± 4.7 |
| F2 C10-C16 | mg/kg | 10 | 5837 ± 430 |
| F3 C16-C34 | mg/kg | 10 | 25633 ± 1193 |
| F4 C34-C50 | mg/kg | 10 | 12033 ± 651 |
| F4 HTGC C34-C50+ | mg/kg | 10 | 36600 ± 7851 |
| Total PHC | mg/kg | | 68070 ± 9387 |

In another study conducted at University of Saskatchewan, Fleming et al (2011) investigated PHC degradation and leaching potential from surficial bitumen accumulations in otherwise clean near-surface sand deposits in certain areas of the Athabasca oil sands region. These have informally been termed "tarballs" and consist of material similar to oilsands or LOS. Similarly to Visser, prior to initiating a column study, Fleming (2012) used freshly collected surficial bitumen material from Syncrude Canada’s Aurora North mine as well as other sites to analyze for the PHC fractions according to CCME tier 1 method and determine other physical/ chemical properties as well. Surficial bitumen materials were mixed with clean sand at a ratio intended to recreate the field conditions during reclamation and were packed into six steel 1m long and 30cm in diameter columns. The equipment used in Fleming's study to measure respiration rates was a highly advanced Micro-Oxymax closed circuit respiratory system developed by Columbus Instruments (Columbus, OH) that measured the production and/or consumption of many gases simultaneously such as $O_2$, $CO_2$ and $CH_4$. The respiration of $CO_2$ and $O_2$ was monitored as a surrogate of microbial activity for 21 months. In result, the total amount of $O_2$ consumed and $CO_2$ produced over that time in the experiment was converted to mg of PHCs using the Zytner's stoichiometric equation such as: ($C_{16}H_{34}+24.5O_2=17H_2O+16CO_2$) (Zytner 2001) from which the rates of HC degradation were estimated. Moreover, Fleming in his column study was monitoring the PHC leaching potential by collecting leached water samples from each of his columns and testing for presence of PHC fractions and TC/TOC.

Table 2.3. Hydrocarbon data mean and standard deviation values in tarballs (Fleming, 2011)

| Fraction | Unit | Regulatory Guidelines[#] | Mean +/- STDEV |
|---|---|---|---|
| F1 C6-C10 | mg/kg | 210 | 17 ± 112 |
| F2 C10-C16 | mg/kg | 150 | 354 ± 1650 |
| F3 C16-C34 | mg/kg | 310 | 3450 ± 9015 |
| F4 HTGC C34-C50+ | mg/kg | 2800 | 9740 ± 14800 |
| F4G | mg/kg | 2800 | 39900 ± 45000 |

[#] Alberta Tier 1 guidelines – Natural area land use for coarse grained soils

The results presented in Table 2.3 show that concentrations of F2-F4 PHC exceeded clean soil Alberta tier 1 guidelines for PHC. Typically, the surficial bitumen materials contain little to no light fractions of PHC (F1 and F2) and significant amount of F3 and F4. The column study showed that these surficial bitumen accumulations did not have any significant impact to water leaching through the soil column and that the only PHC fraction found in the leachate were F2 and F3 in amounts below the clear water guidelines (Fleming at al. 2011). From the respiration rates monitored over 21 months in six columns it was concluded that the total mass of PHC degraded over 21 months ranged from 0.9g to 4.6g, a relatively small amount in comparison to

860g of total HC present in each column and that the degradation rates of tarball material occurred very slowly (Fleming at al. 2011).

Based on the available (though scarce) data on LOS in the literature, it can be anticipated that the column study with LOS material that is presented in this thesis, should show an increased level of hydrocarbon contamination in the leachate (relative to the surficial bitumen material investigated by Fleming et al (2011) and overall increased rates of biodegradation activity in comparison with the more weathered material.

## 2.5 Mass transport processes - Distribution of PHC in the subsurface

In a large oil sands waste storage dump, characterization of and understanding the site specific water flow regimes and PHC distribution in the subsurface is crucial. At the Aurora Fort Hills dump, the subsurface soil may be divided into three zones: unsaturated zone, capillary fringe and saturated zone. PHC's may be present in soil either in aqueous or vapour phases and can migrate within the unsaturated zone. The contaminant migration rates may be enhanced by infiltration of rain water available through precipitation. During the infiltration of rain water through the soil into the saturated zone, some of the PHC may dissolved in water, be adsorbed in soils, vaporized or trapped between soil particles in the unsaturated zone (Chen, 1992). Percolating contaminated rain water eventually gets to the saturated zone. Once the contaminant significantly accumulates in the saturated zone it may pose some issues due to advective contaminant transport. In this case some dissolved petroleum hydrocarbons and other derivatives washed out from the soil contained LOS material could be spread rapidly and reach the Athabasca River.

The distribution of contaminants within the vadose zone can take place either in aqueous or vapour phases. Direction of movement of gas phase is independent and depends on the relative density and pressure gradients while for aqueous phase is usually downward due the gravity forces. A brief overview of mass transport and biodegradation mechanisms such as diffusion and biodegradation related to this project are provided below.

### Diffusion

Molecular Diffusion is described as a mass transport in liquid or gas phases driven by concentration gradients and thus becomes less significant when equalization occurs (Domenico and Schwartz 1990). As long as the concentration gradients exist the diffusion takes place even where there is no water movement. Therefore, contaminant can be often detected in a solute a bit in advance of the advective transport only. In case when the advective flow of solute is too slow the diffusive mass transport may dominate (Fetter 1993). In a field with soil made of mostly of hydrocarbons in unsaturated zone it is expected that diffusion of gas phase will be dominant. However, sporadically due to heavy rains when the air voids in porous media get filled up with water, volatilization of hydrocarbons may stop and only aqueous diffusion takes place. Note that diffusion in the air is approximately 10 000 greater than in the water.

### Biodegradation

Biodegradation is by definition a process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment - (U.S. Environmental Protection Agency, 2009). The organic compound such as PHC are degraded by various bacteria available in the subsurface and produce energy. In the process of biodegradation organic compounds are converted into $CO_2$ and $H_2O$ and this is called mineralization. However, complete mineralization never occurs as a portion of organic compound is converted to biomass and a significant fraction of it is not effectively biodegradable (Eweis et al 1998). The most complex PHC molecules are broken down to simpler forms or in most cases they are degraded to a form of $CO_2$ and water as a final end (Mossop, 1980).

## Factors affecting biodegradation of hydrocarbons in the environment

As mentioned above, PHCs are a mixture of organic compounds derived from geological substances such as oil, bitumen and coal and it may contain hundreds to thousands of various compounds, composed mostly of carbon and hydrogen. The PHC biodegradation rates will vary due to its compositional heterogeneity and its variability in physical and chemical properties such as bioavailability and solubility (Leahy, 1990). However, there is research well described in the literature that suggest the rates of PHC degradation decrease with increase molecular weight of hydrocarbons (Das et al 2011, Visser 2008b, Atlas 1981). The most simple HC molecules such as F1 fraction due to its relative high solubility and volatilization potentials are degrading easily and fast. With increasing molecular weight and complexity of hydrocarbons structure as fractions from F2 to F4, bioavailability of HC for degradation is becoming more limited due to decreased volatilization and solubility resulting in slower degradation rates. Thus, from the fastest degrading PHC fractions are F1 ...F2...F3 to the slowest degrading PHC fractions F4.

Regardless of the composition of PHC there are other biological and physiochemical factors that can influence the biodegradation rates.

Biodegradation of hydrocarbons results from metabolic processes of wide variety of microorganisms including bacteria and fungi, which are capable of degrading the PHC. Thus, PHC degradation rates depend in part on the composition of the microbial community and its adaptive response to the presence of the hydrocarbons (Atlas 1981, Leahy 1990, Das at al. 2011)

Physical and chemical factors affecting biodegradation of hydrocarbons include: temperature, availability of Oxygen and nutrients, soil moisture (water content), solubility, redox potential and pH (Chen 1992; Leahy 1990; Atlas 1981).

- the temperature has a significant effect on degradation of hydrocarbons by its influence on physical nature and chemical composition of the HC, rate of HC metabolism by microorganism and composition of microbial community (Atlas, 1981). Generally, the rates of HC degradation increase within increasing temperature. At low temperatures the PHC degradation process is slowed down due to reduction in volatilization of short chain alkanes and their increased solubility in water (Leahy, 1990)

- the availability of oxygen in soils for the microbial oxidation of HC in the process of HC biodegradation is crucial and depends on rates of microbial oxygen consumption, the type of soil, saturation of soil and other presence of other substrate that can lead to oxygen depletion (Leachy 1990). Zo Bell (Zo Bell 1969) at his work found that hydrocarbons degradation was an order of magnitude faster at 25$^oC$ than at 5$^oC$ and in another study (Ludzack and Kinkead 1956) that motor oil was rapidly oxidized in 20 $^oC$ but not at 5 $^oC$

- microorganisms require nitrogen and phosphorus for decomposition of hydrocarbons therefore availability of such nutrients in the system can be a limiting factor in the microbial degradation of hydrocarbons (Leahy 1990, Atlas 1981, Eweis et al 1998

- soil pH can be highly variable from 2.5 to 11. The extremes values of pH can have negative effect on microbial communities that degrade the hydrocarbons. The soil pH range of 6.5-8.5 is found to be to most optimal for microbial biodegradation efficiency (Leahy 1990, Eweis et al 1998, )

- microbial activity in the soil increases with increasing water content due to the greater availability of nutrient, organic carbon and other oxidizable compounds. However, there is a threshold water content value above which the activity begins to decline. At high levels of saturation water occupies most of the voids in the soil matrix leaving a little space for transport and availability of oxygen to microorganisms. The optimal soil moisture content for remediation is in a range 30-80% by volume (Neale 2000, Das et al 2011, Lyman et al 1992).

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 Introduction

The main purpose of this study was to characterize the natural (in situ) conditions and describe processes taking place in the subsurface of the Aurora Fort Hills Dump, Syncrude Canada Ltd., North of Fort McMurray, AB.  These studies were focused on the degradation rates of PHCs in the subsurface and in the near surface materials and on the rates of gas fluxes from the dump to the surface as well as the mobility of PHC within subsurface materials and the potential for the PHC leaching to the groundwater system.

The scope of this work was divided into field and laboratory studies.

The field study comprised surface gas flux measurements from the unsaturated zone using custom fabricated flux chambers with gas analysis by field portable equipment and subsurface soil gas monitoring using gas vapour probe kit. The purpose of this study was to evaluate the initial field conditions in terms of $CO_2$ flux production (as an indicator of the subsurface microbial degradation of PHCs) and determine of the effect of temperature on gas flux rates with focus on repeatability and spatial variability of collected data. The field measurements of the LOS material were conducted prior to placement of the soil reclamation materials and revegetation.

The laboratory study involved laboratory column experiments intended to mimic some important processes that occur in the field and are associated with PHC biodegradation and mobility. In this study the actual field conditions of the Aurora Soil Capping Study, oil sands waste disposal area, are simulated such as representative temperatures and similar soil densities. The whole analytical lab work and chromatography was carried out in the Geoenvironmental Engineering Laboratory at the University of Saskatchewan and at specialized commercial analytical labs such as Exova, Calgary, AB.

## 3.2 Field Study

### 3.2.1 Gas flux measurements

In 16 selected locations across the Aurora Capping Study area, custom-fabricated gas flux chambers were temporarily installed in order to take measurements of the flux of gases from the subsurface to the atmosphere. The test locations were chosen to be representative of and cover the whole surface area of Fort Hills Dump (Site plan – Appendix A). The measurements were taken during successive field trips to evaluate the repeatability of the data collected and to estimate its sensitivity to variations in weather conditions such as temperature, moisture conditions and wind.

Each gas flux chamber consisted of two parts: the lower part (the ring) and the upper part (cap). Both parts had the same 0.7m diameter and the ring and the cap had 0.2m and 0.15m in height, respectively. The detailed schematic drawing of the gas flux chamber is presented in Figure 3.1. Prior to measurements the ring was installed on the surface (dug into the soil - depending on its hardness usually it was between 0.04-0.08m) and sealed around the edges with bentonite. The next day the cap was put on the ring and the flanges and gasket tightened to ensure a good tight seal. Two tubes were attached to the chamber for gas inlet and outlet, respectively. The outlet was connected to the FTIR (Fourier-Transform IR) equipment and the oxygen sensor and the data were collected on computer (Photo 3.1). The schematic drawing of the system set up is presented in Figure 3.2.

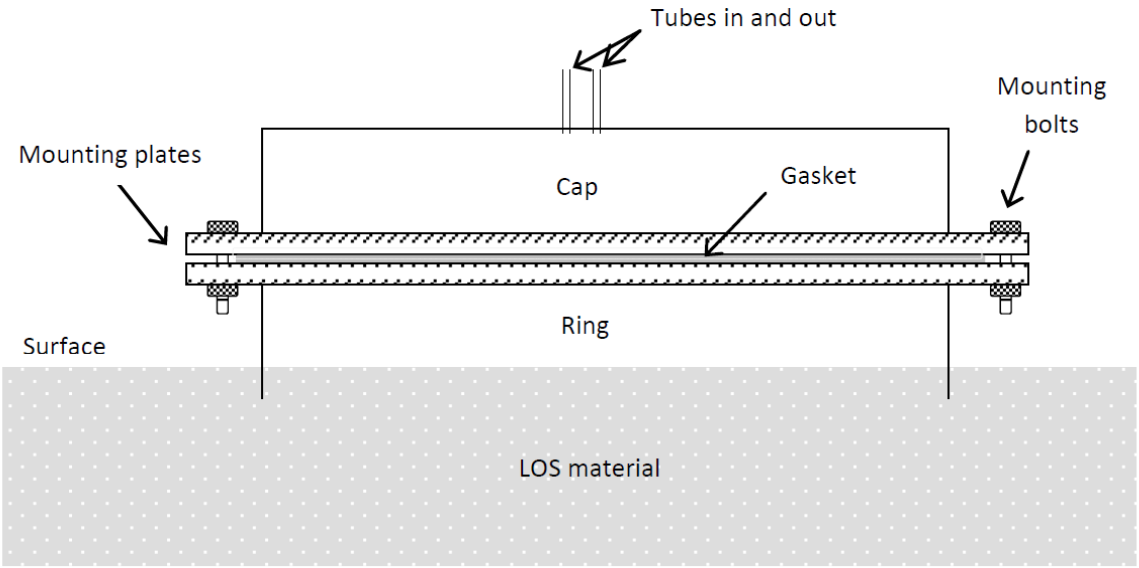


Figure 3.1. Schematic drawing of the gas flux chamber

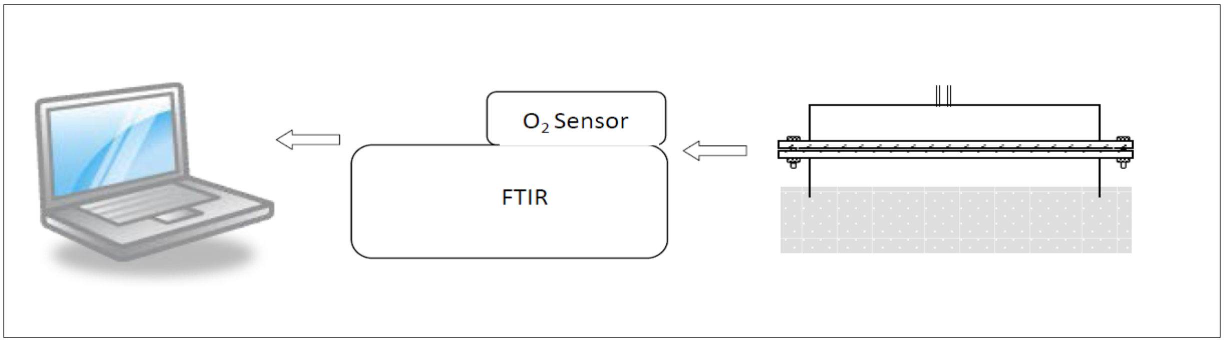


Figure 3.2. Schematic set up of gas flux measurement

Photo 3.1. Gas flux measurement at Aurora Capping Study - facing NE

After an initial FTIR calibration (system flush with pure nitrogen) the data collection began on computer using the Calcmet software. The concentrations of $CO_2$, $CH_4$ and other gases (except $O_2$) in gas flux chambers were measured at each location by GasMet DX-4015 FTIR Analyzer. The oxygen concentration was measured using a Varsalla Paramagnetic Oxygen sensor. After taking the initial reading (ambient) the changing concentrations of $O_2$, $CO_2$, $CH_4$ and other gases were monitored at time intervals : 1, 5, 15, 30, 60, 90, 120, 180, 240 and approx. 360 min, depending on quality of data collected. From the changing concentrations and the known volume of the chamber, the rate of the gas flux from the subsurface to the atmosphere may be determined for each of the various gas components monitored.

### 3.2.2 Soil gas phase concentrations monitoring

In total, 31 subsurface gas sampling probe tips were successfully installed in the ground as a long term sampling points at selected 13 locations at the site (in the close proximity of previously installed gas chambers) using an AMS hand sampling system and its "Gas Vapour Probe Kit" (Photo 3.2). The sampling gas vapour probe that can be used for collecting either gas or water samples was driven into the ground by specially constructed rods (AMS) which were then removed to leave the tip in place with plastic tubing exposed at the surface. Approximately 1m of tubing was left above the ground surface attached to the post with ID number and plugged with a golf tee. The hole made due to installation was backfilled around the tube with bentonite and water to seal out atmospheric gases.

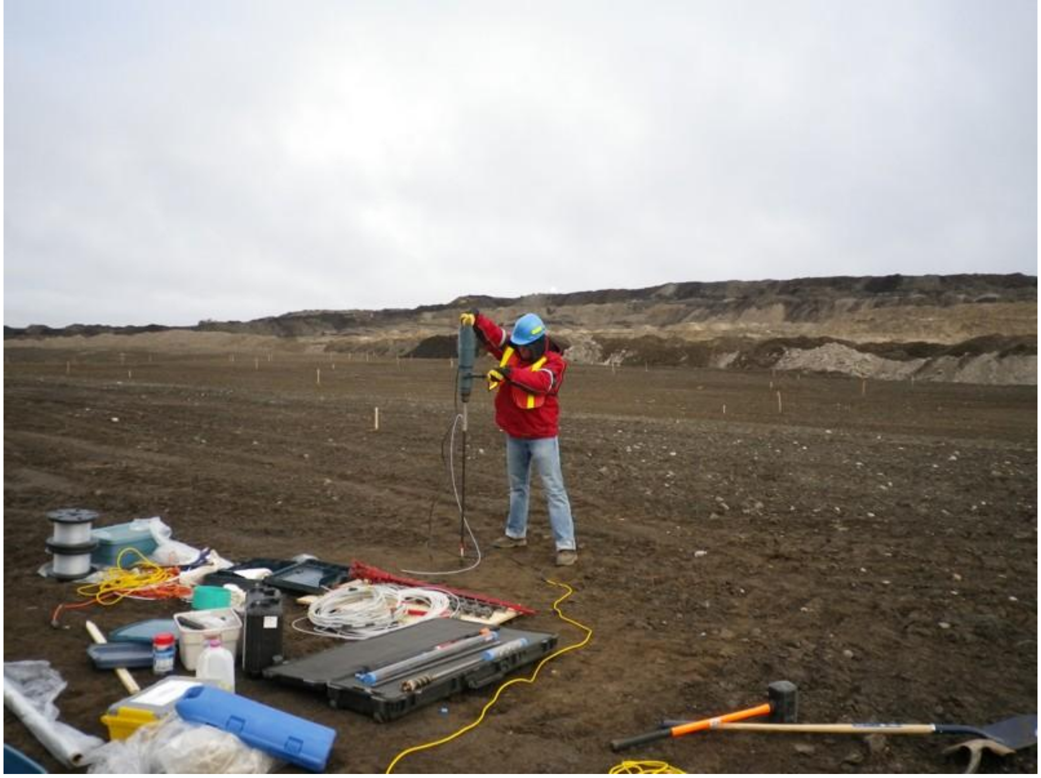


Photo 3.2. Installation of gas vapor tip using AMS sampling system and hammer drill at Aurora Capping Study - facing NW

Initially, it was planned to install three gas vapour probes at the three different depths at a single location to get the profile conditions of gas concentration within the soil, however, due to hardened or occasionally frozen surface and unexpected difficulties with successful installation of the gas probes such as tubing disconnection, certain depths and locations were not achieved. The detailed layout of all gas vapour installations as well as locations of gas flux measurements are presented on a site plan in Appendix A. The schematic drawing presenting the installations of the gas vapour tips is presented in Figure 3.3.

The gas phase concentrations of $O_2$, $CO_2$ and $CH_4$ from the gas vapor probes at each location were measured using Landtec GEM 2000 - portable gas analyser. The measurement were always taken a day after the installations and repeated on few occasions to ensure the repeatability of collected data.

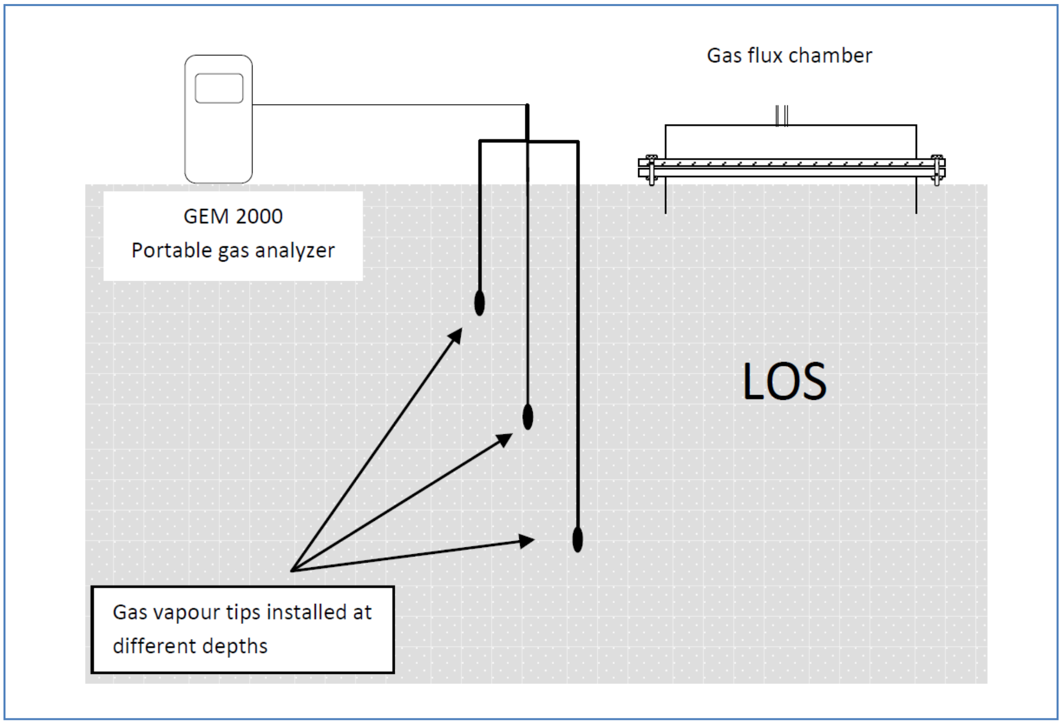


Figure 3.3. Schematic drawing of gas vapour tips installation

## 3.3 Laboratory study

### 3.3.1 Introduction

In this study some important processes that occur in the field were recreated in the lab in order to evaluate the PHC degradation and leaching potential.

### 3.3.2 Column study - design and set up

The six teflon-coated steel columns were designed and fabricated at the University of Saskatchewan machine shop and had previously used in the project “Hydrocarbons in the root zone” (Fleming et al 2011).

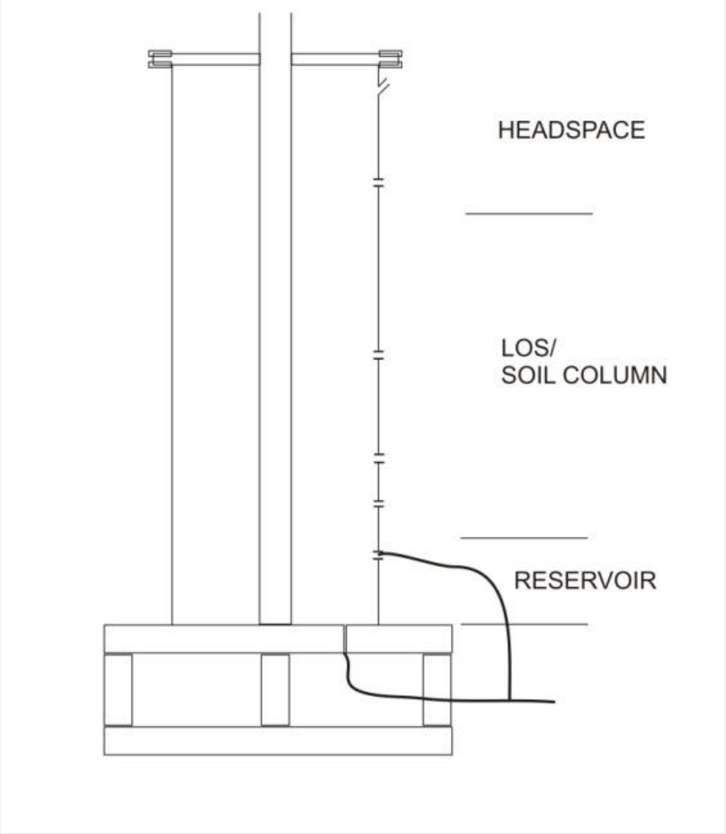


Figure 3.4. Schematic of soil column cross section

The columns are 0.3m in diameter and 1.0m tall. To minimize potential sorption or catalytic effects in the columns, all interior surfaces are lined with teflon or glass. Each column is equipped with a glass access tube running vertically down the centre of the column as shown in Fig. 3.4, to provide access for a Sentek Enviroscan probe, a soil moisture sensor probe which operates on the principle of FDR frequency-domain reflectometer (Sentek Sensor Technologies, Australia). Special connections were made in the wall of each column for the connection to Micro-Oxymax respirometer (Columbus Instruments, Columbus, OH, USA) as well as for water supply and for the access to measure the concentration of gases at various depth. The bottom of each column was filled with 11 to 12cm of coarse silica sand to create a capillary break within the LOS/overburden material. Leachate referred from the LOS/overburden material was collected and sampled for analysis, up to about one litre in volume, every 7 days. Prior to placement, the silica sand was autoclaved in order to avoid introducing additional microbes. Above this sand reservoir, approximately 66-67 cm of LOS/overburden material was placed and packed to the approximate densities of 1.5 to 1.8 $T/m^3$ as an equivalent of averaged densities in the field. The remaining space, approximately 23-24cm, provided a headspace for sampling of volatilized gases. Detailed information regarding each column set up is presented in the Table 3.1.

The columns were operated under unsaturated conditions using a low flow peristaltic pump to provide 30 ml of demineralized water three times per day in order to replicate field conditions. The amount of water provided to each column was determined based on an average annual precipitation for Fort McMurray area which is 460 mm/year. However, these rates used in the experiment do not represent the infiltration rates that would be expected in the field. Alberta

Environment assumes infiltration rates of 10% of average annual precipitation in Alberta in developing contaminated soil guidelines (Alberta Environment 2007).

Table 3.1. Detailed information of the columns CH1-CH6 set up

| Column ID | CH1 | CH2 | CH3 | CH4 | CH5 | CH6 |
|---|---|---|---|---|---|---|
| Date of assembly | 24/03/12 | 23/04/12 | 23/04/12 | 18/06/12 | 18/06/12 | 19/06/12 |
| Reservoir height (cm) | 12.5 | 11 | 12 | 12 | 11.5 | 12 |
| LOS height (cm) | 67.5 | 67 | 66 | 66 | 66 | 65.5 |
| Headspace height (cm) | 21.5 | 23.5 | 23.5 | 23.5 | 24 | 24 |
| Headspace volume (L) | 15.1 | 16.5 | 16.5 | 16.5 | 16.85 | 16.85 |
| Total mass of LOS (kg) | 72.9 | 83 | 78.8 | 83 | 79 | 75 |
| Density T/m3 | 1.54 | 1.74 | 1.7 | 1.82 | 1.65 | 1.64 |

Working with more realistic infiltration rates (around 10 time smaller) in the columns study would extend the experimental project by years. Therefore, the amount of 90 ml water provided on a daily basis (which was based on an equivalent of average annual precipitation rates for Fort McMurray region (460mm/year) was sufficiently enough to maintain unsaturated conditions in the experiment as well as provide adequate amount of leachate for hydrocarbon analysis.

To ensure the accuracy and repeatability of collected data each individual test was carried out in triplicates (three columns were set up and running at room temperature (avg. 22 $^{o}$C) and three columns were running at varying cooler temperatures (around 2$^{o}$C and 14 $^{o}$C) each for several weeks (depending on the quality of collected data).

Once the column was filled and sealed it was connected to Micro-Oxymax, an advanced, fully automated aerobic/anaerobic closed circuit respirometry system. This system monitors continuously the changes in concentrations of oxygen, carbon dioxide and methane in the headspace, thus the production and/or consumption of gases may be used as a surrogate for microbial activity. The Micro-oxymax respirometer consists of a main pump, oxygen sensor (0 - 100 %), Methane sensor (0-10%) and Carbon Dioxide Sensor (0-10%).

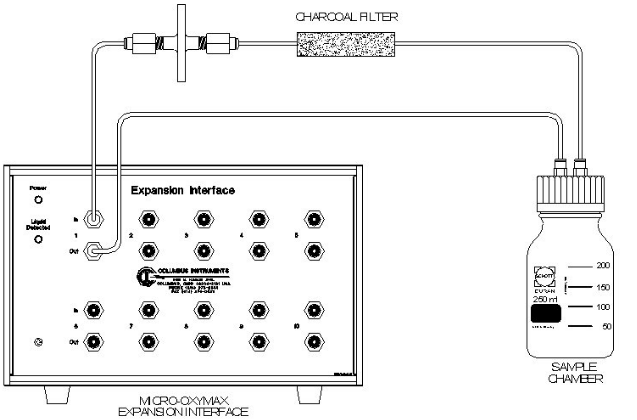


Figure 3.5. The example drawing of typical connection of Micro-oxymax with the charcoal tube (Columbus user's manual)

Prior to starting the experiment the micro-oxymax (sensors) were calibrated with gases in compliance with Columbus instrument manual and tested positively for leaks and proper connections using the Columbus software. The micro-oxymax equipment was calibrated and running at room temperature. Since the material used in the experiment contained a great amount of PHC and potentially volatiles, an activated charcoal trap (in this case Orbo 302 charcoal sorbent tube) was used to collect PHC volatiles in order to evaluate the potential that natural processes in LOS release significant gas-phase VOC's and to prevent the gas sensors from malfunctioning or being damaged (Columbus Instruments Micro Oxymax user's manual). The example drawing (Figure 3.5) shows the connection of the charcoal trap to the Micro Oxymax and sample chamber.

To maintain ambient atmospheric condition same as in the field, periodic refreshing of the headspace was required. Respiration  activity of the material such as LOS (rich in PHCs) could result in a fluctuation of gas, particularly oxygen and carbon dioxide concentrations measured in the headspace. Periodic refreshing of each column avoided this problem by replacing the air in the headspace.

The data obtained from the Micro -Oxymax respirometer system can be presented in two forms: rate and cumulative. These two forms of data are useful in different situations. Rate data present how fast the gas is being consumed or produced over time. This information is useful in toxicity type of tests where the activity level of the organisms is required. However, this representation may have some limitations. For example: while running samples with high moisture content, $CO_2$ may be released in to the headspace just after refresh. This is observed by jumps or spikes in the $CO_2$ rate data, caused by $CO_2$ building up in the head space during the course of an experiment. The $CO_2$ dissolved in solution is in equilibrium with the head space $CO_2$ concentration. After a refresh occurs, the $CO_2$ concentration in the headspace decreases considerably so the $CO_2$ dissolved in solution is then released into the head space reaching equilibrium, and showing a jump in $CO_2$ production rate (Columbus Instruments, Columbus, OH). In such cases, cumulative data for $CO_2$ will be correct and used accordingly in this study. All of the results ($CO_2$ production and $O_2$ consumption) collected by the respirometry system were automatically normalized to STP {standard temperature (0°C - 273.15 K) and pressure 760 mmHg (101325 Pa)} conditions.

### 3.3.3 Lean oil sand and PHC characterisation

During loading of LOS/overburden material into the columns, small representative amounts of samples were collected at intervals averaging 5-10 cm in depth. The collected samples were used to carry out a wide variety of lab standard tests determining a moisture content, loss on ignition (LOI), grain size distribution and PHC content in terms of C fractions.

### 3.3.3.1 Moisture content

In total from six experimental columns 44 samples were collected (averaging seven samples per column) and moisture contents were measured according to the standard test method for laboratory determination of water content in soils by mass (ASTM D2216 - 98). The results from the tests allowed to establish the initial profile conditions of moisture content in each column.

### 3.3.3.2 Loss On Ignition (LOI)

Loss on ignition is a standard method estimating the organic and carbonate content by determining the mass loss of a specimen upon combustion while heated under controlled conditions of temperature, time, atmosphere and specimen mass (ASTM D7348-08). The purpose of this test was to characterize the initial conditions in each column in terms of the organic content. From each column, four samples were taken and tested in triplicates (about 2 g of each sample) to ensure the accuracy of obtained results for LOI. At first, the samples were held in a high temperature furnace at 550 °C for 2 hours. During that time organic content was oxidized at 550 °C to carbon dioxide and ash. Correspondingly, the loss in mass may be used to estimate the organic content of the sample. Subsequently, the same samples were combusted at 950°C for an additional two hours. During that time, at 950°C carbon dioxide was evolved from carbonates. In this reaction the loss in mass may be used to estimate the total carbon in the sample. The tests were conducted in compliance with standard test methods for loss on ignition of solid combustion residues (ASTM D7348-08).

### 3.3.3.3 Grain size distribution

Grain size analyses were performed on 12 samples (two from each column) according to the standard test method for particle size analysis of soil (ASTM D422-07). Prior to grain size analyses, the bitumen present in the soil samples was extracted according to procedure supplied by Syncrude, Canada (APPENDIX C). In this method, approximately 100g of each sample was loaded to four or six 37ml teflon tubes evenly and shaken in a solution with Dichloromethane (DCM), then centrifuged and decanted. The procedure was repeated (on average 6-8 times) till the solution was visibly clear after shaking.

### 3.3.3.4 Petroleum hydrocarbon analysis

Total number of 60 soil samples were collected from all six experimental columns and analyzed for PHC content according to the Reference Method for the Canada Wide Standards for Petroleum Hydrocarbons in soils described previously in section 2.5. All of the 60 samples were analysed by Exova, a commercial analytical lab located in Calgary. In compliance with Exova sample requirements, each collected soil sample was placed in a glass jar with a teflon-lined lid and tightly packed with no headspace and kept cool at 4$^{o}$C.

Soil samples were packed into a cooler and sent overnight to Exova and then they were analysed for:

- Monoaromatic hydrocarbons: BTEX - Benzene, Toluene, Ethylbenzene and Total Xylenes (m,p,o)
- Volatile petroleum hydrocarbons: F1 C6-C10
- Extractable petroleum hydrocarbons:
    - F2 C10-C16
    - F3 C16-C34
    - F4 C34-C50
    - F4HTGC C34-C50+
- Gravimetric heavy hydrocarbons: F4G

The results from these tests provided information about the amount of PHC in each fraction and based on that it was concluded which PHC fractions were dominating in LOS material and what was the total amount of PHC in each column.

#### 3.3.3.5 PHC degradation from respiration data

As previously described in section 3.2.2 the micro-oxymax respirometry system was simultaneously monitoring the changing concentrations of oxygen, carbon dioxide and methane in the headspace of each column. The Microoxymax software determines the cumulative consumption of oxygen and generation of carbon dioxide and methane. During biodegradation, in the presence of oxygen (aerobic conditions), oxygen is consumed by microorganisms in order to degrade hydrocarbons into simpler organic compounds and eventually reduce them to mineral compounds such as carbon dioxide and water. During biodegradation of hydrocarbons in the absence of oxygen (anaerobic conditions), microorganisms consume other elements than oxygen such as sulphur or nitrogen which results in production of carbon dioxide and methane. Monitoring of methane production allows to determine if system is running primarily under aerobic or anaerobic conditions.

Microbial degradation of hydrocarbons in an aerobic environment can be expressed as the consumption of hydrocarbon, oxygen and nitrogen in order to yield biomass or $CO_2$ and $H_2O$. Further, biomass can be oxidized to $CO_2$, $H_2O$ and $NO_3$. The detailed stoichiometric equations for production of biomass and complete mineralization of hydrocarbons are described in R.J Baker et al (2000). In Baker's work a simplified stoichiometric general formula for complete hydrocarbon degradation was provided and it is presented below: $C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + (y/2)H_2O$. Depending on the hydrocarbon complexity, the stoichiometry of each reaction will vary. Zytner in his work for example used a diesel molecule as an approximation for heavy hydrocarbons and presented the simplified formula for complete degradation of diesel oil: $C_{16}H_{34}+24.5O_2=17H_2O+16CO_2$ (Zytner, 2001). LOS material investigated in this thesis contained primary heavy hydrocarbons therefore estimation of PHC degradation rates was based on Zytner's general formula.

In result, the total aerobic PHC degradation rates can be estimated from cumulative volumes of $O_2$ consumed and $CO_2$ produced resulting from microbial activity over the time of the experiment. The cumulative volumes of $O_2$ and $CO_2$ were converted into grams and used in Zytner's equation provided above in order to estimate the PHC degradation rates. Based on the cumulative generation of $CO_2$ the long term gas fluxes for each column were estimated. Further, the variety in generating rates with varying temperature were evaluated and described in chapter 5.

The charcoal trap (Orbo 302 charcoal sorbent tube) was attached to each column and used in the experiment to collect volatiles (described in section 3.2.2). At the end of the experiment one of the charcoal tubes was sent to Exova for analysis of any PHC volatiles that had accumulated over a period of several months.

### 3.3.4 PHC leaching potential and mobility

Addition of DDI (Demineralized) water to each column on a daily basis in amount of approximately 90 ml/day resulted in production of leachate over time. Leachate was collecting from a reservoir at the bottom of each column on a weekly basis and analysed for TC (total carbon) and TOC (total organic carbon) using the Tekmar-Dohrmann Phoenix 8000 UV/persulphate analyser.

As well, every 3 weeks the leachate was sent to Exova to check for leachable chromatographable PHC fractions such as BTEX, F1, F2 and F3. Additionally, on one occasion, at the end of the experiment, the water sample was also checked for "oil and grease", according to partition-gravimetric standard method for water/environmental protection agency (APHA/USEPA). This gravimetric method weighs all organic material (not just hydrocarbons). The results from the leachate analysis showed that organic carbon concentrations were several orders of magnitude higher than the reported concentration of hydrocarbons. It was concluded that some other organic compounds may be present in the leachate in increased concentrations. Accordingly, additional leachate analyses were conducted at Environment Canada for presence of naphthenic acids and other acid-extractables.

### 3.3.5 Volumetric water content measurements

The EnviroScan probe is a device for monitoring of water content at multiple depths in a soil profile. Each probe can be equipped with several moisture sensors depending on applications. The moisture sensors produce a high frequency electrical field, what extends into the surrounding soil. The sensors detect the changes in dielectric constant, or permittivity, of the soil over time. At high frequency the measurement is affected mostly by water molecules. The greater the amount of water, the smaller the frequency measured between the two rings of the sensor. The output of this measurement is expressed as volumetric water content which is converted from a scaled frequency reading using a default calibration equation, which is based on data obtained from numerous scientific studies in a range of soil textures (Sentek technologies).

The probe used in the course of this study was 1m long and consisted of one moisture sensor installed 12cm from the bottom as it is presented in the Figure 3.6. The volumetric water content within each column was measured on a regular basis using a Sentek EnviroScan probe (Fig. 3.6). Each column was equipped with glass access tube for EnviroScan probe (Fig. 3.4) allowing the moisture probe for direct measurement of volumetric water content across the length of the column. In this study, moisture contents were measured every 10 cm along the soil columns. The continuous monitoring of changes in moisture content within columns over time (especially at the initial period of soil wetting) allowed for establishing the flow regimes as well as potential water retention spots within the LOS material.

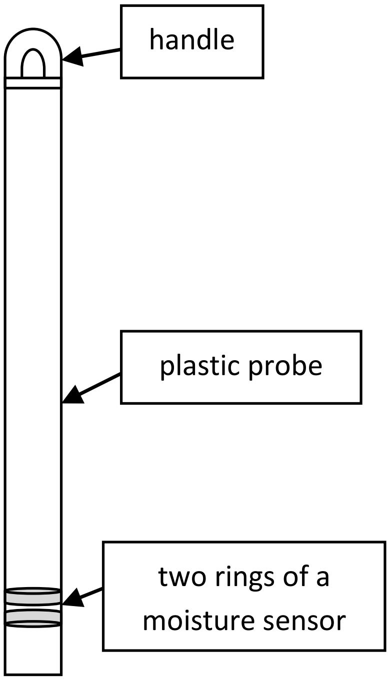


Figure 3.6. Schematic drawing of EnviroScan probe with one sensor

# CHAPTER 4

## FIELD STUDY

### 4.1 Introduction

The purpose of this field study was to evaluate the rates of gas flux from subsurface to the atmosphere from LOS and overburden materials disposed at the "Aurora Fort Hills" oil sands waste disposal area. All of the field measurements were conducted prior to soil cover placement. Surficial gas fluxes represent indicators of subsurface microbial degradation of PHCs. Significant gas flux may potentially affect the performance of reclamation covers. Additionally, biodegradation of PHC's within the dump may result in more mobile daughter products which may be loaded by percolating pore water. The field study comprised surface gas flux measurements from the unsaturated zone using custom fabricated flux chambers with gas analysis by field portable equipment and subsurface soil gas monitoring using gas vapour probe kit as previously described in section 3.2.

### 4.2 Temporal and spatial variations of surficial gas flux rates

At 16 selected locations across the Aurora Capping Study site (Appendix A), 25 gas flux measurements were successfully carried out. Additionally, 11 replicate readings were taken. The locations were selected in order to cover as much of the Capping Study site as possible with special focus on spatial, seasonal variability and repeatability of collected data. The data were collected on three separate occasions. The summary of the results from gas flux measurements are presented in Table 4.1.

Table 4.1. Summary of the results from gas flux measurements

| Location | Estimated $CO_2$ fluxes mg/m$^2$/h | Estimated $CO_2$ fluxes mg/m$^2$/h | Estimated $CO_2$ fluxes mg/m$^2$/h |
|---|---|---|---|
| | October 2010 | July 2011 | September 2011 |
| CH-1 | 13 | - | 71 |
| CH-2 | 26 | - | |
| CH-3 | 39 | - | 56 |
| CH-4 | 13 | - | - |
| CH-5 | 16 | - | - |
| CH-6 (CH 14) | 120 | 810 | 263 and 258 |
| CH-7 (CH 12) | 87 | 107 | 89 |
| CH-8 (CH 11) | 10 | 75 | 100 |
| CH-9 | - | 140 | - |
| CH-10 | - | 130 | - |
| CH-13 | - | 72 | - |
| CH-15 | - | 27 | - |
| CH-16 | - | 12 | 166 |
| CH-17 | - | 69 | - |
| CH-18 | - | 35 | - |
| CH-19 | | | 51 |

In Table 4.1, each column represents different time of year when gas flux measurements were taken. In October 2010, the temperatures were oscillating between 6 to 10$^{o}$C on average and dropping to 0$^{o}$C with the -15 $^{o}$C at wind chill at the end of the sampling event. In July 2011, the conditions were moist from precipitation events and the daytime temperatures ranged from

20 to 30°C. In September 2011, the weather was dry (due to lack of precipitation the previous 3 to 4 weeks) with daily high temperatures ranged from 15 to 25°C.

In October 2010, measured $CO_2$ flux rates ranged from 10 to 40 (mg/m$^2$/h) with peaks of 90 to 120 (mg/m$^2$/h). In July and September 2011, measured $CO_2$ flux rates ranged from 12 to 140 (mg/m$^2$/h) with peak of 810 (mg/m$^2$/h), and 50 to 165 (mg/m$^2$/h) with peaks of 260 (mg/m$^2$/h), respectively. It was observed that the very high rate of 810 (mg/m$^2$/h) was associated with the area of relatively loose sand (compared to more compact, fine textured LOS material with increased bitumen at the surface across most of the site) and may this represent preferential flow in a zone of high air permeability. It should also be noted that the significant drop in gas flux rates (12 to 27 mg/m$^2$/h) in July 2011 at locations CH-15 and CH-16 were due to heavy rain that occurred in the morning. The photos 4.1 and 4.2 show the field site after a heavy rain and the inside of the flux chamber to illustrate the degree to which the soil was saturated which resulted in drop in gas fluxes.

Photo 4.1. Aurora Capping Study after heavy rain, facing S

Photo 4.2. Apparent increased level of saturation inside the flux chamber after heavy rain, at location CH-15

## 4.3 Gas flux rate calculations and example plots

The gas flux rates were measured over intervals of time as described in section 3.2. Each individual measurement was taken at least twice to ensure accuracy and repeatability. The final data points collected during the test were plotted on the chart of $CO_2$ concentration versus time. A few examples of gas flux plots are presented in Figures 4.1 and 4.2.

The individual $CO_2$ gas fluxes were estimated based on calculations using best fit linear regression applied to the slopes of the $CO_2$ production plotted on the chart of $CO_2$ concentration versus time as presented in figures 4.1 and 4.2. The concentration of $CO_2$ accumulated over time in a gas chamber (expressed in ppm) was used along with the volume of the chamber and the density of $CO_2$ 1.96 mg/ml (based on ideal gas law - 1 ml of $CO_2$ is equal 1.96 mg at $0^{o}$C and 1 atm). The calculated amount of $CO_2$ accumulated over a certain interval of time can thus be expressed as a total mass of $CO_2$. The calculated mass of $CO_2$ (mg) in the chamber was then divided by time (h) and the surface area of the ground surface within the chamber ($m^2$). The measured gas flux rates are thus expressed as $mg/m^2/h$ as summarised in Table 4.1.

The plots shown in Figure 4.1 represent different trends of gas flux rates for the same location measured during two separate field trips in late October 2010 and September 2011. These plots show a significant variety in gas fluxes which evidently illustrate that temperature had an significant influence on gas flux rates. The plots of $CO_2$ concentration versus time (Figures 4.1 and 4.2) show a general linear relationship. This indicates the $CO_2$ gas fluxes were not readily affected by reduction in the diffusion rate caused by increasing $CO_2$ concentrations in the chamber during each test. Sporadically, due to unstable weather conditions such as strong wind (estimated as 60 km/h) and sudden temperatures variations, the FTIR monitoring system which was affected the analysis results and the accuracy of the measurements that resulted in having an odd/erroneous data collection points (outliers) such as in Figure 4.2.

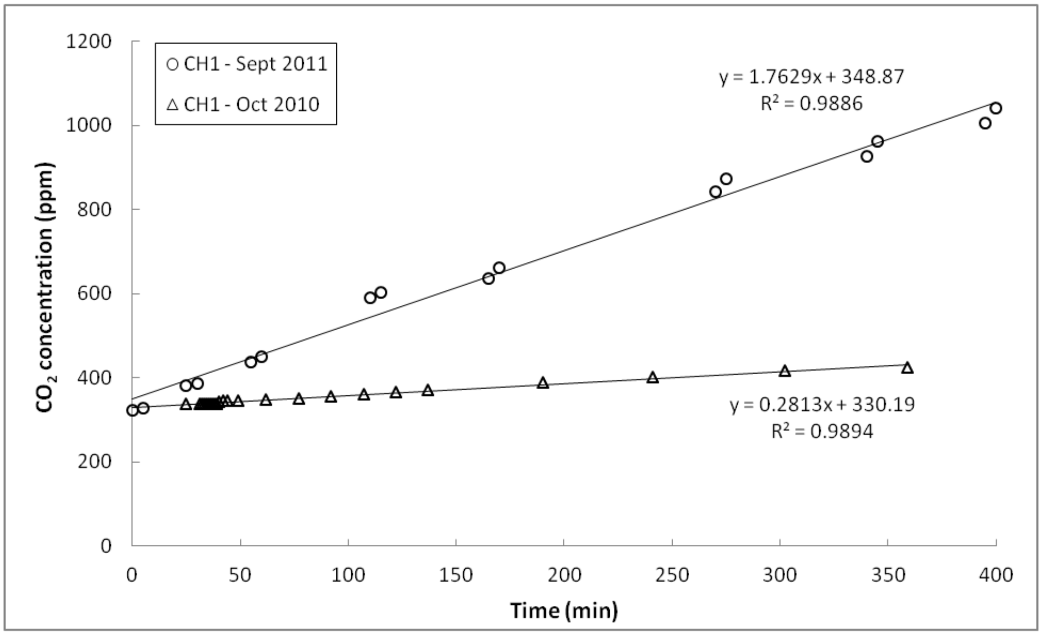


Figure 4.1. Examples of CO2 gas fluxes at CH1 location taken at different times of year (Oct. 2010 and Sept. 2011).

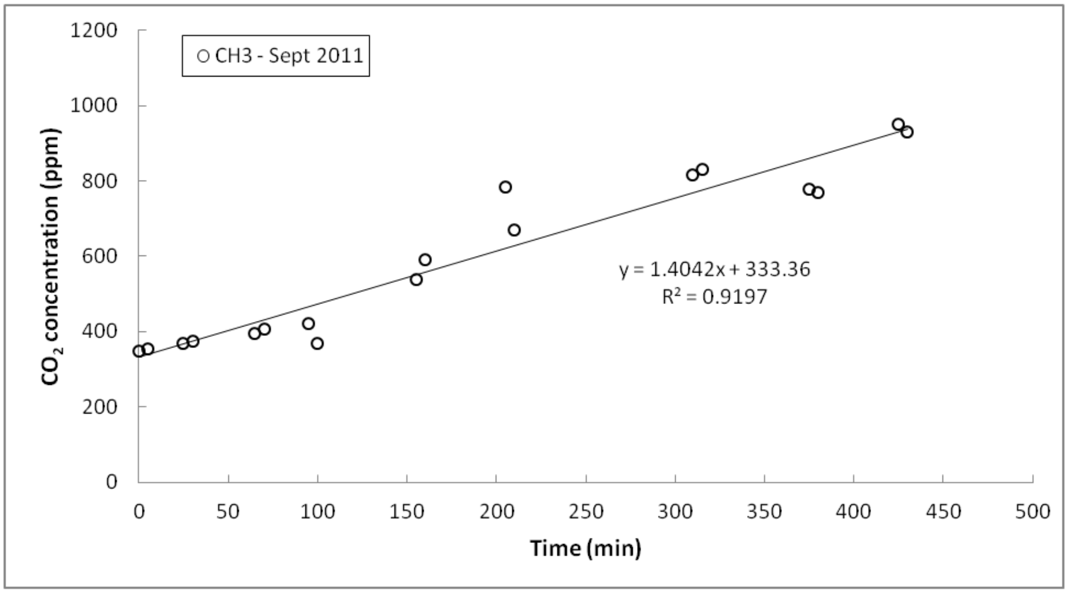


Figure 4.2. Gas flux measurement at location CH 3 (Sept. 2011)

## 4.4 Subsurface gas phase concentrations

In total 31 gas vapour probes were installed at 13 locations across the site in a close proximity to locations of the gas flux tests. Probes were installed to depths ranging from 0.5 to 7m. During field data collection it was found that at several installations the gas vapour probes became clogged. Clogged probes held vacuum of 60 to 70 kPa for 30 seconds with no noticeable change in suction. It is believed that clogs were caused by bitumen and/ or clay moving in and sealing the gas vapour vents. On several occasions water was drawn through the probes in measurable quantities indicating zones of perched shallow groundwater conditions below the surface. Additionally at three locations during soil gas measurements leaks were detected. All in all, from 31 gas vapour probes successfully installed only 18 of them showed consistency and reliability in collecting data.

Soil vapour concentrations depth profiles typically ranged from 0-2% Oxygen with peaks between 13 to 18%, 3 to 9% $CO_2$, and 0 to 4% methane. Occasionally concentrations were found up to 21% for $CO_2$ and 12% for $CH_4$. The detailed summary table with the all gas vapour concentrations is presented in the Appendix B. Some of the examples of gas-phase concentrations profiles are illustrated in figures 4.3 to 4.6.

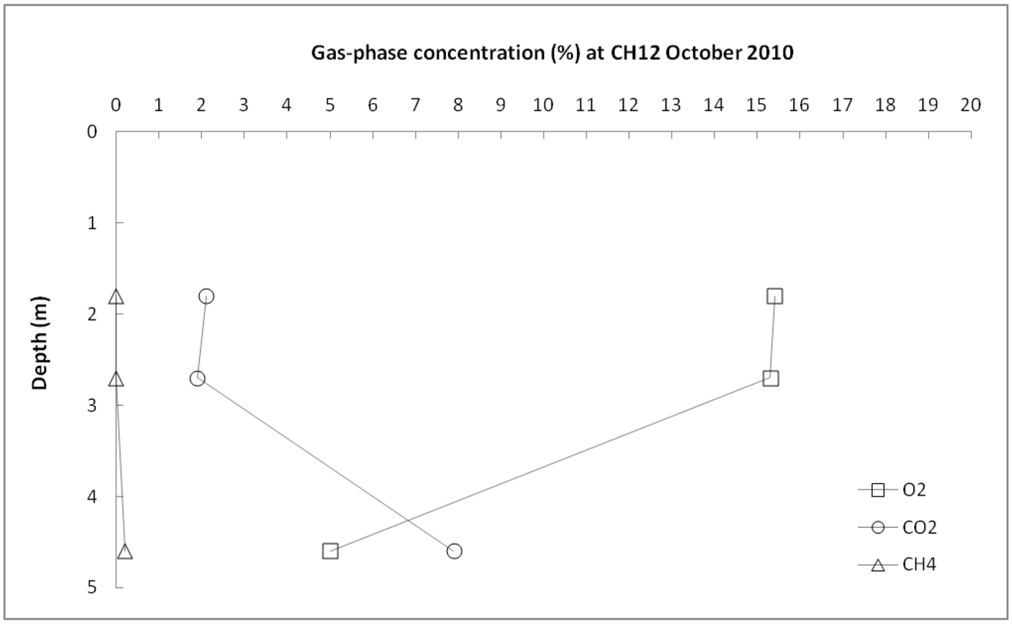


Figure 4.3. Depth profile for gas-phase concentrations at location CH12 measured in October 2010

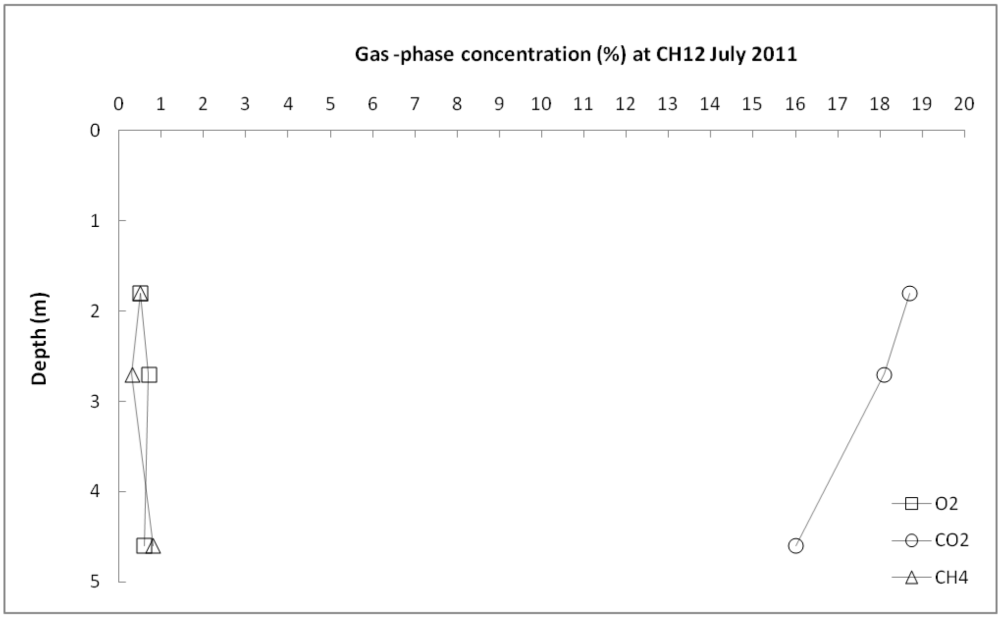


Figure 4.4. Depth profile for gas-phase concentrations at location CH12 measured in July 2011

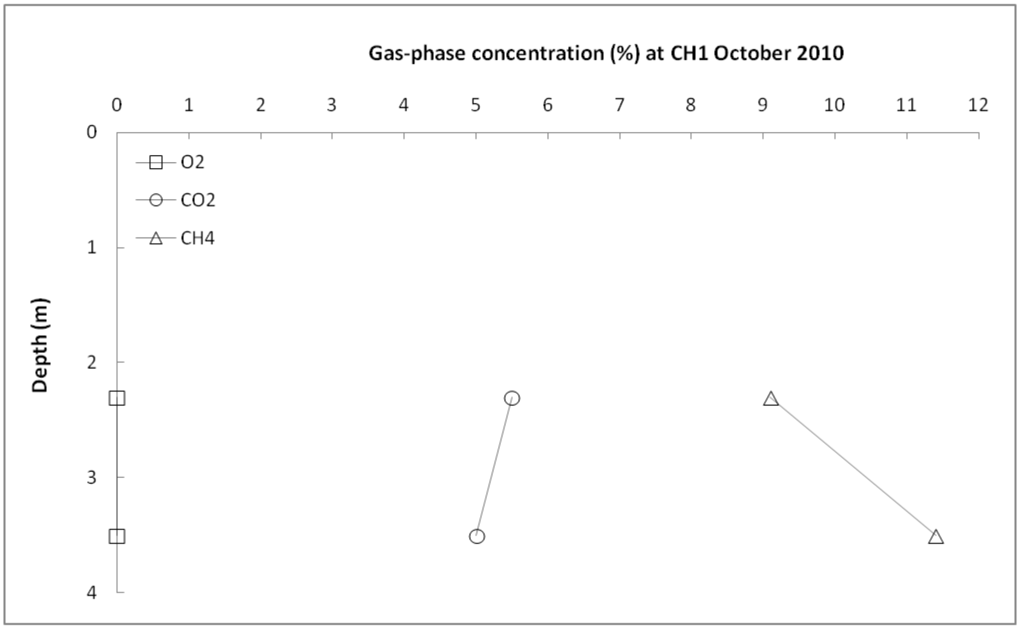


Figure 4.5. Depth profile for gas-phase concentrations at location CH1 measured in October 2010

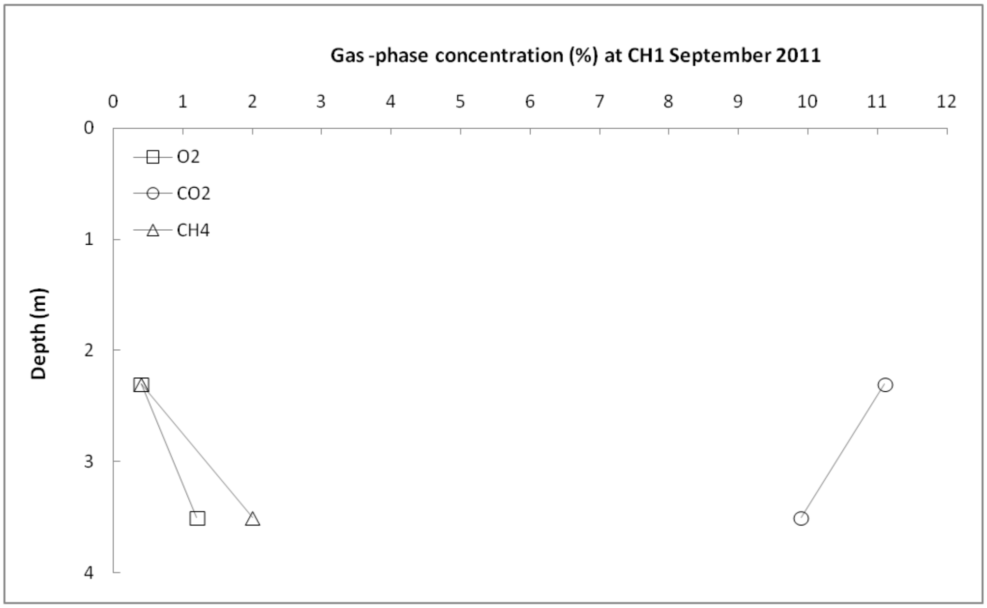


Figure 4.6. Depth profile for gas-phase concentrations at location CH1 measured in September 2011

Figures 4.3 to 4.6 show the examples of gas-phase concentration depth profiles for chosen locations CH1 and CH12 measured in October 2010 and Summer 2011. Figure 4.3 presents a typical gas-phase concentration depth profile in which the concentration of $O_2$ and concentration of $CO_2$ are inversely promotional with depth below the ground surface ($O_2$ decreases with depth and $CO_2$ increases with depth showing approximately volume for volume replacement of $O_2$ over the entire depth profile) (Hinchee, 1994) (Davis et al 2009). In Figure 4.3 a sudden change in $O_2$ consumption and $CO_2$ production was observed at depth of 2.8m. This represents an increased microbial activity enhancing $O_2$ consumption and $CO_2$ production that may have been caused by number of contributing factors described below. It was also observed that in in-situ experiments the carbon dioxide appearance may differ from a typical gas-phase concentration depth profiles found in text books or might be smaller than it would be accounted for by oxygen disappearance as illustrated in Figures 4.4 to 4.6. This trend may be caused by a number of contributing factor such as soil properties, hydrocarbon content, biomass production, oxidation processes or $CO_2$ dissolved in water as carbonates (Hinchee, 1994). The analysis of the collected data from the field study showed that $CO_2$ gas phase concentrations in the subsurface varied seasonally. For example, soil $CO_2$ concentration ranged between 2-7% and 16-19%, in the Fall 2010 and Summer 2011, respectively. It was observed that, this trend in increased soil gas concentrations reflected an increase in surficial gas flux rates at the same locations. The $CH_4$ concentrations found in the subsurface showed decreasing trend toward the ground surface as a result of methane oxidation. Figures 4.5 and 4.6 illustrate the evident example of methane oxidation. Here, $CH_4$ concentration from 9 - 12% was oxidized to 1 - 2 %. In this reaction carbon dioxide was evolved as a final end product the concentration of $CO_2$ increased from approximately 5% to 11%.

As was described in Chapter 2, diffusion governs soil gas migration in this study and it is a function of the concentration or partial pressure gradient. In general, the atmospheric $O_2$ concentration is higher than soil $O_2$ which means that $O_2$ will diffuse vertically into soil and vice versa the soil $CO_2$ concentration is higher than atmospheric $CO_2$ hence the soil $CO_2$ will diffuse from soil to the atmosphere. In oil contained soils a substantial amount of oxygen is consumed by microbes in a process of hydrocarbon biodegradation resulting in formation of decreasing vertical gradient of oxygen in the unsaturated zone. This process may lead to depletion of oxygen and an increase in carbon dioxide concentration as a final product of hydrocarbon degradation. The oxygen consumption rates can also be affected by numerous environmental parameters, such as: temperature, pH, oxygen levels, nutrients concentration, hydrocarbon type and concentration, microbial population and soil type (Reddy et al 1983).

## 4.5 Summary

Based on the results collected in the field study it was observed that there is a substantial variability in gas fluxes at different locations. In general, gas flux rates were ranging from approximately 10 to 260 ($mg/m^2/h$) with one peak of 810 ($mg/m^2/h$) and varied by up to 2 orders of magnitude. Moreover, in addition to observed spatial variability, temporal and seasonal variations in gas flux rates, were also observed.

Temperature was observed to have a significant effect on the observed gas flux rate (Parkin et al 2003) - possibly reflecting diffusion rates of PHC degradation in the near subsurface. Additionally, the level of soil saturation also had an effect of gas flux rates. It appears that after the addition of water from precipitation events, the observed gas flux rates increase significantly resulting from soil air displacement (Reddy et al 1983), (Parkin et al 2003. It was also observed that high levels of soil saturation caused by rainfall events resulted in a temporary reduction in gas flux rates, inhibiting free gas flux to almost zero. When the water content of the soil increases subsequent to heavy rain, the amount of air space for $CO_2$ to travel within the soil is significantly reduced and, greater amount of $CO_2$ dissolved in water, which altogether results in drop in flux rates. Diffusion rate of $CO_2$ in air is 10000 times faster than in water. All in all, temperature and level of soil saturation should have an influence on the gas flux rate measured on the surface. Temperature has an effect on the microbial activity thus production of $CO_2$ due to degradation of HC. The level of soil saturation affects the air space availability in the soil matrix which controls the gas-phase diffusion toward the surface of the $CO_2$ produced.

Low concentrations of oxygen (near depletion) and increased concentrations of carbon dioxide in the subsurface indicate that biodegradation of hydrocarbons was taking place. In general, it was observed that soil $CO_2$ concentrations were varying seasonally and were changing accordingly with the trends of gas flux rates. However, no direct correlations between gas-phase concentrations and gas flux rates were found, therefore further detailed study is required.

The $CH_4$ concentrations found in the subsurface showed trend of decreasing concentrations (to about 0%) towards the ground surface as a result of methane oxidation. It would explain low $CH_4$ concentrations measured at the surface.

Occasionally, elevated concentrations of soil $CO_2$ (up to 21%) and $CH_4$ (up to 12%) were detected. It is been hypothesised, that the high concentrations of soil $CO_2$ (21%) and $CH_4$ (12 %) found on a single occasion, may have been caused by presence of low permeability layers of bitumen in the subsurface inhibiting free flow of gas to the surface. This would explain why elevated gas concentrations were measured below these layers. High concentrations of methane at these depths in the soil may have some temporary negative impact on plant growth. Therefore, further study will be required to investigate these random anomalies.

In addition to $CO_2$, $O_2$ and $CH_4$, other trace gases were measured such as Nitrous oxide $N_2O$, Ammonia $NH_3$, Sulfur dioxide $SO_2$, Nitrogen dioxide $NO_2$, Ethylene $C_2H_4$ and Carbon disulfide $CS_2$ and were found at low (up to 1ppm) or zero concentration so determination of their flux rates were not possible. The reason for that may be: dimensions/volume of the gas flux chamber and time interval measurements. The actual dimensions and volume of the gas flux chamber together with assigned time intervals for collecting data were specifically designed for measurements of high $CO_2$ respiration rates where $CO_2$ concentrations were 3 to 4 order of magnitude higher than other trace gases.

# CHAPTER 5

# LABORATORY STUDY

## 5.1 Introduction

The laboratory component of the research involved column experiment intended to recreate some of the important conditions that occur in the field in order to evaluate PHC biodegradation and mobility under controlled conditions. The results of this column study are presented in this chapter, along with an evaluation of the implications of those results in terms of potential environmental impacts of LOS material used in reclamation and its potential effect on the quality and performance of remediation activities.

## 5.2 Characterization of PHC fraction and LOS

LOS/overburden material was collected from the Aurora Capping Study site for use in the column study. This material was characterized in terms of PHC concentrations/content. These data allowed the amount of PHC in each individual column to be determined for each of the CCME-defined PHC fractions. Additionally, grain size information and LOIs data were also collected.

### 5.2.1 PHC concentrations in LOS

A total of 60 soil samples were collected from all six columns and analyzed for PHC content by fraction according to the Reference Method for the Canada Wide Standards for Petroleum Hydrocarbons in soils (described previously in section 2.5). The results from the tests are presented in Table 5.1, regarding the amount of each PHC fraction present. Based on these data, conclusions may be reached regarding the total mass of PHC in each column and which fraction dominate the LOS material. A summary of the collected data is provided in Table 5.1 and Figures 5.1 and 5.2.

Table 5.1. Summary of HC data mean and standard deviation values for each set of columns

| PHC Fractions | | Regulatory | Columns 1-3 | | Columns 4-6 | |
|---|---|---|---|---|---|---|
| | Units | Guidelines* | Mean | STDEV# | Mean | STDEV |
| BTEX | mg/kg | N/A | non-detect | N/A | non-detect | N/A |
| F1 C6-C10 | mg/kg | 210 | 37 | 17 | 29 | 8 |
| F2 C10-C16 | mg/kg | 150 | 2894 | 767 | 1678 | 351 |
| F3 C16-C34 | mg/kg | 310 | 16328 | 5671 | 9442 | 1831 |
| F4HTGC C34-50+ | mg/kg | 2800 | 15549 | 6665 | 9288 | 2179 |
| Total F4G | mg/kg | 2800 | 53313 | 14998 | 23383 | 3696 |

*Alberta Tier 1 guidelines – Natural area land use for coarse grained soils

#STDEV - Standard Deviation

Table 5.1 summarizes the results for all samples analyzed for PHC content from two sets of columns. The Figures 5.1 and 5.2 represent the same data set as Table 5.1 but in a form of box graphs. Median and quartile, max - min values, average and outliers hydrocarbon concentration are presented as normal lines, +/- whiskers, solid black circles and open circles, respectively.

The LOS material/overburden was collected at one location at the site thus collected data, as anticipated, showed relatively the same PHC content among all columns. However, the LOS material in the field may differ slightly or significantly from location to location in terms of PHC content. This may be caused by presence of high variability LOS material placed on the site in which the bitumen content may vary between 0 and 7%.

As expected initial characterisation of LOS material found the results showed that LOS was comprised mostly of F3 (47%) and F4 (45%), high molecular hydrocarbons, which are not readily degradable (CCME 2008a). It was detected that LOS material contains significant PHC fraction with carbon numbers exceeding C50 so additional methods of PHC quantification were required.

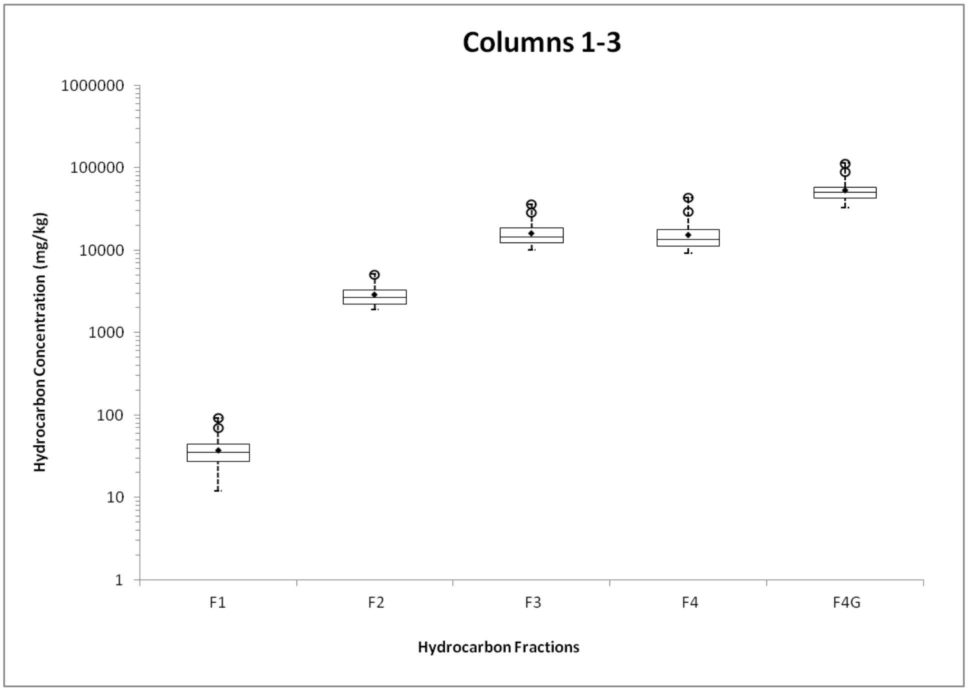


Figure 5.1. LOS PHCs by fraction for columns 1-3

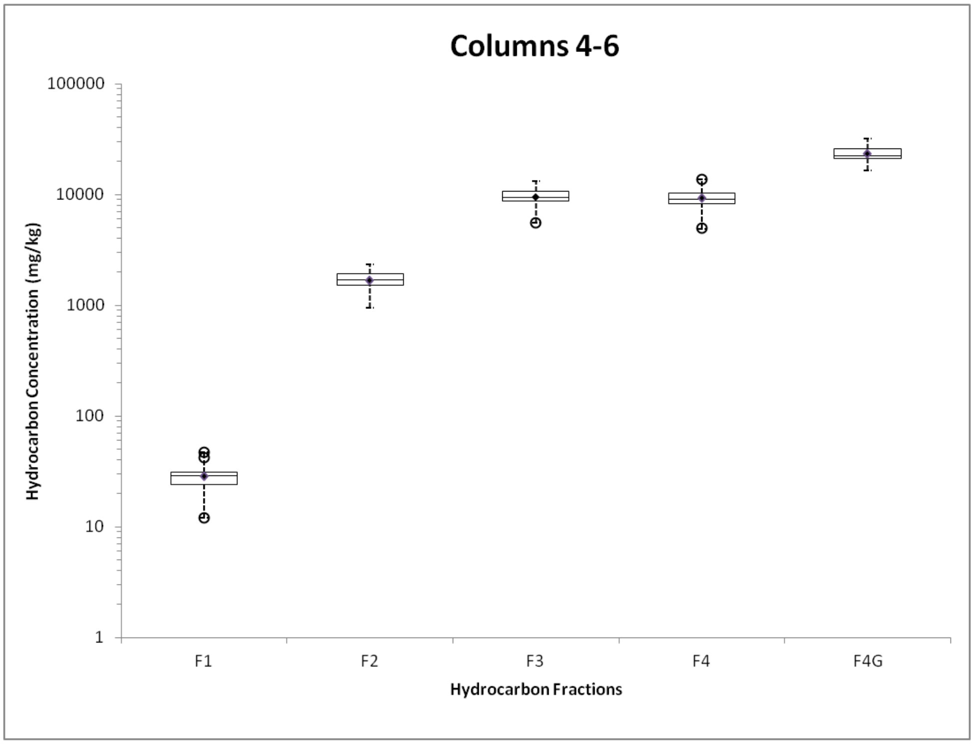


Figure 5.2. LOS PHCs by fraction for columns 4-6

High temperature chromatographic method (CCME 1993), mentioned in section 2.3, was reported as F4HTGC C34-C50+ and was used in this study. This high temperature chromatography HTGC is capable of detecting  carbon up to around C90 (Swyngedouw, 2010). Additionally, the other gravimetric method (CCME 2001b) of analysing the PHC with C>50, (also mentioned in 2.3 section) was used and reported as F4G. In this method soil sample is extracted with 50:50 hexane:acetone. The solvent is evaporated and the weight of residue determined. The results from the gravimetric method provided the PHC concentrations in a range from F2 to the heaviest molecular weights of hydrocarbons. Using this method even the heaviest hydrocarbons molecules over C100 can be detected included in a bulk assay. Based on the results of chromatographable hydrocarbons, F4 HTGC and gravimetric method (F4G) summarized in the Table 5.1, it was inferred that LOS material contains some (approximately ranging from 15 to 35%) heavier material exceeding the upper limit of the HTGC system (around C90).

The rest of the PHC fractions present in LOS contained small amounts of F1 (0.1% with no detectable BTEX) and F2 (8.3%). These lighter fractions volatilize and biodegrade easily. Among all PHC fractions only F1, representing light volatize hydrocarbons, was below the CCME clean soil guidelines. The other PHC fractions F2, F3 and F4 exceed the clean soil guidelines at least an order of magnitude. Based on the known mass of material placed in the columns and the average PHC composition of the material, an estimate can be made of the total mass of PHC in each set of columns CH1-3 and CH4-6. This estimate was 2.8 kg and 1.7 kg, respectively.

The results from chromatographable/gravimetric HC analysis (Table 5.1) showed that PHC content in columns 1-3 was higher than in columns 4-6. The standard student's t-test within 95% of confidence was performed to determine the statistical difference between two sets of PHC data. The results showed the difference between these two sets of PHC data are statistically significant. Initially, it was believed the differences in PHC content were due to presence of highly different levels of bitumen content, however upon further study, this was not consistent with the LOI data. Based on the data obtained from both tests it is hypothesized that this inconsistency may have been caused by a variation in the standard used by the commercial lab for the two sets of samples which were separated by approximately two months.

### 5.2.2 LOI

Volatile solids, or loss on ignition is used as an easy, quick and low cost method to evaluate the relative organic and carbonate content in the soils. The main purpose of this test was to quickly evaluate the LOS material placed in each column in terms of organic carbon and carbonates content. The results obtained in this test were used as a rough indicator of the weight percent of organic and carbonates content found in LOS material. The summary result are presented in Table 5.2.

Table 5.2 Summary results from LOI method for organic and carbonate content in LOS

| Organic/ Inorganic carbon | CH1-3 | | CH4-6 | |
|---|---|---|---|---|
| | AVG % | STDEV % | AVG % | STDEV % |
| Carbonates | 8.7 | 0.58 | 9.1 | 0.48 |
| Organic carbon | 7.8 | 0.59 | 8.1 | 0.49 |

### 5.2.3 Moisture content

The moisture content of the LOS material placed in the experimental columns was consistent and averaging around 11% on a wet weight basis. Summary results of averaged water contents for all columns are presented in Table 5.3. These data were used as a starting point in monitoring water regimes during the wetting period for the columns which will we discussed in detail in section 5.4 below.

Table 5.3. Summary of mean initial water contents for all columns

| Column No | Gravimetric Water Content % | STDEV % |
|---|---|---|
| CH1 | 11.0 | 1.2 |
| CH2 | 10.9 | 0.8 |
| CH3 | 10.9 | 0.5 |
| CH4 | 11.3 | 1.4 |
| CH5 | 10.8 | 0.7 |
| CH6 | 11 | 0.6 |
| CH1-6 | 10.9 | 0.9 |

### 5.2.4 Grain size distributions

Grain size analyses were performed on total 12 samples (two from each column) in order to determine the particle size distribution among the columns. The particle size distributions are shown in Figure 5.3. This is evident that this material may be classified as SM (silty sand)

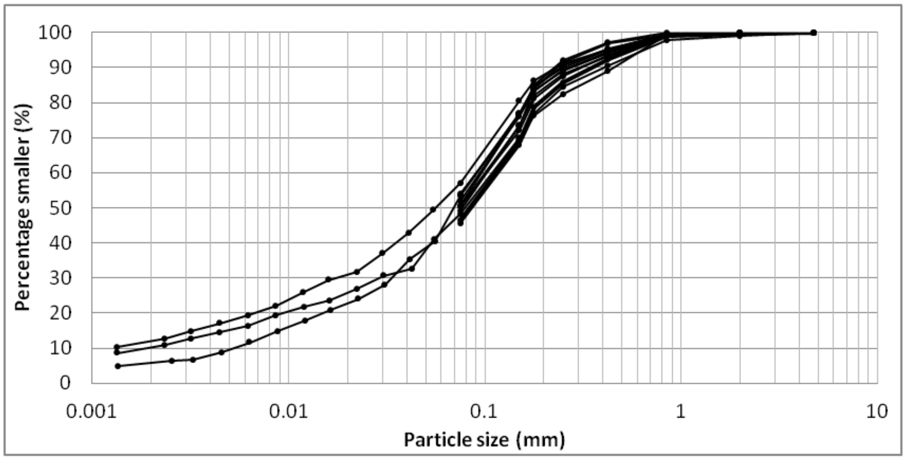


Figure 5.3. Particle size distribution curves for all columns

according to USCS.

On average, LOS contained approximately up to 10% of clay, 35% of silt and 55% of sand. This values were relatively consistent within all 6 columns however in a field scenario the ratio between sand and fines may vary due to high variability of dumping material.

### 5.2.5 Summary

In this section the characterization of the LOS material was summarized. The LOS/overburden material collected from ASCS and used in the column study generally exceeded clean soil guidelines by a factor of 10 to 20 and showed consistency in terms of PHC content, water content, organic and carbonates contents, and sand to fines ratio among all columns.

LOS was predominantly composed of F3 (47%) and F4 (45%) hydrocarbon fractions (i.e. very heavy molecular hydrocarbons that are not readily degradable). The remaining PHC fractions present in the LOS contained small amounts of volatile and easy degraded F1 (0.1% excluding undetectable BTEX) and F2 (8.3%). Only the F1 fraction was below the clean soil guidelines limit of 210mg/L.

Similar to the study conducted by Visser (2008b) in which she assessed the impact of fresh and weathered LOS material incorporated into reclamation material, it was inferred that weathered LOS material which is composed predominantly of heavier molecular hydrocarbons, should have a minimal impact on capping study reclamation activities.

## 5.3 PHC biodegradation potential

### 5.3.1 Introduction

In this section, the results of the column study are presented. These results have shed light regarding the biodegrability of the LOS material. In this study, oxygen consumption and carbon dioxide and methane production were continuously monitored in the headspace of each column over period of several months as a indicator of the rate of microbial activity. The LOS material used in column study was compacted to the densities 1.5 to 1.7 T/m$^3$, the same as the range of densities measured in the field. Respiration rates were monitored in the lab at various temperatures which varied over time between 2$^{\circ}$C and 22$^{\circ}$C, in order to assess the sensitivity of the biodegradation rate of the LOS to seasonal temperature variations reflecting the field conditions.

The columns tests were carried out under unsaturated conditions. Daily, 90 ml of DDI (demineralized) water was added to the system repeating the annual precipitation of 460mm at Fort McMurray. At the bottom of the columns the leachate was collected and the vertical distribution of the water content was periodically measured using a Sentek EnviroScan probe (Sentek technologies), described earlier in section 3.3.5.

### 5.3.2 Biodegradation potential monitoring

Six columns were set up for the experiment to monitor the biodegradation potential of LOS material. To ensure accuracy and repeatability of collected data, two individual tests were conducted in triplicate. Three columns were set up at room temperature with average temperature 22°C and three columns were set up in a climate chamber where temperatures varied over time between 2°C and 14°C. Details of the column set up are described in section 3.3.2 and Table.3.1 and are shown in Photos 5.1 and 5.2.

Photo 5.1. Column study set up (Geoenvironmental lab, U of S)

The first column CH1 (room temp) was set up at the end of March 2012 and was run as a trial for learning purposes in order to get familiar with respirometer system and to ensure everything was working properly. During the commissioning period, leaks were repaired and the respirometry monitoring system had to be restarted on a few occasions. Once this initial trial period was complete two additional columns were set up and connected approximately 1 month after the initial start of the experiment.

Over the next two months, three additional columns were set up in a climate chamber (initially at 5°C) and connected to the system. All of the dates and other detailed information of the columns CH1-6 set up are shown in Table 3.1. Each time an additional column was connected the respirometer system had to be restarted - the resulting time lags were relatively short and the datalogged respiration data were subsequently corrected in this regard. Unfortunately, on September 18, 2012 the $CO_2$ sensor broke down and required repair by manufacturer (Columbus Instruments'). Accordingly, $CO_2$ data were not collected for 24 days, however, the experiment continued running as usual, with water supply and refreshment rates, etc. Thus for this period, the cumulative data of $CO_2$, $O_2$ and $CH_4$ were extrapolated using a number of values from the previous data set.

Photo 5.2. Columns set up in room temp (left) and climate chamber (right)

The representation of test results vary thus cumulative approach is more useful for biodegradation type experiments like in the case of column study, where the total amount of $CO_2$ produced maybe detected over time. The cumulative data represent the total amount of gas expressed in (ml at STP) or (mg) that has been produced or consumed since the beginning of the experiment. This includes any $CO_2$ produced or $O_2$ consumed during a refresh which was already mentioned in section 3.3.2.

Figures 5.4 and 5.5 show the summary of total cumulative $CO_2$ production and $O_2$ consumption measured for all chambers during the course of this study. The results illustrate how temperature had an effect on production and consumption of gases in the experiment. As shown in Figures 5.4 and 5.5, the column tests at room temperature were carried out for 196 days. The columns in the climate chamber on the other hand, ran continuously for 166 days. The total cumulative averaged $CO_2$ production and $O_2$ consumption for room temperature columns over the period of 196 days were approximately 45L and 86L, respectively. The total cumulative averaged $CO_2$ production and $O_2$ consumption for the columns exposed to various temperatures over certain amount of time but averaging 6°C over the period of 166 days were approximately 8.8L and 21.6L, respectively. In result, the total cumulative volume at STP of $O_2$ consumed and $CO_2$ produced resulting from microbial activity over the time of the experiment was converted into grams and used to estimate the amount of PHC degradation. The PHC degradation was estimated using the stoichiometric simplified relationship ($C_{16}H_{34}+24.5O_2=17H_2O+16CO_2$) proposed by Zytner (2001) for complete biodegradation of diesel fuel. Using this, the rates of PHC degradation were estimated using either the amount of oxygen consumed or carbon dioxide produced, which ideally should yield independent but relatively similar estimates assuming that all the observed gas flux was associated with microbial degradation of PHC.

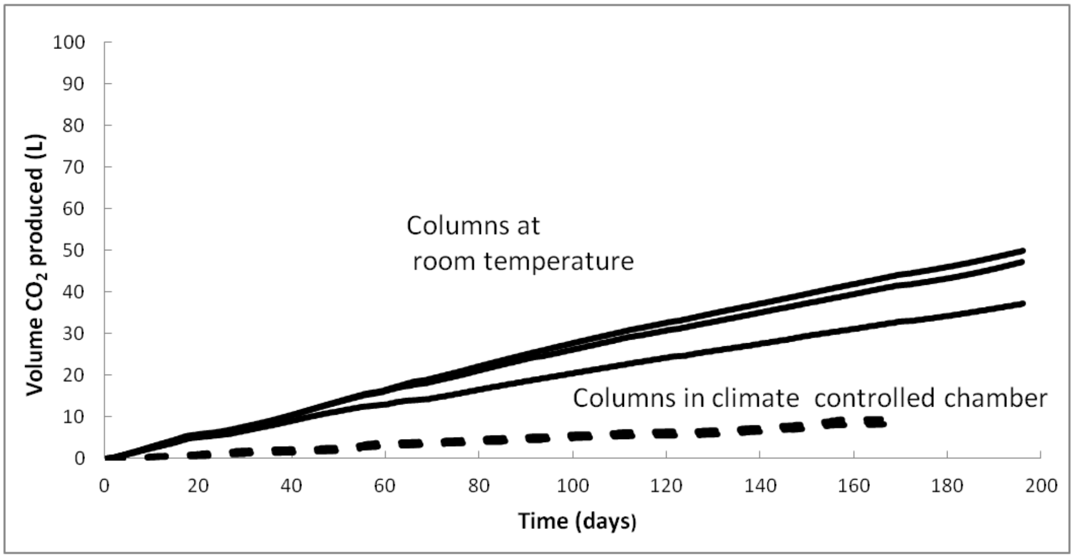


Figure 5.4. Total cumulative $CO_2$ production measured by respiration

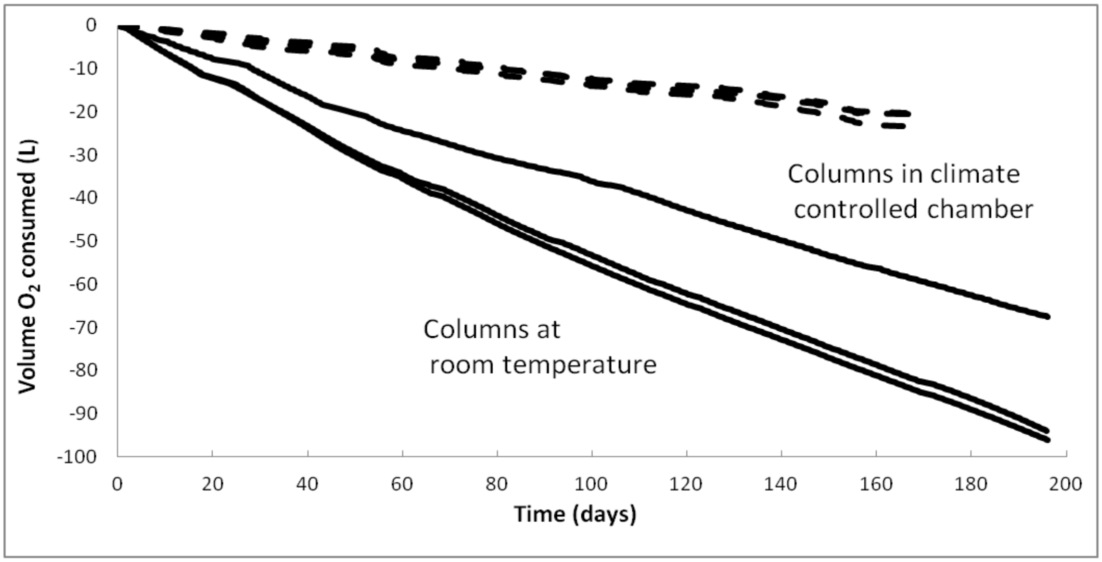


Figure 5.5. Total cumulative $O_2$ consumption measured by respiration

As shown in Figures 5.4 and 5.5 the ratios of cumulative $O_2/CO_2$ were different and did not match the expected stoichiometric ratios from the Zytner's (2001). The PHC degradation rates were estimated from $CO_2$ production and $O_2$ consumption data. The results, which are presented in Table 5.4 show that the degradation of PHC calculated from $CO_2$ production data was on average 28g and 6g for columns 1-3 and columns 4-6, respectively. However, the degradation of PHC calculated from $O_2$ consumption data was on average 36g for columns 1-3 and 9g for columns 4-6. Since the results of hydrocarbon degradation rates from these independent estimates vary, an average rate was taken as a final which is 32g and 7g of PHC degraded for columns 1-3 and 4-6, respectively. The difference in the calculated PHC degradation rates may have resulted from several factors such as either there was a significant sink for $O_2$ that was not accounted for or not all of the $CO_2$ was accounted for all the $CO_2$ produced. The excessive oxygen consumption that was observed relative to carbon dioxide production, indicates that in the columns, other processes were taking place.

The processes that would consume oxygen (oxygen sink) might include oxidation of reduced species into LOS/overburden material, production of biomass, incorporation of oxygen into organic acids etc. Given the very low metabolic rate inferred by the gas monitoring, accumulation of biomass is not expected to represent a significant oxygen sink. A limited amount of additional tests conducted on leachate samples from the bottom of the columns revealed the presence of significant amounts of naphthenic acids (averaging 150 mg/L). Unfortunately, due to high variability and complexity of these organic acids it was not possible to reliably quantify this potential oxygen sink, although it is evident that naphthenic acid accounts for at least some of the excess of the oxygen consumption.

In the case of carbon dioxide, it is assumed that respiration rates are primarily due to microbial activity, however some of the $CO_2$, so produced was dissolved in the infiltrating water. Weekly analysis for TC and TOC in leachate (discussed in section 5.4.2.1) confirmed that significant amount of $CO_2$ was dissolved in water. This corresponded to approximately 20 mg of $CO_2$ per day which is about 5% of the rate inferred by the gas phase respirometry measurements.

Monitoring of TIC (Total Inorganic Carbon) along with the amount of water supplied to and withdrawn from the system through the course of the experiment allowed for estimation of the total amount of $CO_2$ dissolved in water. The total $CO_2$ produced ($CO_2$ measured through respiration and $CO_2$ dissolved in water) was estimated and the results were compared with the theoretical $CO_2$ produced calculated from known $O_2$ consumption based on the Zytner's equation. The results of these calculations are presented in Table 5.4. The total $CO_2$ produced calculated from known $O_2$ consumption was in a range of 80-85% of the theoretical $CO_2$ produced. This confirms the presence of a significant sink of oxygen in the system. Based on the collected data it was concluded that the hydrocarbon degradation rates calculated directly from estimated total $CO_2$ ($CO_2$ collected through respiration and dissolved in water) may provide a more reliable estimate.

It was assumed that all dissolved $CO_2$ comes only from TIC found in water and $CaCO_3$ content is unknown. The calculations for $CO_2$ dissolved in water were based on the following:

- regular monitoring of the volume of leachate removed from the system;
- measured values of TIC;
- concentration of TIC was converted to a mass of total dissolved $CO_2$ by using the relationship $C+O_2=CO_2$; and
- $CO_2(g)+H_2O= CO_2(l)$ and then it forms carbonic acid $H_2CO_3$

Table 5.4. Summary of CO2 and O2 respiration results

| Columns ID | units | CH1 | CH2 | CH3 | CH4 | CH5 | CH6 |
|---|---|---|---|---|---|---|---|
| AVG O2 consumed | g/day | 0.53 | 0.70 | 0.69 | 0.20 | 0.17 | 0.17 |
| AVG CO2 produced | g/day | 0.37 | 0.49 | 0.47 | 0.12 | 0.10 | 0.10 |
| AVG CO2 removed in leachate | g/day | 0.02 | 0.03 | 0.02 | 0.02 | 0.01 | 0.01 |
| AVG CO2 dissolved in remaining water in column | g/day | 0.02 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 |
| Total CO2 | g/day | 0.41 | 0.54 | 0.51 | 0.15 | 0.13 | 0.13 |
| Theoretical CO2 production from known O2 consumption based on Zytner's equation | g/day | 0.46 | 0.63 | 0.62 | 0.18 | 0.16 | 0.16 |
| Known CO2/day as (%) of the theoretical | % | 89 | 85 | 82 | 83 | 79 | 79 |
| Total CO2 measured by respiration | g | 73 | 96 | 92 | 20 | 17 | 17 |
| Total O2 measured by respiration | g | 104 | 137 | 135 | 33 | 28 | 28 |
| Degradation of PHC based on known O2 consumption | g | 30 | 40 | 39 | 10 | 8 | 8 |
| Degradation of PHC based on know CO2 production | g | 23 | 31 | 30 | 6 | 5 | 5 |
| AVG degradation of PHC based on known CO2 production CH1-3 | g | | 28 | | | | |
| AVG degradation of PHC based on known CO2 production CH4-6 | g | | | | | 6 | |
| AVG degradation of PHC based on known O2 consumption CH1-3 | g | | 36 | | | | |
| AVG degradation of PHC based on known O2 consumption CH4-6 | g | | | | | 9 | |
| AVG degradation of PHC based on known AVG of O2 and CO2 CH1-3 | g | | 32 | | | | |
| AVG degradation of PHC based on known AVG of O2 and CO2 CH4-6 | g | | | | | 7 | |

Measured pH of leachate water was at 6.8. At this pH, $H_2CO_3$ dissociates to bicarbonate HCO3- ion only; therefore, $CO_2$ dissolved in the leachate is present mostly as bicarbonates and free $CO_2$ (as equivalent of $H_2CO_3$). So calculated values of dissolved $CO_2$ in water together with $CO_2$ cumulative respiration rates data provided a new approach in estimation of total $CO_2$ released due to microbial respiration which allowed to estimate the PHC degradation according to Zytner's formula. The results obtained from this approach were compared with the data from average PHC degradation rates calculated from known $O_2$ and $CO_2$ data.

For columns CH1-3 running at room temperature (22C) for 196 days, the total averaged amount of $CO_2$ produced through microbial activity (including $CO_2$ dissolved in water) was approximately 100 grams which was an equivalent of 32 grams of degraded PHC. For columns CH4-6 running at various but generally lower temperatures averaging 6°C over 166 days, the total averaged amount of $CO_2$ produced through microbial activity (including dissolved $CO_2$) was 22 grams which was an equivalent of 7 grams of degraded PHC. It is interesting that the results of PHC degradation rates calculated from total $CO_2$ produced (including dissolved $CO_2$) and calculated from known averages $O_2$ and $CO_2$ data are consistent.

Cumulative methane production was also measured for all sets of columns are presented in Figure 5.8. The total amount of $CH_4$ produced in room temp (196 days) and cool temps (166 days) was approximately 0.03g and 0.007g, respectively, confirming that aerobic conditions prevailed in most of the columns.

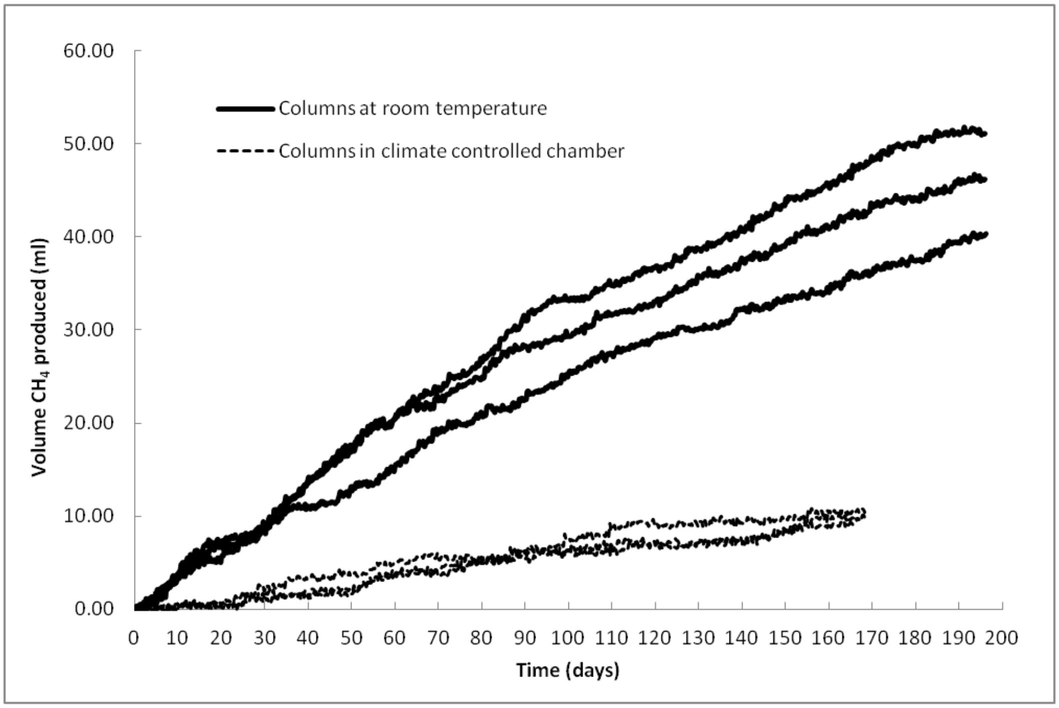


Figure 5.6. Cumulative $CH_4$ production for columns CH1-6

### 5.3.3 Volatile hydrocarbons

The LOS material used in the experiment contained a significant amount of PHCs and their volatiles. Accordingly, an activated charcoal trap (Orbo 302 charcoal sorbent tube) was used to collect volatiles and prevent the Micro-Oxymax gas sensors from being damaged (Columbus, Microoxymax user's manual). At the end of the study, one such charcoal tube that had collected the volatilized gases for 5 months was eluted for analysis of volatile PHC. The results of the analysis are shown in Table 5.5. Results indicated the presence of hydrocarbons on the downstream module of the two-module trap, suggesting that the tube may have been overloaded; accordingly the mass of the hydrocarbons reported in Table 5.5 underestimate by unknown margin the true mass volatilized. The relative mass of volatilized PHC of the various fractions may provide some insight into the sort of PHC's that may partition to the gas phase under field conditions. The total amount of volatilized PHC collected in the tube was 131 mg, of which 123 mg was within lighter part of the F2 fraction (up to C20) reflecting the limitation of the GC instrument used which could quantify up to C20 so the F3 fraction content only represents PHC in a range from C16 to C20.

Table 5.5. BTEX and other PHC in the air (CH2)

| **Analyte** | **Mass volatiles mg/tube** |
|---|---|
| **BTEX** | 0.093 |
| **F0 (C4-C6)** | 0.025 |
| **F1 (C6-C10)** | 5.8 |
| **F2 (C10-C16)** | 122.8 |
| **F3 (C16-C34)** | 2.4 |
| **Sum** | 131.2 |

### 5.3.4 CO2 gas flux rates

Based on the cumulative slopes of $CO_2$ production, the long term gas fluxes for each column were estimated and plotted versus temperature in Figure 5.7. Figure 5.7 also contains averaged cumulative slopes superimposed on the chart and associated with them various temperatures and estimated gas fluxes. The highest gas flux measurement found on this plot represents a time of thermostat breakdown in the climate chamber where temperature increased to 23 $^{o}$C within 24h. Initially, the thermostat in the climate chamber failed to keep low temperatures and was oscillating between 14-20 $^{o}$C. After next 1.5 days it totally broke down and temperature jumped up to 22-23 degrees within following hours. It was decided to take average temperature during climate chamber breakdown which was approximately 21$^{o}$C. Thermostat was broken down for approximately 3 days.

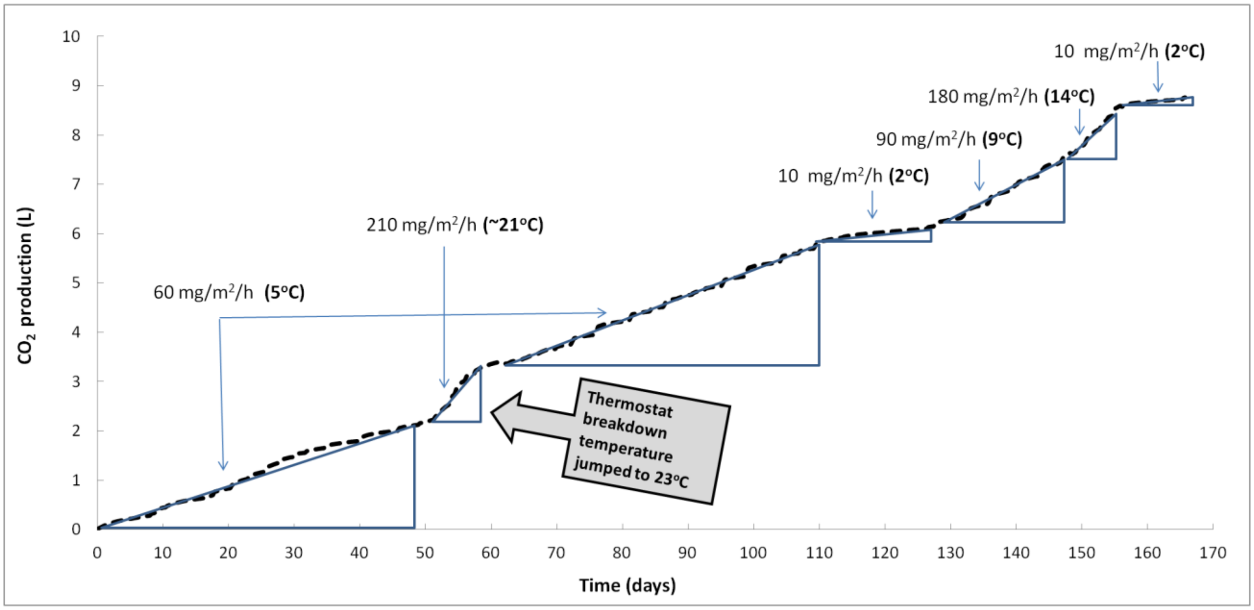


Figure 5.7. Averaged cumulative CO2 production from 3 columns at various temperatures with averaged cumulative slopes superimposed on chart

Each $CO_2$ gas flux was estimated based on calculation using best fitted regression lines applied to cumulative slopes of $CO_2$ production at various temperatures. The outcome of this estimates are illustrated in Figure 5.8 which also show the linear relationship between $CO_2$ gas fluxes and temperatures.

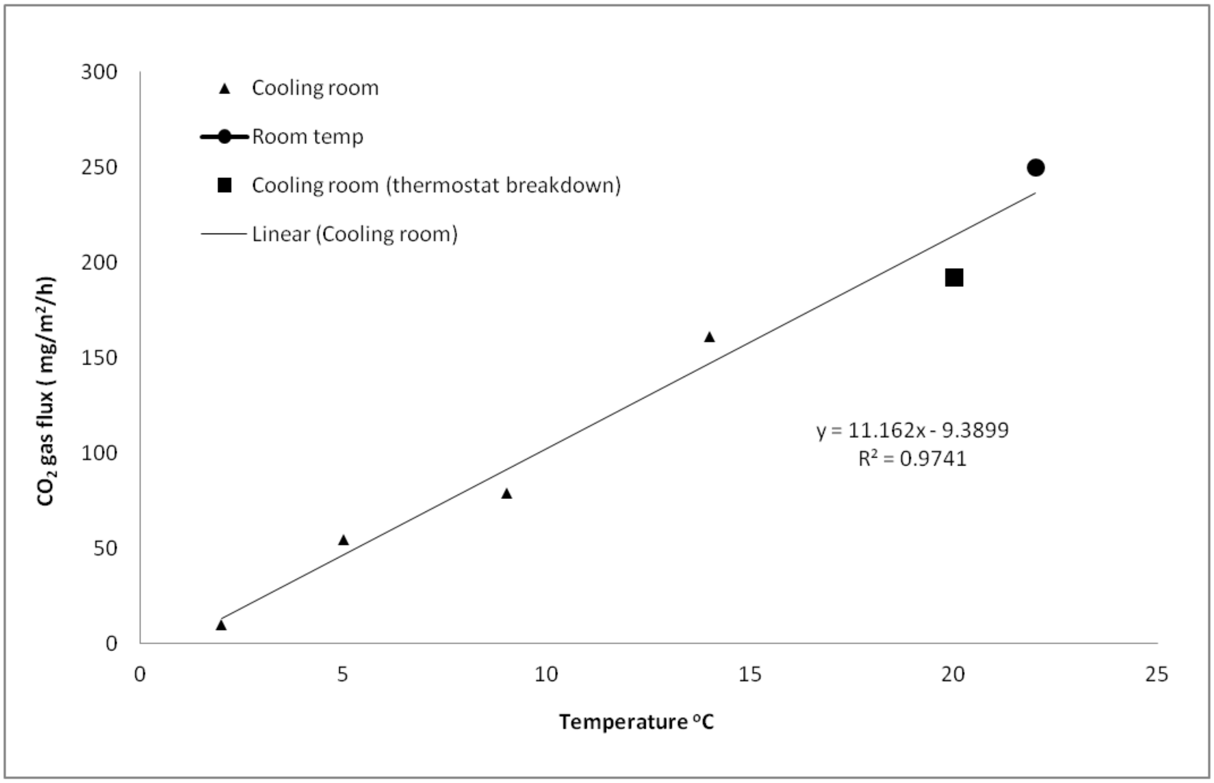


Figure 5.8. Gas flux rates versus temperature for all columns

Another way of presenting gas flux rates was to express it as averaged incremental $CO_2$ volume produced over time dV/dt (ml/d) versus cumulative time (d). For the clarity of presented data best results were achieved by eliminating some of the outliers and presenting data as 2 day average incremental dV/dt. The results of the flux rates expressed as ml/d were provided for most representative samples CH2 (room temp) and CH4 (cool temps) and are presented in Figures 5.9 and 5.10. The results presented in Figure 5.9 were measured in relatively constant temperature at around 22 $^{o}$C and illustrated a decreasing trend of gas flux rate over time. Just to note that at the beginning of the experiment the system was flushed with oxygen for the experimental reasons which altered the flux rate. At the very end of the experiment it was observed the gas flux rates jumped within all columns at room temp. It was concluded that it was due to water supply shut down that took place at 180th day of the experiment.

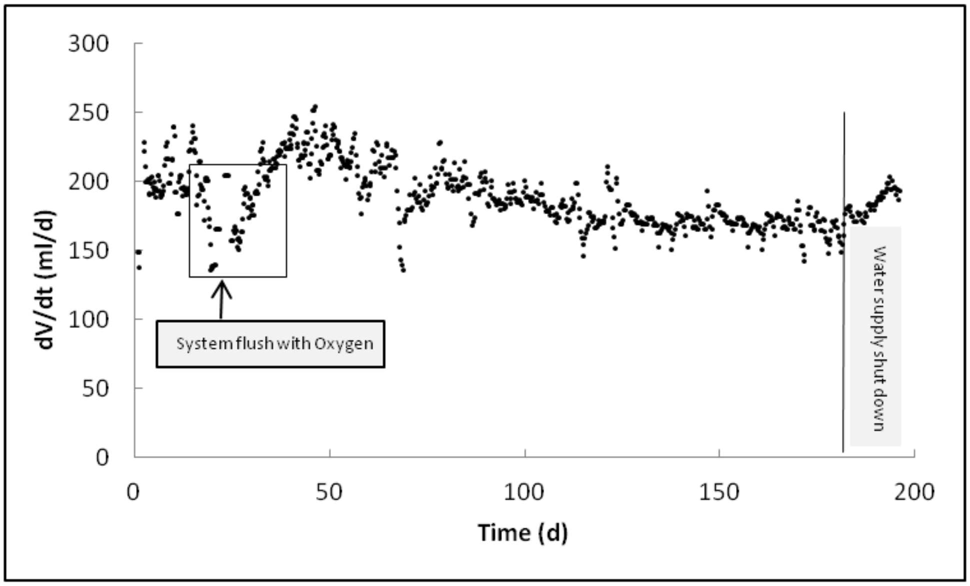


Figure 5.9. Two day averaged incremental dV/dt vs cumulative time for CH2

The results presented in Figure 5.10 were measured in temperatures that varied over time between 2 and 14 $^{o}$C. This plot can be correlated with Figure 5.7 to illustrate variability of gas flux rates versus temperature. The highest rate on the plot in Fig. 5.10 represent the thermostat breakdown in climate chamber which is associated with temperature increase.

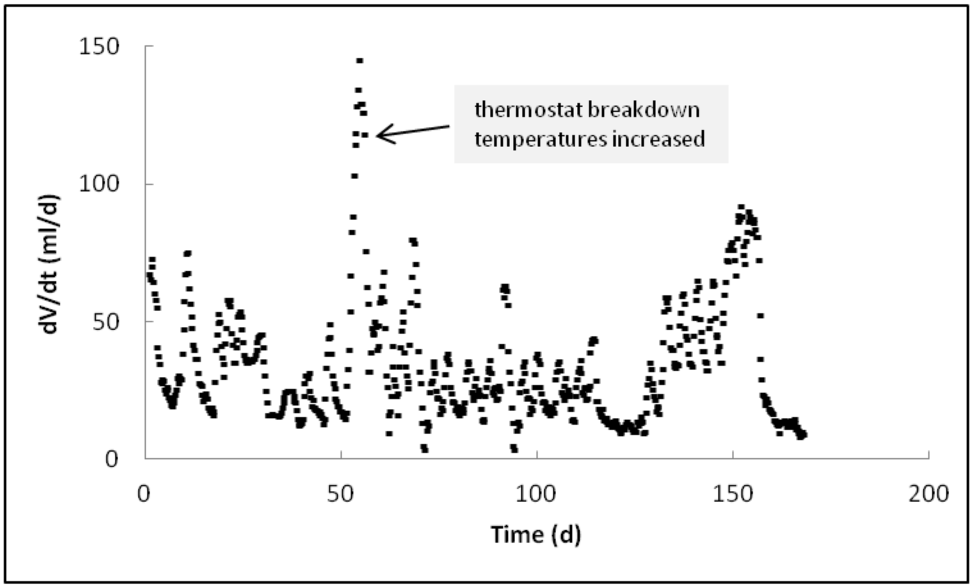


Figure 5.10. Two day averaged incremental dV/dt vs cumulative time for CH4

### 5.3.5 Summary

In this section LOS material was characterized in details in terms of PHC biodegradation potential. The respiration rates of $CO_2$ and cumulative consumption of $O_2$ and production of $CO_2$ were monitored for the period of several months during which the LOS material was exposed to various temperatures which varied over time between 2 and 22°C.

Based on soil respiration, biodegradation is apparently dependant on temperature. The total estimated PHC degradation from respiration was 60g/year at 22°C and 15g/year at temperatures from 2 to 14°C. However, these amounts constitute only a small portion of the approximately 2.8kg of hydrocarbons present in each column. Thus, the results indicate that the degradation of hydrocarbons from LOS material is occurring at relatively slow rates. PHC volatilization at rates of 0.3g/yr was observed to be two orders of magnitude less than that of PHC degradation.

Controlling temperature during the experiments allowed the effects of temperature on hydrocarbon degradation and CO2 production to be investigated. Temperature dependence became evident during climate chamber failure when the temperature in the climate chamber abruptly increased from 5 to 23°C within 24h and resulted in a spike in gas flux rates. The estimated $CO_2$ flux rates showed a linear relationship between $CO_2$ gas fluxes and temperatures. Interestingly, the gas flux results obtained under controlled steady lab conditions ranged from 10 to 260 mg/m$^2$/h were comparable with the gas flux rates obtained in the field ranged from 13 to 263 mg/m$^2$/h.

## 5.4 PHC mobility as leaching potential

### 5.4.1 Introduction

In this section a potential risk/impact of LOS material used in reclamation will be assessed in terms of PHC mobility as leaching potential to ground water and its potential effect on quality and performance of remediation processes. Additionally, the column moisture regime will be evaluated.

### 5.4.2 LOS leaching potential

Addition of DDI (demineralized) water to each column on a daily basis in amount of approximately 90 ml/day resulted in production of leachate over time. Leachate was collected from reservoir at the bottom of each column on a weekly basis and analysed for TC (total carbon) and TOC (total organic carbon). Additionally, every three weeks a small sample of leachate was collected and analysed for chromatographable hydrocarbons such as BTEX, F1, F2 and F3.

#### 5.4.2.1 Leachate Total Carbon and Total Organic Carbon

Main purpose of this test was to estimate mobility and quantity of organic/inorganic material in the leachate. The leachate analyses were performed on a weekly basis through the course of the study. The summary of results collected in this study for room temperature columns (1-3) and cooling room columns (4-6) are plotted in Figures 5.11 and 5.12.

The results of TC/TOC concentrations show a general typical decreasing trend over time. The organic carbon concentrations measured in the leachate analysis were several orders of magnitude higher than the reported concentration of chromatographable hydrocarbons. However, there is no direct regulations on TC/TOC in natural ground water in Alberta.

Based on the leachate data it was concluded that some other organic compounds may be present in the leachate at increased concentrations. Accordingly, additional leachate analyses were conducted at Environment Canada for presence of Naphthenic acids and other acid-extractables. The ratio of TC/TOC between two sets of columns were relatively similar. It should be noted, TC/TOC concentrations at the field scale would have less significant effect due to lower infiltration rate which is only 10% of the annual precipitation for Fort McMurray region.

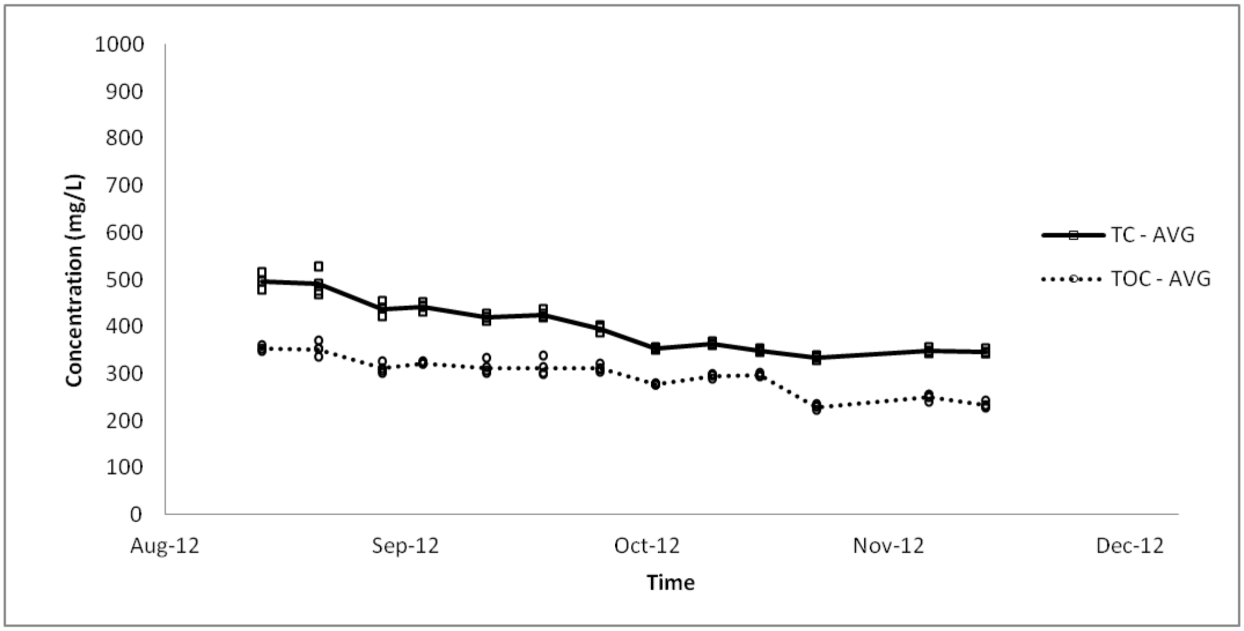


Figure 5.11. TC and TOC concentrations in the leachate (Columns 1-3)

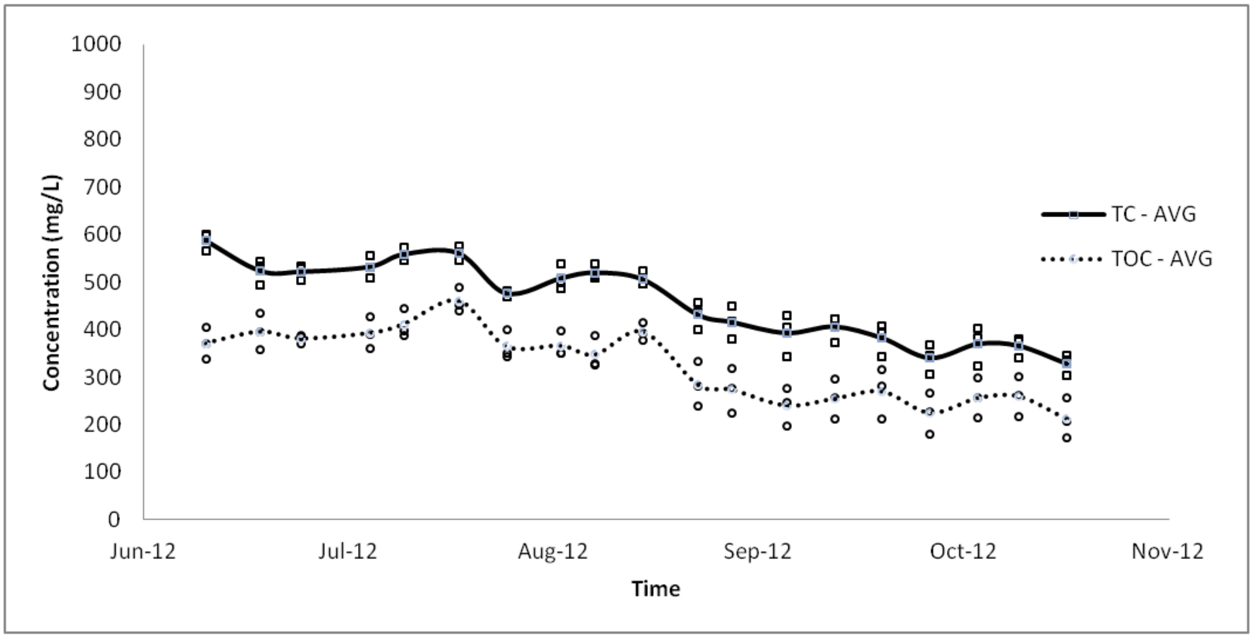


Figure 5.12. TC and TOC concentrations in the leachate (Columns 4-6)

#### 5.4.2.2 Leachate Hydrocarbons

In this section, hydrocarbon leaching potential will be discussed. On a regular basis, approximately every 3 weeks, the leachate was monitored for chromatographable PHC fractions such as BTEX, F1, F2 and F3. Additionally, on one occasion, at the end of the experiment, the leachate water sample was also checked for heavy gravimetric PHC called "oil and grease". The water analyses for chromatographable PHCs measured a small amount of F2 and F3 fractions in the leachate, but did not detect F1 or BTEX fractions. The results of F2 and F3 fractions content for each set of columns are presented in Figures 5.13 and 5.14. At the beginning of the experiment, the concentration of F2 at room temperature exceeded the 1.1mg/L clean water guidelines on several occasions. The F3 fraction due to its low solubility in water it is not regulated for water quality. Similarly to TC/TOC results the chromatographable hydrocarbons show general typical tendency of decreasing concentration over time. Concentrations of chromatographable hydrocarbons for the columns at room temperature (columns 1 to 3) decreased over time as expected. Concentrations of chromatographable hydrocarbons for the columns in the climate chamber (columns 4 to 6) were low at detectable limits and spiked at the end of the experiment due to the temperature in climate chamber increasing from 5°C to 9°C (Figure 5.14), which implies that PHC mobility is temperature dependent.

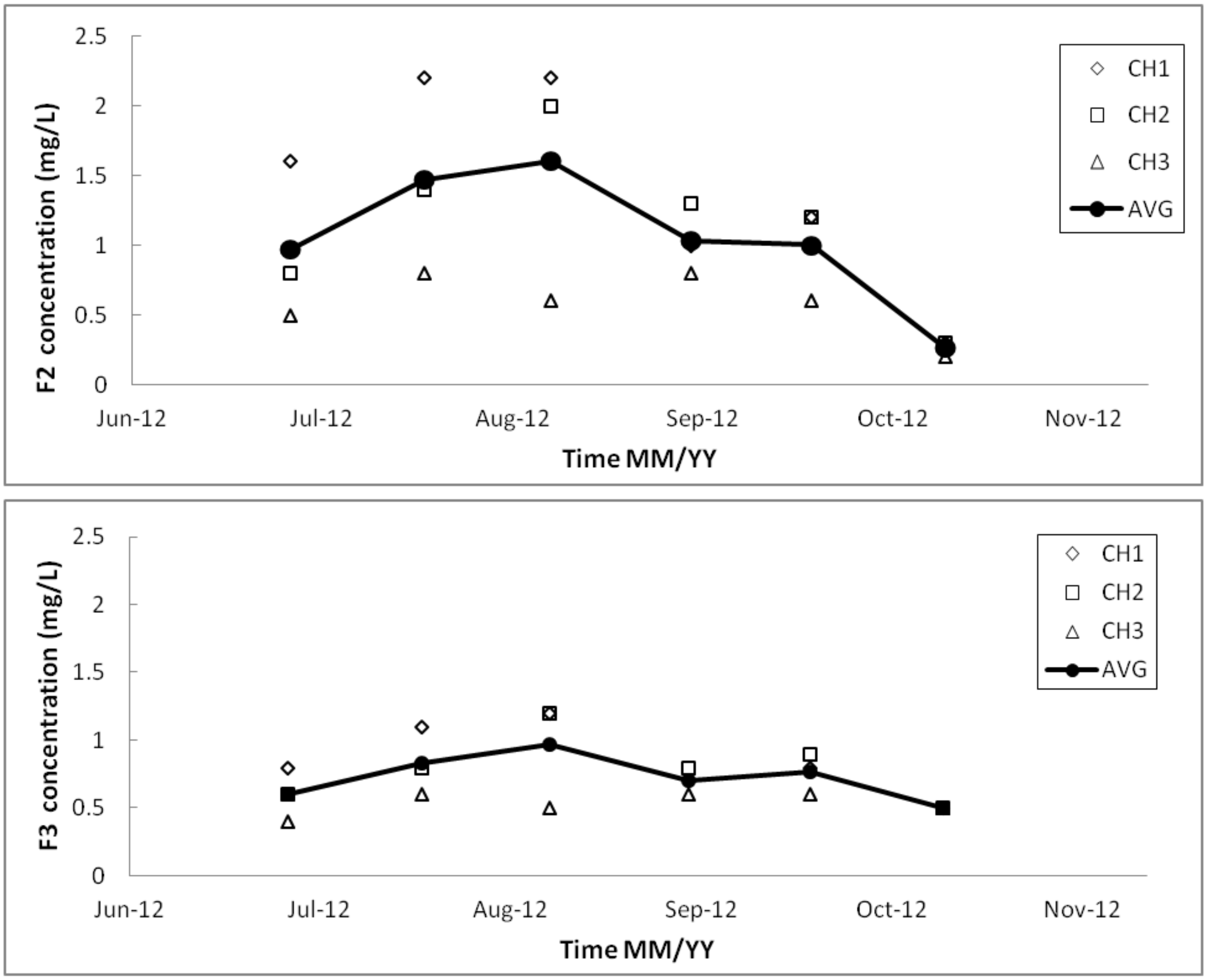
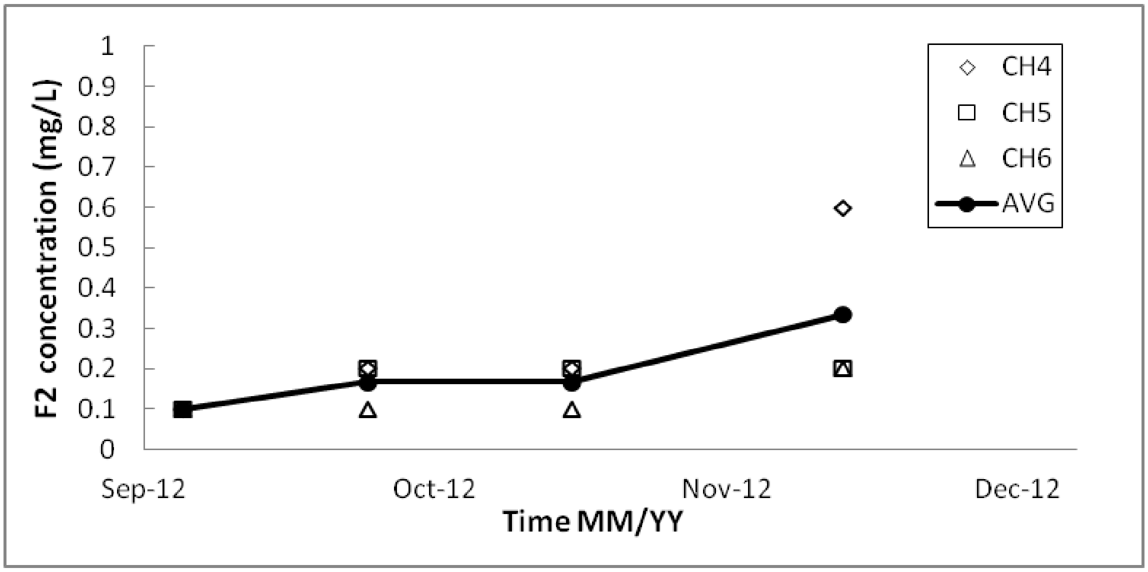


Figure 5.13. F2 and F3 Hydrocarbon concentrations in the leachate (Columns 1-3)



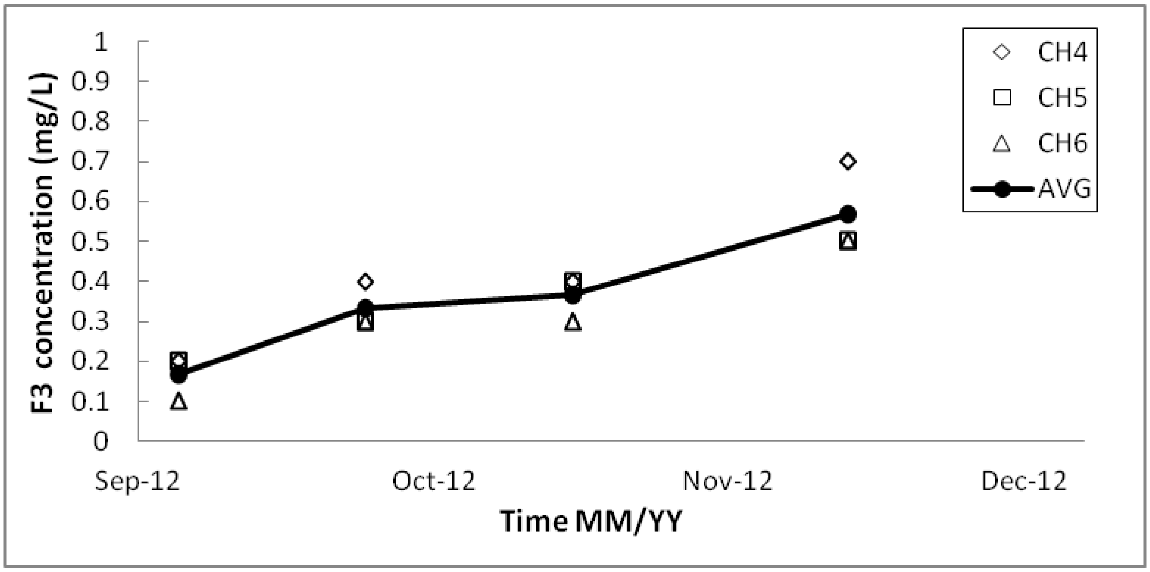


Figure 5.14. F2, F3 Hydrocarbon concentrations in the leachate (Columns 4-6)

Additionally, a water sample was analyzed for "oil and grease" at the end of the experiment using the partition-gravimetric standard method for water/environmental protection agency (APHA/USEPA). This gravimetric method weighs all organic material (not just hydrocarbons). The results from oil and grease tests revealed the presence of some BTEX and light diesel (most abundant at ~C20). There were also some indications of heavier materials not detected by the chromatograph. The total average concentrations of oil and grease in the leachate was 49 mg/L.

#### 5.4.2.3 Leaching of organic acids

As it was briefly mentioned in section 5.3.2., based on the leachate collection data of TC/TOC it was concluded that some other organic compounds may be present in the leachate at increased concentrations. Therefore, additional leachate analyses were conducted on selected samples at Environment Canada for presence of organic acids and other acid-extractables.

The results from these tests revealed a presence of significant amount of organic acids and other acid-extractables averaging approximately 150 mg/L. In cooperation with EC staff a quantification of organic carbon as well as oxygen within was attempted. However, due to high variability and complexity of detected organic acids estimation of approximate values for oxygen content as well as for organic carbon were not successful. The results from these test however allowed to account for at least some of the excess of oxygen consumption mentioned earlier.

### 5.4.3 Moisture regime

The volumetric water content within each column was measured on a regular basis (initially once per week) by Sentek EnviroScan probe described in more details in section 3.3.5. The continuous monitoring of changes in moisture content within columns over time (especially at the initial period of soil wetting) allowed for establishing the flow regimes as well as the water retention spots within the LOS material.

The readings were taken every 10 cm along the soil column using EnviroScan moisture probe and specially made glass access tube in each individual column (described in section 3.3). Water was supplied three time daily in a total amount of approximately 90ml as a equivalent of annual precipitation for Fort McMurray area. Water was released at 3 to 6 discrete points on the soil surface by specially fabricated rings.

It was hoped that water will be released from all of the discrete points made on the rings in order to be distributed evenly over the soil cross section. In result, some of the holes were not working as previously tested resulting in probably uneven distribution of water across the soil. The Results from water moisture distribution are presented in Figure 5.15. The bold black lines on the plots represent initial conditions before water was applied to the system. These initial readings of moisture content at the beginning of this study are very consistent with the results for water content obtained from soil samples presented in Table 5.2. During the wetting period, water found its way to seep through the soil column and as it was observed on plots in Figure 5.15, some areas within LOS column profile seemed to be wetter. The elevated water content spots may be caused by characteristic properties of LOS material that is capable of retaining water or due to PHC content that may create a low permeability layer of bitumen where water is collected (similar to perched water table found in the field). Maximum water content detected within columns, usually at the bottom part of the columns, was approximately 25%.

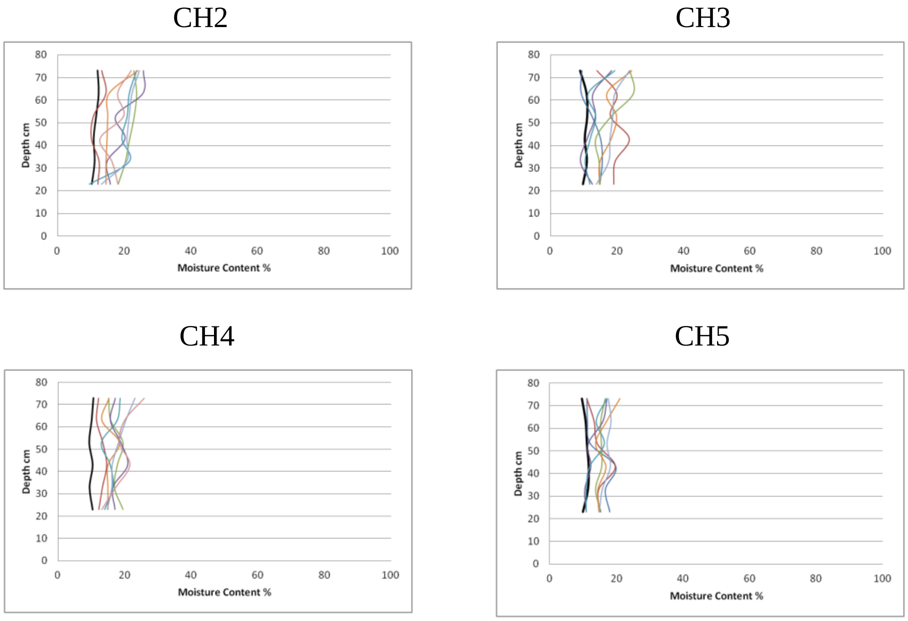


Figure 5.15. Examples of water moisture distribution among 4 columns

### 5.4.3 Summary

In this section the PHC mobility as leaching potential of LOS material was evaluated. The results from the PHC mobility study suggest that the LOS material will have low environmental impacts to surface or groundwater quality. The F1 fraction (including BTEX) was not detected in the column leachate. The F2 fraction slightly exceeded clean water guidelines on a few occasions at temperatures ≥22 °C (which does not reflect average field conditions). Overall, however, the concentrations of F2 hydrocarbons remained below clean water guidelines and decreased over time. Furthermore, at low temperatures (≤4°C), the concentration of F2 hydrocarbons was close to the 0.1mg/L detection limit. The F3 hydrocarbons were present at concentrations below F2 regulatory limits and are not regulated for groundwater.

The results from the leachate analysis showed that organic carbon concentrations were several orders of magnitude higher than the reported concentrations of chromatographable hydrocarbons, which indicates the presence of other organic compounds. Additional tests conducted on leachate water revealed the presence of 49mg/L concentrations of oil and grease and 150mg/L of organic compounds known as Naphthenic Acid Fraction Component (NAFC) and other acid extractables. Organic acids found in the leachate were complex and detailed quantification of separate compounds were not possible. However, further detailed investigation and interpretation of data in regards to oil and grease and NAFC is recommended to evaluate the potential impact to the environment and on reclamation activities.

It should be noted that water was supplied to the columns in a rate of 460 mm/year which was equivalent of annual precipitation rates for Fort McMurray area. However, these rates used in the experiment do not represent the infiltration rates that would be expected in the field. Alberta Environment assumes infiltration rates of 10% of average annual precipitation in Alberta in developing contaminated soil guidelines (Alberta Environment 2007). Working with more realistic infiltration rates (around 10 time smaller) in the columns study would extend the experimental project by years.

# CHAPTER 6

## CONCLUSIONS AND RECOMMENDATIONS

### 6.1 Overview

The purpose of this study was to describe the effects of in situ processes on the reclamation research being conducted at the Aurora Fort Hills disposal area in terms of:

a) characterization of hydrocarbon composition in LOS material

b) determination of the effect of temperature on gas flux rates

c) biodegradation potential of petroleum hydrocarbons (PHCs) in the subsurface and near surface materials as a result of microbial activity

d) estimation of PHC leaching potential

Based on the results obtain in this study we can conclude that:

- Temperature has a significant effect on the rate of HC degradation as indicated by gas flux measurements taken at 16 locations across ASCS at different times of the year
- High levels of soil moisture caused by rainfall events resulted in a temporary reduction of the gas flux rates
- Gas flux rates in the field varied spatially and temporally
- Occasionally, elevated concentrations of soil $CO_2$ (up to 21%) and $CH_4$ (up to 12%) were detected. The high concentrations of $CO_2$ and $CH_4$ may have been caused by the presence of low permeability layers of bitumen in the subsurface inhibiting free flow of gas to the surface. This would explain why elevated gas concentrations were measured below these layers. High concentrations of methane at these depths in the soil may have some temporary negative impact on plant growth

- The LOS/overburden material collected from ASCS and used in the column study generally exceeded clean soil guidelines by a factor of 10 to 20. LOS was predominantly composed of F3 (47%) and F4 (45%) hydrocarbon fractions (i.e. very heavy molecular hydrocarbons that are not readily degradable). The remaining PHC fractions present in the LOS contained small amounts of volatile and easily degradable F1 (0.1% excluding undetectable BTEX) and F2 (8.3%).

- LOS material should have low environmental impacts on surface or groundwater quality. The F1 fraction (including BTEX) was not detected in the column leachate. The F2 fraction slightly exceeded clean water guidelines on a few occasions at temperatures ≥22 °C (which does not reflect average field conditions). Overall, however, the concentrations of F2 hydrocarbons remained below clean water guidelines and decreased over time. Furthermore, at low temperatures (≤4°C), the concentration of F2 hydrocarbons was close to the detection limit of 0.1mg/L. The F3 hydrocarbons were present at concentrations below F2 regulatory limits and are not regulated for groundwater

- Organic carbon concentrations were several orders of magnitude higher than the reported concentrations of chromatographable hydrocarbons, which indicates the presence of other organic compounds. Additional tests conducted on the leachate water revealed the presence of 49mg/L concentrations of oil and grease and 150mg/L of organic compounds known as Naphthenic Acid Fraction Component (NAFC) and other acid extractables. Organic acids found in the leachate were complex and detailed quantification of separate compounds was not possible

- Based on soil respiration, biodegradation rate appears to depend on temperature. The total estimated PHC degradation from respiration was 60g/year at 22°C and 15g/year at temperatures from 2 to 14°C (averaging about 6°C). However, these amounts constitute only a small portion of the approximately 2.8kg of hydrocarbons present in each column. Thus, the results indicate that the degradation of hydrocarbons from LOS material is occurring at relatively slow rates. For comparison, Fleming (2012) showed that degradation of PHC from surficial bitumen materials (at 20°C) was on average 8.5g/yr, which is significantly slower than in the case of LOS. The observed PHC volatilization rate (0.3g/yr) was two orders of magnitude lower than that of PHC degradation

- Controlling temperature during the experiments allowed the effects of temperature on hydrocarbon degradation and $CO_2$ production to be investigated. Temperature dependence became evident during climate chamber failure when the temperature in the climate chamber increased abruptly from 4 to 23°C within 24h resulting in the spike in gas flux rates. The estimated $CO_2$ flux rates showed a linear relationship between $CO_2$ gas fluxes and temperatures. The gas flux rates ranged from 11mg/m2/h at 2°C to 265mg/m2/h at 22°C. Interestingly, the gas flux results obtained under controlled steady lab conditions were comparable with the gas flux rates obtained in the field, which ranged from 10 to 166mg/m2/h with peaks of 260 and 810mg/m2/h

- The results from the field and laboratory respiration studies were also relatively similar, confirming that the column study could be used to produce meaningful and low cost estimates of in situ PHC degradation.

## 6.2 Recommendation for Future Work

Based on the results from this study a few recommendations could be made for the future studies.

- High concentrations of methane detected on a few occasions at various depths in the soil may have some temporary negative impact on plant growth. Further studies will be required to investigate these random anomalies

- On one occasion, the additional tests were conducted and revealed a significant amount of oil and grease and NAFC in the leachate water. Further detailed investigation and continuous monitoring and interpretation of data with respect to oil and grease, and NAFC is recommended to evaluate the potential impact on the environment and on the reclamation activities

- The results from the charcoal tube that had collected PHC volatilized gases for 5 months indicated the presence of hydrocarbons on the downstream module of the two-module trap, suggesting that the tube may have been overloaded. It is recommended to monitor the volatiles from all of the columns and in shorter intervals (depending on the volatilization rate of PHC) to avoid overloading the charcoal tube, which may underestimate, by an unknown margin, the true mass volatilized

- It would be valuable to assess the PHC fraction content immediately after the cessation of the experiment. These additional data could facilitate the determination of the actual rate of separate PHC fraction degradation.

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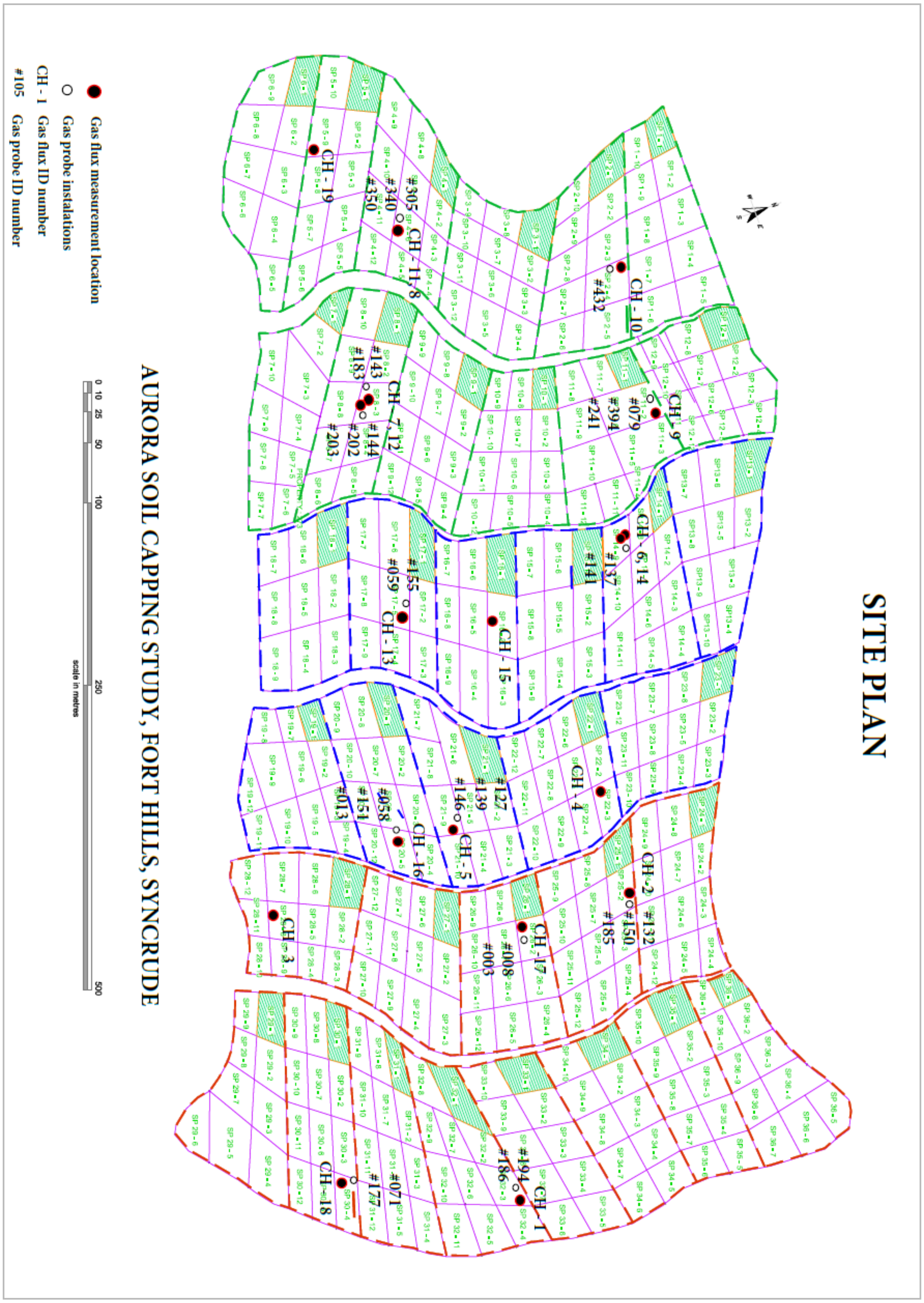
# APPENDICES

# APPENDIX A


SITE PLAN
AURORA SOIL CAPPING STUDY, FORT HILLS, SYNCRUDE
● Gas flux measurement location
○ Gas probe instalations
CH - 1 Gas flux ID number
#105 Gas probe ID number
0 10 25 50 100 250 500
scale in metres

# APPENDIX B

## Summary table of soil gas concentration

| probe No | Depth **(m)** | concentrations % (Oct 2010) | | | concentrations % (July 2011) | | | concentrations % (Sept 2011) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | **$O_2$** | **$CO_2$** | **$CH_4$** | **$O_2$** | **$CO_2$** | **$CH_4$** | **$O_2$** | **$CO_2$** | **$CH_4$** |
| # 186 | 2.3 | 0 | 5.5 | 9.1 | 0.4 | 11.1 | 0.4 | 0.1 | 13.8 | 0.4 |
| # 194 | 3.5 | 0 | 5 | 11.4 | 1.2 | 9.9 | 2 | 0.2 | 13.9 | 3.7 |
| # 150 | 2.4 | 0 | 8.1 | 7.5 | 20.3 | 0.4 | 0.2 | | | |
| # 132 | 3.6 | 10.1 | 5 | 0.1 | 20 | 1 | 0 | | | |
| # 185 | 7.3 | 10.4 | 6.6 | 0.4 | 12 | 5.5 | 0.9 | | | |
| # 146 | 1.8 | 19.2 | 0 | 0.1 | 19 | 1.3 | 0.1 | 20.7 | 0.4 | 0.4 |
| # 142 | 3.2 | 17.6 | 0.2 | 0 | 20 | 1 | 0 | 20.4 | 0.5 | 0.6 |
| # 139 | 5.5 | 12.3 | 1.4 | 3.1 | 1.8 | 16.4 | 0.2 | 9.1 | 9.2 | 0.1 |
| # 141 | 1.8 | 14.3 | 3.6 | 0 | 15.6 | 4.7 | 0.1 | 16 | 5.8 | 0.1 |
| # 137 | 6.3 | 15.7 | 0.6 | 0 | 20.5 | 0.8 | 0 | 20.2 | 1.2 | 0.4 |
| # 202 | 1.8 | 15.4 | 2.1 | 0 | 0.5 | 18.7 | 0.5 | 0 | 21.2 | 0.5 |
| # 144 | 2.7 | 15.3 | 1.9 | 0 | 0.7 | 18.1 | 0.3 | 0 | 21.2 | 0.4 |
| # 203 | 4.6 | 5 | 7.9 | 0.2 | 0.6 | 16 | 0.8 | 0 | 19.1 | 0.8 |
| # 183 | 1.8 | 7.7 | 2.4 | 0.7 | 1.6 | 8.3 | 6.2 | 0 | 10.4 | 0.6 |
| # 143 | 4.5 | 8.5 | 4.8 | 0.4 | 1.6 | 12.6 | 0.7 | 0 | 14.4 | 0.6 |
| #340 | 0.9 | | | | 2 | 14.5 | 0.1 | 2 | 12.2 | 0.1 |
| #305 | 2.0 | | | | 14.5 | 4.1 | 0.1 | 0 | 12.5 | 0.2 |
| #350 | 2.8 | | | | 1.35 | 12.2 | 0.1 | 23 | 0 | 0 |
| #432 | 0.9 | | | | 19 | 1.4 | 0.1 | | | |
| #079 | 0.6 | | | | 1.6 | 2.4 | 2 | | | |
| #394 | 2.1 | | | | 2.3 | 3.3 | 2.2 | | | |
| #241 | 3.4 | | | | 0.65 | 4 | 2.4 | | | |
| #059 | 1.7 | | | | 0.6 | 18 | 0 | 0 | 20.6 | 0.2 |
| #155 | 3.8 | | | | 4 | 7.5 | 12 | 14.3 | 4.1 | 0.4 |
| #058 | 1.8 | | | | 15.9 | 3.9 | 0.2 | 18.4 | 3.5 | 0.2 |
| #151 | 2.8 | | | | 2.6 | 18.5 | 2 | 5.3 | 9 | 0.2 |
| #013 | 5.3 | | | | 0.4 | 19 | 3 | 1.2 | 12 | 4 |
| #003 | 1.4 | | | | 20.4 | 0 | 0 | | | |
| #008 | 1.8 | | | | 20.6 | 0 | 0 | | | |
| #177 | 1.7 | | | | | not measured | | | | |
| #071 | 2.6 | | | | | not measured | | | | |

Shaded spots in the table represent locations in which either gas vapour probes become clogged, water was drawn through the probes in measurable quantities or leaks were detected.

# APPENDIX C

## Bitumen removal method supplied by Suncor LTD.

**Procedure:**

**Note: 250 mls Nalgene bottles are kept under coulter A and the caps are kept in the drawer under fumehood#10.**

1. Transfer the oil sand sample plug to a 250 mls Nalgene bottle. Put all the plugs from the glass jars to bottles.
2. Put a new sticky on the Nalgene bottle with the Hole # and the bottle no copied from the Geologist sheet. Be sure to tape the label again. Put the bottles in the racks meant for 250 mls bottles.
3. Fill the 250-mL Nalgene bottle just below neck with IPA/ Toluene to dissolve the oil from the sample.

**Note: For composite samples mark C at the top of the bottle for easy balancing later.**

4. Balance the bottles to within ±0.4g using a top loading balance by adding IPA/Toluene. Repeat this step till all pairs of samples are balanced.
5. Shake the samples for 6 minutes in the paint shaker. Centrifuge the samples at 2200 rpm for 20 minutes.
6. When the centrifuge has completely stopped, remove the bottles and remove the solvent by suction, taking care not to lose any solids. Remove suction from the liquid layer when the liquid level is within about 1 inch of the solids layer.
7. Repeat steps 3 to 5.until the liquid that is decanted after centrifuging is very clear. You can compare the solvent by taking some in a disposable pipette and comparing it.

**Note: Keep an eye on the Waste Bottle. When it gets full, discard the solvent in Fumehood#10**

8. Transfer the sample from 250-ml Nalgene bottles to the evaporating dishes and use acetone to rinse all the solids from the bottle. Transfer the sticky from the bottle and put on the Evaporating dishes. Cover with the tape.

9. Place the samples in the fume hood in large evaporating dishes and leave it there until all solvent has been evaporated

**Note: Label the dishes with lab labels or sample ID tags.**

10.Crush the clean, dry samples using a pestle to break up any (clay lumps).

11.Place the crushed samples in clean, labeled C-tubes. They are now ready to be sub sampled. Transfer the label as well.

**Note: If any vial fills more than 25 mls. It needs to be riffled, when finished, take vial 1& 3 from the riffler.**

12. Mark the samples with rocks as **R** on top of the lid. Weigh the vial and put the weight on the sheet.

13. Every 15th sample is done in duplicate. The samples, which we do in duplicate, are marked as 15A and 15D.

14. After extracting the oil, riffle the sample. For sample #15, take the sample from glass vial 1&3 and transfer the sample into vial marked 15A. Similarly take sample from vial 2&4 and transfer it to vial marked 15B. Riffle sample 15D and transfer the sample from 1&3, call it 15C. Similarly transfer the sample from vial 2&4 and call 15D

15. Do the same for sample#30

**Note: If after extraction of oil, we have more than 1 vial then riffle both the vials take vial#1 only from the refiller as sample.**