PETROLEUM HYDROCARBON CONTENT, LEACHING AND DEGRADATION FROM SURFICIAL BITUMENS IN THE ATHABASCA OIL SANDS REGION

A Thesis Submitted to the
College of Graduate Studies and Research
in Partial Fulfillment of the Requirements
for the degree of Master of Science in Civil Engineering
in the Department of Civil and Geological Engineering
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ABSTRACT

Mine reclamation has become a topic of considerable research in the Athabasca Oil Sands Region of Northeastern Alberta, Canada. In this area some of the largest open pit mines in the world extract bitumen, a type of heavy oil, from the oil bearing McMurray Formation. At the close of mine operations, lease holders are required to return the land to equivalent capability. To achieve this, several existing waste piles will need to be capped and a functioning ecosystem re-established.

Proposed borrow pits for capping material were recently found to contain reworked bitumen materials of various shapes and sizes. This reworked bitumen has been named tarballs by local industry. The use of that name is maintained throughout this study. The tarball accumulations are very abundant in some areas but also occur infrequently in apparently clean areas. In this study, the petroleum hydrocarbon signature and leaching characteristics of the tarballs were determined. The hydrocarbon content and composition of the tarballs were assessed using the Canadian Council of Ministers of the Environment (CCME) methods. The data were presented in terms of the four CCME fractions. Leaching characteristics were determined using a custom designed, unsaturated soil column experiment carried out at the University of Saskatchewan. The soil column was monitored for petroleum hydrocarbons, total carbon and total organic carbon in leachate water and soil respiration as a surrogate for biodegradation.

The bitumen was found to consist primarily of heavy hydrocarbons, CCME Fractions 3 and 4, at levels of thousands and tens of thousands of mg/kg respectively. Gravimetric analyses indicated that a significant proportion of the tarball materials are very heavy hydrocarbons beyond the range of high temperature gas chromatography. These very heavy hydrocarbons are greater than carbon number C90. Lighter and more mobile hydrocarbons were occasionally identified at the core of larger accumulations. Where identified, the lighter fractions were typically accompanied by F3 and F4 hydrocarbons at one to two orders of magnitude greater than typical tarball material.

Leachate was found to contain F2 hydrocarbons at less than 0.2 mg/L, a small fraction of the CCME clean water guideline of 1.1 mg/L. F3 hydrocarbons were identified at levels up to 0.6 mg/L. Soil respiration indicated a very low activity system, suggesting limited potential for biodegradation. Tarball materials are concluded to be of little concern for potential impacts to groundwater based upon the hydrocarbon fingerprint and the observed leaching characteristics of the tarball materials.

ACKNOWLEDGEMENTS

This thesis would not have been possible without significant contributions from many people. Sponsors, colleages, mentors, family and friends have all played a roll in it's preparation.

Particular acknowledgements go to Doug, Alex and Cynthia in the Department of Civil and Geological Engineering at the University of Saskatchewan. Help, ideas and support from fellow students Heather, Amanda, Julie and Chris has been especially valuable. Assistance in fieldwork from the good people at Paragon Soil and Environmental Consulting, especially Len and Wade. Significant help from John, Du and Kerry of Environment Canada with many chemical analyses, among other things, made much of this work possible.

Special mention is also due to industry sponsors, the Environmental Research Group (ERG) of the Canadian Oil Sands Network for Research and Development (CONRAD). Financial support was also provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada and the University of Saskatchewan.

But most importantly, the unending support and energy of my supervisor, Dr. Ian Fleming, is acknowledged with a debt of gratitude that cannot be repaid.

Thank you all.

To all of the strong women in my life, my grandmothers, mother and future wife, without whose constant love and dedication I would not be who and what I am today.

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List of Abbreviations

CCME	Canadian Council of Ministers of the Environment
CEMA	Cumulative Effects Management Association
CLAS	Clearwater - Lower Athabasca Spillway
CWS	Canada-Wide Standard
ERCB	(Alberta) Energy Resources Conservation Board
GC-FID	Gas Chromatography with Flame Ionization Detection
GC-MS	Gas Chromatography with Mass Spectrometry
LAPBD	Late Pleistocene Athabasca Braid Delta
LOS	Lean Oil Sands
PHC	Petroleum Hydrocarbon
SMA	Surface Mineable Area
USTPHCWG	United States Total Petroleum Hydrocarbon Criterion Working Group

Chapter 1

Introduction

1.1 Background

Steady growth in global demand for oil has brought significant attention to the Athabasca Oil Sands Region in Northeastern Alberta, Canada. This deposit is estimated to contain 1,804 billion barrels of bitumen, of which 38.7 billion barrels are estimated to be recoverable by surface mining (ERCB 2011). According to the Alberta Energy Resources Conservation Board (ERCB), as of early 2011, there were four operators with mines in production and two additional mines under development but not yet in production. The total permitted area of these projects covers almost 152,000 ha of land. When mining is completed, operators in the region are required to reclaim mined areas to an equivalent land capability relative to pre-disturbance conditions. This requirement poses a significant challenge to mine operators, with the potential for substantial legacy costs if anticipated reclamation performance is not achieved.

One major component of reclamation operations involves locating, stockpiling and eventually placing significant quantities of clean soil for cover systems and ecosystem reconstruction. Recent cuts in undisturbed proposed borrow areas have uncovered naturally occuring deposits of bitumen in surficial materials proposed for use in reclamation. This bitumen typically occurs in layers that can range from a few centimetres to half a metre in thickness and extend several metres horizontally. Also present are isolated balls of bitumen that can range from a few centimetres to half a metre, and occasional large chunks, several metres in diameter. Accumulations of thicknesses greater than 35 to 40 centimetres rarely occur. However, the core of these accumulations often contains high concentrations of less weathered bitumen. These rich cores sometimes exhibit hydrocarbon contents and fingerprints (including more mobile fractions) approaching those of the ore mined at depth. Bitumen affected soils have been found to extend from the top of mineral soils to beyond six metres below ground surface. These accumulations of bitumen are often referred to as ‘tarballs.’

1.2 Objectives

A regional study was carried out by Paragon (2006) that outlined the broad geographic extent of tarball affected soils in the Athabasca Oil Sands Region. This report emphasized that much of the geologic study in the region has centered around the economically-significant, bitumen-bearing McMurray Formation. Surficial geology and post glacial geologic processes, on the other hand, have been studied by a few, but even these make only passing references to ‘reworked bitumen’ in glacial and post-glacial drift. The origin and nature of these materials is often taken for granted, or not discussed at all. This thesis addresses two distinct but related questions. “What is the hydrocarbon content and composition of the tarballs?”; and “what are the potential impacts in terms of hydrocarbon mobility if they are incorporated in reclamation covers?”

The work in this thesis was carried out in order to add to the growing knowledge base surrounding these materials. More specifically, this thesis represents an attempt to address several gaps in knowledge. Specific objectives are as follows:

- determine the hydrocarbon composition of typical upland tarball samples according to Canadian Council of Ministers of the Environment benchmark methods,
- investigate potential correlations to physical properties or appearance and their potential use as field screening indicators of hydrocarbon concentration,
- determine the potential for hydrocarbon leaching from cover systems containing tarball affected soils to surface water and/or groundwater,
- investigate potential tarball hydrocarbon biodegradability, and
- as an additional outcome of this study, provide comments related to the genesis of the material where possible.

This information is essential to determine the suitability of these materials for use in reclamation soils.

1.3 Thesis Organization

This thesis represents the first known major work on the geologic material presented herein. The tarballs are thought to be unique on a global scale. Although the forces of geology which created them are universal, it is unlikely that a similar set of circumstances would have come together in any other location on a similar scale.

The format of a typical five chapter thesis is generally followed in this six chapter thesis: Chapters 1, 2 and 3 provide an Introduction, Literature Review and a review of Experimental Methods respectively. The presentation of data is then divided into two chapters. Chapter 4 presents a characterization of detectable hydrocarbons, in an effort to define the potential contaminant source. Chapter 5 presents an assessment of potential mobility to groundwater, a significant contaminant transport pathway. A brief summary and conclusions are provided in Chapter 6, the final chapter.

Chapter 2

Background and Literature Review

An understanding of potential impacts to the environment from tarball disturbance and incorporation in reclamation covers requires a thorough understanding of the tarball materials in terms of hydrocarbon content and leaching potential. This information must be understood in the context of the regional geology, the mine reclamation process, environmental regulations and the mechanisms of contaminant transport. This background information and the current body of knowledge on tarball materials are presented in this Chapter. The findings and conclusions of this study have been presented in a recent publication, Fleming et al. (2011)

2.1 Physiography and Geologic Setting

2.1.1 Geography

The Athabasca Oil Sands region is located in the northeastern Alberta, Canada, as shown in Figure 2.1. The major population centre is the town of Fort McMurray, surrounded by large expanses of natural terrain. Fort McMurray and its associated mining industry are located in the Boreal Forest Region of Canada (AOSERP 1982). More than half of the area is covered by organic soils, defined as having more than 30 cm of peat, which represents decomposed or slightly decomposed organic material, at the surface. In areas of improved drainage, vegetation is primarily aspen poplar, however stands of jack pine and white and black spruce are common (Carrigy and Kramers 1973) The climate is sub-arctic with average daily temperatures of 0.7 °C and average annual precipitation of 455 mm (Environment Canada 2008).

The largest deposit of heavy crude bitumen in the world is found in the Cretaceous McMurray Formation north of Fort McMurray. The Alberta Energy Resources Conservation Board (ERCB) has jurisdiction over these resources. The ERCB defines a Surface Mineable Area (SMA) as the area in which overburden and deposit conditions are technologically and economically amenable to open pit mining. The SMA occupies 51.5 townships approximately 30 to 70 km north of Fort McMurray. Several open pit mines are currently in operation in the SMA.

Figure 2.1: The location of Fort McMurray within Alberta, Canada

2.1.2 Geology of the McMurray Formation

A representative east-west crossection of the regional geology just north of Fort McMurray is provided in Figure 2.2. The oil-bearing McMurray formation is a member of the lower Cretaceous Mannville Group. It is composed primarily of very fine to medium grained quartz sand (Mossop 1980) interbedded in places with relatively thin ironstone (Carrigy and Kramers 1973). These sands are also interbedded with shales in a highly complex series of channels and deltas. The McMurray formation transgresses, in a general fining upward pattern, from coarse grained river-sand reservoirs in the lower McMurray to fine grained sands with mudstone filled channels in the upper McMurray (Carrigy 1966; Hein and Cotterill 2006).

The McMurray formation is capped in places by the Wabiskaw member of the Clearwater formation. This consists of a relatively thin layer of bitumen bearing sands and shales. The regionally extensive Clearwater marine shale and superjacent Grand Rapids sand formations complete the Mannville Group (Flach 1984). On a regional scale, these formations represent a transgression from fluvial to estuarine to lacustrine depositional environments in early Albian time (Hein and Cotterill 2006).

The McMurray, Clearwater and Grand Rapids formations represent bedrock throughout much of the SMA (Green 1970). Bedrock trends older to the north and west and is overlain by several to tens of metres of drift.

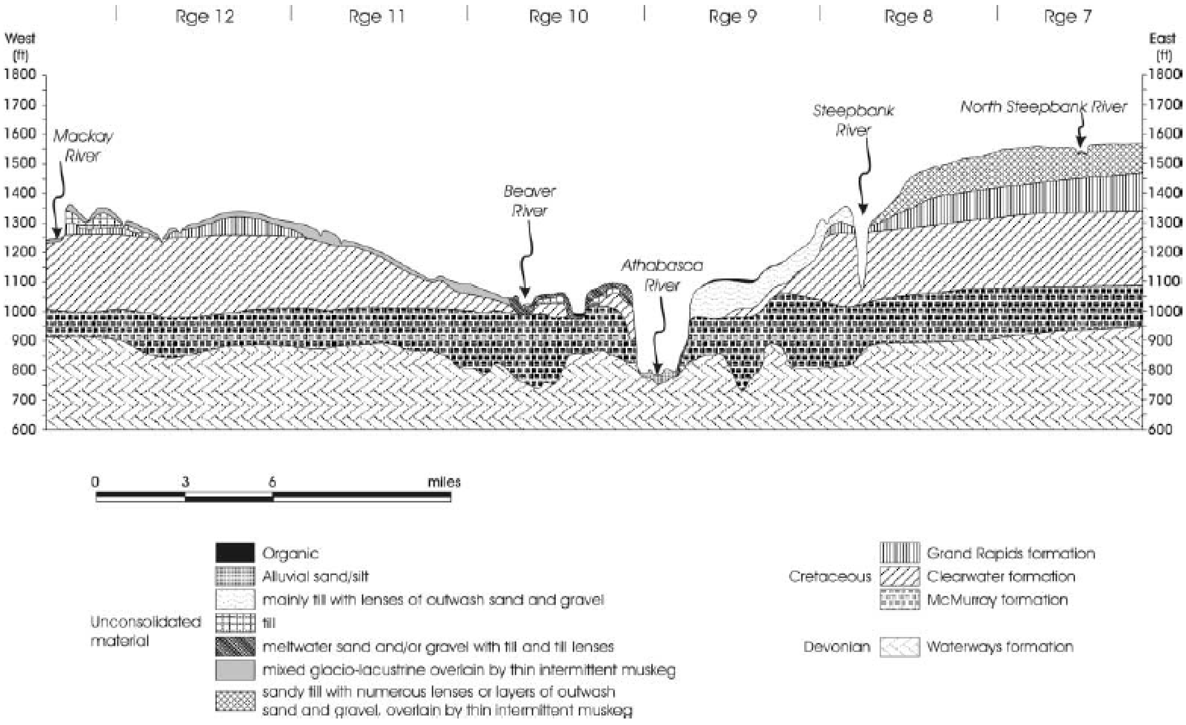

Figure 2.2: Representative geological cross section of the Fort McMurray area Conly et al. (2002)

2.1.3 Glacial Geology

Much of the surficial geology of the Athabasca Oil Sands Region consists of glacial drift or organic soils on glacial drift (Carrigy 1959; McPherson and Kathol 1977). This drift is found as Pleistocene ground moraine and kame deposits, with a significant portion of the active mining area overlain by glaciofluvial and glaciolacustrine deposits (Bayrock 1974).

The glacial and organic soils occur along a major glacial meltwater channel that follows the approximate course of the present Athabasca River from Fort McMurray to Lake Athabasca. This meltwater channel is known as the Clearwater - Lower Athabasca Spillway (CLAS). Its presence and likely glacial origins have been noted since the earliest geological investigations were made in the late 1800's (Carrigy and Kramers 1973).

2.1.4 Glacial Lake Agassiz

It is commonly accepted that the CLAS derives from glacial meltwater associated with Glacial Lake Agassiz, a post-glacial lake that occupied a large portion of central North America at the end of the last ice age, approximately 10,000 years before present. Recent estimates suggest that Lake Agassiz ranged in size from that of Lake Michigan to many times the total volume of all modern Great Lakes. (Leverington et al. 2002). The progression and recession of the Laurentide ice front and the opening and closing of multiple drainage outlets (Leverington 2000; Leverington et al. 2002) subjected Lake Agassiz to lateral transgression and periods of dramatic rise and fall. The chronology of Lake Agassiz is very complex and remains a topic of debate among geologists.

Among the commonly accepted outlets for Glacial Lake Agassiz is a Northwest Outlet through the CLAS. Although the specific chronology and quantity of drainage through the CLAS elude scientific consensus at the present time, it is generally agreed that some drainage must have occurred through this outlet at some time about 9,000 to 10,000 ^{14}C years before present (Smith 1993; Leverington 2000; Fisher 2009). It is also widely accepted that this channel grades into the Late Pleistocene Athabasca Braid Delta (LPABD) (Rhine and Smith 1988). See Figure 2.3.

Timothy Fisher (2002; 2009) presents a scenario for the development of the CLAS based on spillway geology. In several papers from the mid 1990's, Fisher and others developed the theory of a catastrophic post-glacial flood initially proposed by Smith (1993).

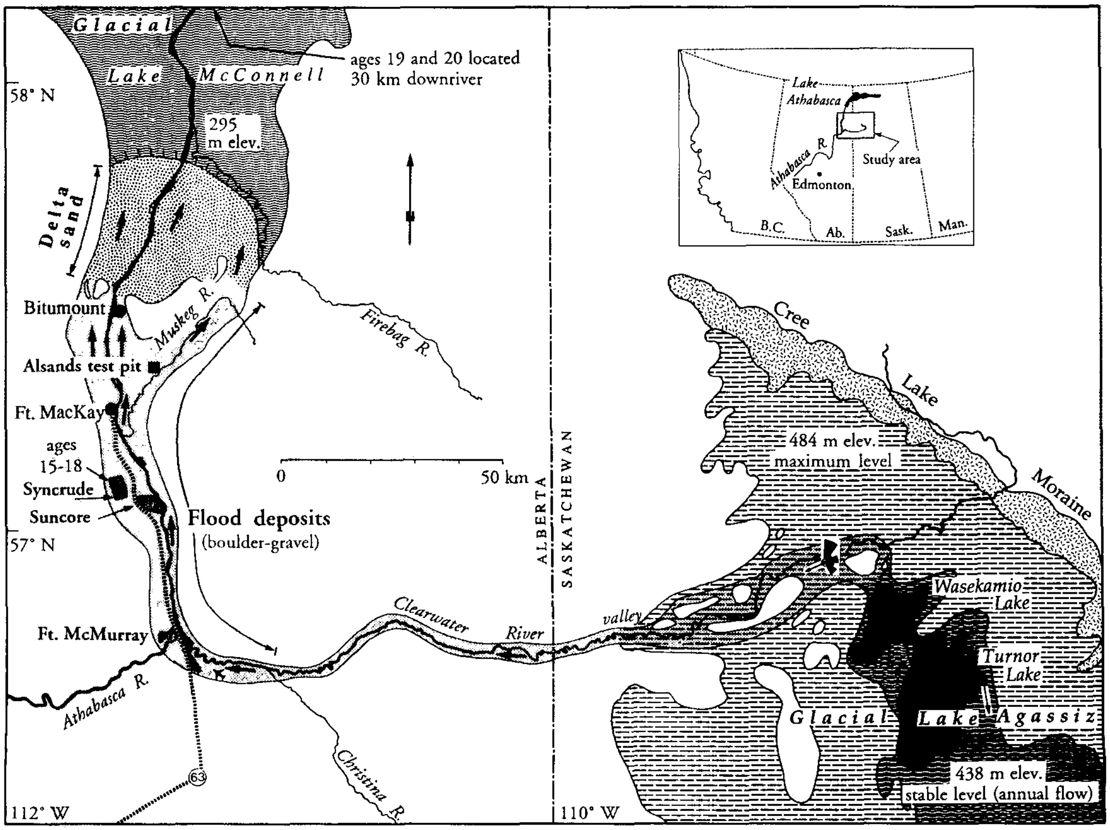

Figure 2.3: Location of the CLAS from Smith (1993)

This flood was initially thought to have occurred 9,900 ^{14}C years before present with the break-up of an ice dam and the overtopping of the Cree Lake moraine in northern Saskatchewan. According to the theory, this produced a flood of catastrophic proportions. Bank-full velocities calculated by Fisher at a location just upstream of Fort McMurray range from 6.3 to 28.0 m/s, with 12 m/s as a reasonable estimate. This is calculated to have continued over a 78 day period (Fisher and Smith 1994; Fisher 2002). Fisher and Smith (1994) suggest that this flood carved the CLAS in a very short period of time, leading to the buildup of the braid delta (LPABD) as floodwaters graded into Glacial Lake McConnell, upstream of the present Lake Athabasca.

New evidence, recent papers and discussion regarding this theory have led to the suggestion of multiple, smaller, flood events. This may eventually lead to the abandonment of the catastrophic flood theory (Teller 2006). However, the presence of significant fluvial and lacustrine deposits in the SMA north of Fort McMurray is not in question. Recent investigations have revealed the widespread occurrence of residual bitumen in these surficial fluvial materials. Lacking an appropriate and concise geological name or descriptor, the term 'tarball' has been adopted by the oil sands industry. The name is derived from the breaking apart of these bitumens during excavation of overburden soils, leaving a landscape of bituminous chunks strewn across the pit floor. The term tarball is employed throughout this thesis to denote any type of surficial bitumen accumulation.

2.2 Tarball Affected Soils

2.2.1 Material Description

Ells (1926) commented on these materials in several reports prepared for the Mines Branch of the Canadian Department of Mines. Ells began his investigations of the Oil Sands in 1914, and throughout several decades produced many reports on the deposit. His work culminated in a significant 1926 report outlining the size and nature of the reserves as well as their economic potential. This report devoted some considerable attention to what he termed "marginal partings" of bituminous sand in quaternary formations of gravel, sand and clay (Ells 1926). Ells included several pictures of these "partings" such as in Figure 2.4. With a clear note that these materials are accompanied by significant variability, Ells provided one outcrop log as typical of these deposits. Capped by a thick layer of bitumen are deposits consisting:

> "...chiefly of clean sand, many thin partings of bituminous sand, from 2 to 5 inches in thickness occur. The thicker and more continuous of these are largely unaltered bituminous sand, but thinner and interrupted partings, particularly in the lower strata, consist of non-cohesive, leached-out fragments. Interbedded between these partings are sand strata, varying in colour from reddish brown to light gray, and entirely unimpregnated by bitumen."

Recent work by Paragon Soil and Environmental Consulting (2005; 2006) in compiling existing field data and an additional field study indicates that tarball affected soils cover a wide geographic area and occur in various different physical manifestations. Tarball bitumen is generally hard and brittle relative to the pliable in-situ McMurray oil sands (Carrigy 1959). Subsequent field investigations by Paragon (2006) have indicated the general consistency between the grain-size of host material (ie. within the tarball itself) and the adjoining soil matrix. Although no measurements were made, it was repeatedly observed that those tarballs surrounded by coarse sand contained coarse sand, and that those in silt or clay would contain primarily silt or clay, respectively.

Tarballs have been observed as continuous bands of material from a few millimetres to tens of centimetres in thickness. They typically extend from centimetres to several metres in length. Bands often repeat, sometimes with tens of thin layers resembling varved clays. Also present are layers of distinct balls, which also range from millimetres to tens of centimetres in diameter. Isolated balls have also been recovered, sometimes surrounded by metres of apparently clean sand. Large chunks several metres in diameter have also been observed in the field. Occasionally, areas of dispersed hydrocarbon staining have been found, ranging from millimetres to tens of metres in diameter. However, none of these occurrences are mappable at even the finest resolution of pre-mining investigation (Lanoue 2009).

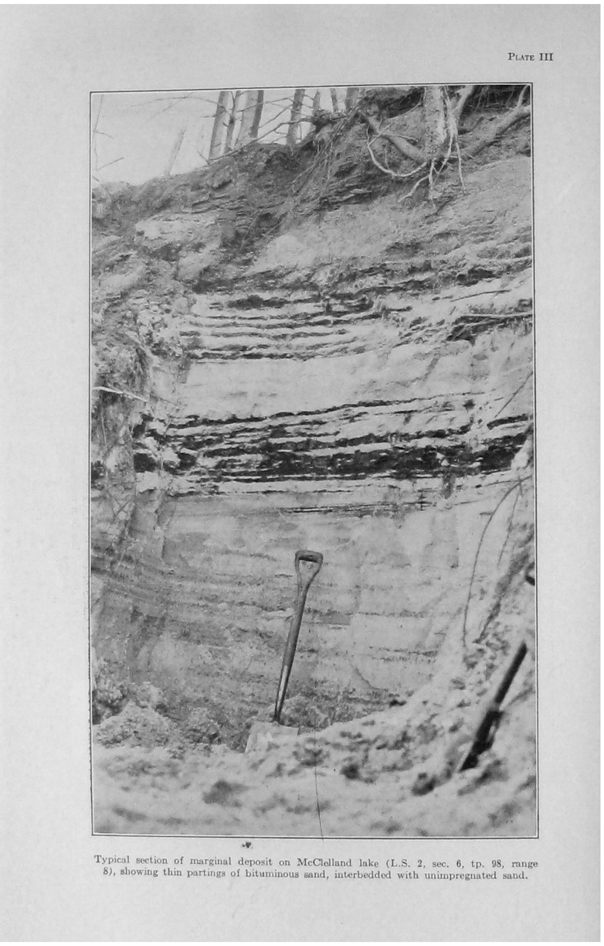

PLATE III

Typical section of marginal deposit on McClelland lake (L.S. 2, sec. 6, tp. 98, range 8), showing thin partings of bituminous sand, interbedded with unimpregnated sand.

Figure 2.4: An early photograph of in-situ tarball material (Ells 1926)

2.2.2 Tarballs Throughout the Literature

Surficial bitumens are found primarily in glaciofluvial sediments (Paragon 2006). These comprise the Firebag, Mildred and Fort Soil Series in the Muskeg River Plain and Clearwater Plain Ecodistricts (AOSERP 1982; Paragon 2005). The Soils Inventory for the Alberta Oil Sands Environmental Research Program (AOSERP) Study Area (1982) describes these soils as containing, in places, "a relatively high percentage of reworked bitumen" or "lenses or slabs of tar sand." Little other attention is given to these occurrences.

Similar mention was made of these materials in various reports and papers throughout the last century. Tracing some of their history provides a meaningful overview of the geographic extents of tarball occurrence.

An Alberta Research Council report entitled Surficial Geology of Potential Mining Areas in the Athabasca Oil Sands Region (Report 1977-4) (McPherson and Kathol 1977) indicates that the Fort Hills contain a "relatively high percentage of reworked bitumen." With reference to the AOSERP Soils Inventory and many subsequent field investigations, the report made mention of reworked bitumen present in outwash sands in the area. The report noted that the sands generally do not occur above an elevation of about 1,000 ft.

Ells (1926) carried out a series of regional outcrop studies from the Clearwater River to Lake Athabasca, reporting on both the exposed oil sand and tarball deposits. Ells noted the greatest accumulations of tarballs along the Athabasca River from Townships 98 to 104, with another noteworthy accumulation on the Firebag river in Township 99. The Athabasca River location corresponds well with the Glacial Meltwater Deposits of Bayrock's surficial geology (1974). The Firebag River location is at the heart of outwash sands associated with the LPABD (Bayrock 1974; Smith 1993).

In subsequent drilling reports, Ells (1932) also described 7 feet of coarse gravel with bitumen fragments at 14 feet depth. The borehole was located in the area south of Beaver Creek and north of Mildred Lake, in the general vicinity of Syncrude's Mildred Lake Mine.

Smith (1993) discussed the glaciofluvial deposits at length, tracing their evolution from large cobbles at Fort McMurray to delta sand north of Bitumount. Mega blocks of tarsand several metres thick and 5 to 10 metres wide are reported in gravel pits at Syncrude's Mildred Lake Mine, about 30 km north of Fort McMurray. Downstream from this location, at the northwest corner of the present Shell Muskeg River Mine, deposits of plane-bedded sand, with lags of tar sand balls and pebbles were common. This transition is illustrated by idealized core logs included in the paper, as shown in Figure 2.5.

2.2.3 Genesis

The likely glacial origin of the tarballs was noted as long ago as 1926 by S.C. Ells. During exploratory work conducted throughout the 1920's and 30's, Ells hypothesized his "marginal partings" to have been deposited in a lacustrine environment - presumably after having been eroded upstream. This he associates with a greatly enlarged Lake Athabasca at the close of the last ice age (Ells 1932).

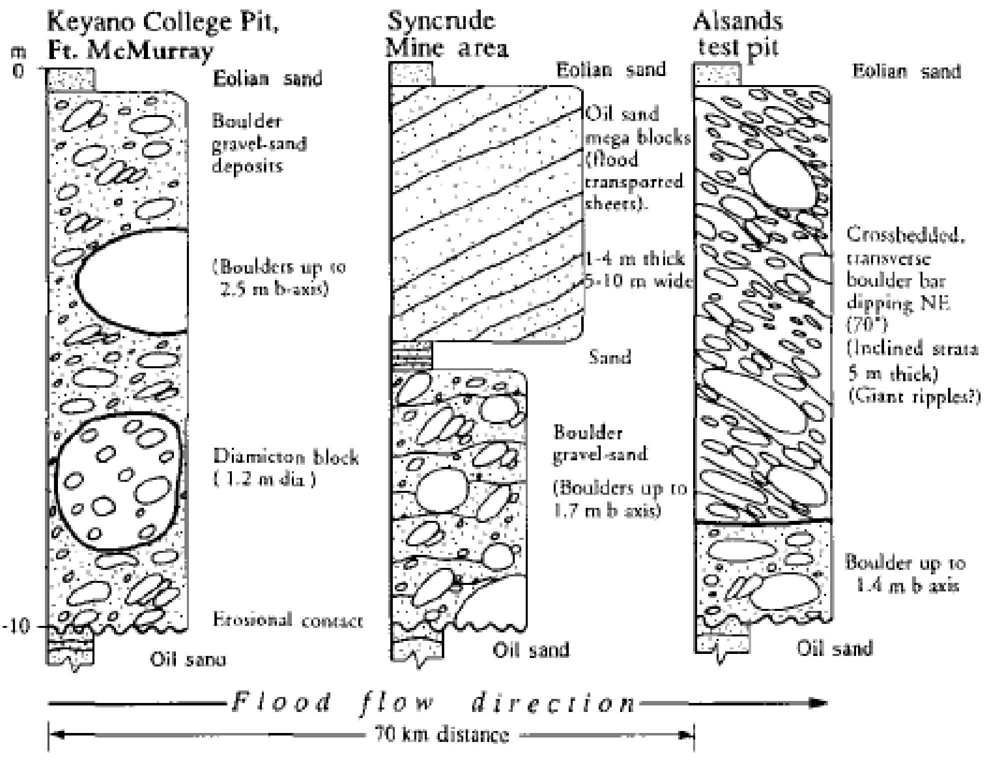

Figure 2.5: Tarsand debris in flood deposits as presented by Smith and Fisher (1994)

Ells (1932) speculated that lower quaternary deposits were likely deposited in colder conditions because these bitumen accumulations are less compacted than their upper counterparts. Warmer temperatures would have given rise to more compressible deposits of bitumen, although the possibility of cold water extraction in some fluvial or lacustrine environment was not ruled out. In fact Ells himself reported on various occurrences of river bottom extraction at seeps and the reworking of surficial bitumens on the Marguerite River, north of current mining activity (Ells 1926, 1932).

Smith (1993) drew a strong link between the presence of tarballs and the outwash channel deposits. Smith argued that the rafted and reworked oil sand among their interpreted sand and gravel flood deposits indicate a large scale flood event. This hypothesis is continued by the Paragon reports (2005; 2006).

The physical appearance and layering structures of the tarball deposits in-situ led the authors of the Paragon report (2006) to comment on potential modes of deposition. Given the commonly observed similarity of grain-size between tarball and adjacent material, it would seem as though the bitumen was deposited as slicks or blobs on existing beach or channel bottom then soaked into the soil matrix. However, large chunks of several metres in diameter do not share this property and appear to have been rafted into place. Perhaps there were two mechanisms in effect, the deposition of extracted bitumen on beach sands with remnants of a traction load deposited as well.

The lack of scientific knowledge regarding the mechanisms of bitumen transport was noted by Ells (1926). This lack of knowledge is again cited by Conly et al. (2002) in their attempt to determine natural hydrocarbon inputs to the Athabasca River. Portions of this study produced information that contributes to an understanding of oil sand deposition processes in a fluvial environment.

2.3 Oil Sands Reclamation Considerations

2.3.1 Industry Concerns

Lease holders in the SMA are required to return leased land to an equivalent land capability at the close of mining. Reclamation must be certified before the land can be returned to government ownership. Equivalent land capability is measured by the productivity of maintenance-free, self-sustaining ecosystems with respect to what existed prior to disturbance (CEMA 2006). A very important step in this process is the reconstruction of a near surface soil profile. In the case of upland reclamation, this generally requires the placement of clean sands to develop a subsoil (B and/or C horizon) capped by a mixture of generally sandy soils and organic overburden intended to mimic natural soil profiles in the region.

Two primary "reclamation recipes" for soil reconstruction are currently in use. These are one-lift and two-lift soil reconstruction. One lift reconstruction involves the placement of 15 to 50 cm of a mixture of peat and mineral soil materials. This material is spread directly over the area to be reclaimed. Two lift operations involve the placement of about 50 cm of suitable subsoil material selected to ensure adequate root zone conditions. About 15 to 25 cm of peat-mineral cover soil is then placed above the subsoil. It is important to note that both of these operations will require significant quantities of suitable mineral soils.

In selecting economical borrow areas for reclamation soils, regional geology leaves few options. The Grand Rapids formation is not continuous throughout the surface mining area. Given its high salinity, the marine Clearwater Shale formation is unsuitable for all but the most salt-resistant plants. For many operators, glacial drift is the only source of suitable reclamation material. As the widespread occurrence of tarball material has become apparent throughout the SMA, oil sands operators have begun to investigate the potential environmental impacts resulting from incorporating these materials in reclamation covers.

2.3.2 Bitumen Toxicity Studies

The most significant study dealing directly with tarball toxicity to date was conducted by Visser, (2008b) of the University of Calgary. This study consisted primarily of phytotoxicity assays on species of vegetation significant to oil sands reclamation. The study included earthworm toxicity as a surrogate for soil macrofauna. The study also provided an initial investigation into tarball Petroleum Hydrocarbon (PHC) composition and potential for leaching into soil.

Visser (2008b) characterized soil nutrients and PHC concentrations in tarballs. These analyses were carried out by Bodycote Labs, Calgary (now Exova). Soil nutrients consisted of high levels of sulphur as sulphate and trace nitrogen as ammonium. Nitrogen as nitrate, available phosphorus and potassium were not detected. PHCs were analyzed by high temperature gas chromatography. PHCs were predominantly heavy hydrocarbons, which represented about 95 % of total PHC (Visser 2008b). These are represented by Fractions 3 and 4 under the CCME system discussed in Section 2.4.1. Levels in these two fractions exceeded clean soil guidelines from several multiples to over an order of magnitude. Fraction 2 hydrocarbons were also detected, frequently at levels above clean soil guidelines. Fraction 1 was not detected (Visser 2008b).

Significant inter-tarball and intra-tarball variability was noted in PHC concentration. Five tarballs were analyzed in the course of the study. Two samples were taken from each tarball. Mean and standard deviation were determined and compared within and across the tarball samples. The coefficient of variation (Cv = standard deviation divided by mean) across the five tarballs was 25 %. Coefficients of variation for multiple analyses undertaken on the same tarball ranged from 9 to 62 %, with four of the five being under

Table 2.1: Average PHC concentrations from Visser (2008b)

CCME Fraction	Carbon Number	Mean Concentration
F1	C6 to C10	nd [a]
F2	C10 to C16	3,423
F3	C16 to C34	27,420
F4	C34 to C50	34,730

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[a] not detected

30 %. Mean PHC concentrations in mg/kg are given in Table 2.1.

In the course of this study it was found that the presence of tarballs had no significant effects on root or shoot growth of Barley, Aspen Poplar or White Spruce (Visser 2008b). In fact these species developed significant root growth and copious root hairs at the contact with the tarball surface. In Jack Pine, shoot growth was not significantly affected, however a marked decrease in root growth was noted in the presence of tarballs. Study of ectomycorrhizal fungi confirmed these results. Similar populations were observed in both control and tarball soils for Barley, Aspen Poplar and White Spruce. Jack Pine fungi were inhibited, showing decreased populations and a reduced variety of species in tarball soils. Adult earthworms were unaffected in terms of survival, growth and reproduction. Juvenile survival was not affected, however rates of growth were slower in tarball affected soils.

These results are particularly meaningful when contrasted with similar studies conducted on fresh and weathered low grade ore from the McMurray Formation, known as Lean Oil Sands (LOS). The LOS study was conducted to assess the impacts of LOS incorporated in reclamation material (Visser 2008a). Toxicology and petroleum hydrocarbon signatures for LOS were determined in this study. Barley, Aspen Poplar and Jack Pine were exposed to various concentrations of both fresh and weathered LOS homogenized with two different host soils. One host soil consisted strictly of reclamation mineral sand, whereas the other consisted of equal parts peat and mineral by volume. Species responses varied significantly, however a general trend of increased inhibition with increasing PHC content is clear (Visser 2008a).

A notable and marked exception to this rule was improved growth for several species in sands with low concentrations of PHC. Regardless of the state of weathering, low doses of PHC were seen to increase plant productivity over control levels (Visser 2008a). This is attributed to visible improvements in soil structure such as aggregation and aeration as well as moisture and the addition of nutrients, such as the carbon, sulphur and other trace components found in the tarballs.

In Visser's 2008 study, weathering was achieved by incubation of LOS samples at 22 °C for 130 days in the presence of a forest soil inoculum. This weathering procedure reduced LOS total PHC concentrations by an average of 24 %. PHC reductions were determined by High Temperature Gas Chromatography (HTGC) and are given by fraction in Table 2.2. This weathering was found to reduce, in some cases significantly, the inhibitory effects of LOS PHCs. Thus it was recommended by Visser (Visser 2008a) that all soils containing LOS be weathered prior to use in reclamation. Table 2.2 presents Visser's recommendation regarding the maximum concentration of weathered LOS PHCs on the basis of not more than 25 % inhibition of plant growth or earthworm reproduction.

Table 2.2: LOS toxicity thresholds from Visser based on 25% toxicity

CCME Fraction	Reduction in PHCs %	Plant Toxicity mg/kg	Earthworm Toxicity mg/kg
F1	100	0	0
F2	75	94	39
F3	31	1,333	787
F4	1	3,730	1,610
Mean	24	5,160	2,440

2.3.3 Conclusions from Bitumen Toxicity Studies

These studies seem to indicate that tarball PHCs are considerably less toxic to plants and soil macrofauna than the presence of weathered or unweathered LOS. Several factors are likely associated with this observation, such as differences in hydrocarbon distribution and composition. In Visser's tarball study, hydrocarbons were present as isolated disks in the test soil, whereas the LOS and receiving soil were homogenized to produce uniform PHC concentration. This uniform concentration offered no refuge for earthworms or roots adversely affected by the presence of PHCs. However this cannot be the only explanation as low concentrations of LOS were seen to improve growth in a sand medium, and root and root hair growth were visually greater adjacent to tarball material. Thus it seems that tarball composition may be different from that of LOS. The LOS material would be expected to have characteristics similar to that of the McMurray formation ore body - from which the tarballs are hypothesized to have been derived. On the other hand, surface soil processes have had an impact on tarball material, such as infiltration, aeration, and microbial activity for approximately the past 9,000 years. These processes would selectively remove volatile and biologically available hydrocarbons, resulting in a low toxicity carbon source for plants and associated microbes.

2.4 Environmental Regulation

2.4.1 Canada Wide Standard for Petroleum Hydrocarbons in Soil

Management of contaminated sites falls under provincial jurisdiction in Canada. Many remediation standards have been harmonized across Canada by the Canadian Council of Ministers of the Environment (CCME) as Canada-Wide Standards (CWS). In the late 1990's CCME undertook the development of a CWS for petroleum hydrocarbons which were previously subject to widely varying standards of management and remediation (CCME 2001a).

Petroleum hydrocarbons (PHC) represent over 60 % of Canada's contaminated sites (CCME 2001a). They are defined by CCME (2001a) as mixtures of organic compounds found in or derived from geological substances such as oil, bitumen and coal. PHCs can represent thousands of chemical compounds, depending upon the source of the contamination and the degree of refining and/or weathering. PHCs are regulated in soil so as to address six primary concerns (CCME 2001a):

1. Reactivity / volatility,
2. Toxicity,
3. Mobility and transport in ground, water or air,
4. Environmental persistence of larger and branched molecules,
5. Aesthetic concerns (odour, taste and appearance in environmental media), and
6. Degradation of soil quality (water retention, transmission and nutrient cycling).

The Canada-Wide Standard for Petroleum Hydrocarbons in Soil (PHC CWS) provides a standard for remediation based on the principles of risk assessment. This risk assessment is conducted for several hypothetical situations defined by land use, soil characteristics and depth of burial. Maximum PHC concentrations in soil are determined for each case based on (CCME 2001a):

1. Identification of receptors and resources to be protected,
2. Potential pathways of exposure, and
3. Tolerable exposure to each receptor.

The PHC CWS offers three management options (CCME 2001a):

- Tier 1 - Remediation to generic numerical levels contained in the Standard,
- Tier 2 - Remediation to adjusted Tier 1 levels based on site specific information, and
- Tier 3 - Site specific risk assessment with possible continued risk management.

The CCME limits are based on a substantial study undertaken by the United States Total Petroleum Hydrocarbon Criterion Working Group (USTPHCWG), a multi-party research panel charged with developing safe and achievable guidelines for petroleum hydrocarbons in soil (Gustafson et al. 1997). The USTPHCWG identified 13 compounds or fractions (based upon carbon number) of interest. These consist of two specific target compounds, benzene and toluene, and 11 hydrocarbon fractions. Each compound or fraction is subject to maximum concentrations in soil (Gustafson et al. 1997). The CCME has combined the USTPHCWG's 13 groups into 4 fractions based upon carbon number and 4 target compounds (CCME 2008). Both systems are illustrated in Table 2.3.

Research by the CCME has indicated that typical hydrocarbon contamination is composed of 80% aliphatics and 20% cyclics. This distribution was used to consolidate the PHC carbon number fractions under the CCME system. The CCME states that by using this approach the Canadian system provides a similar degree of protection with much reduced analytical requirements (CCME 2008).

2.4.2 Analytical Methods

To ensure consistency in analytical data, the CCME has prepared a Reference Method or Benchmark Method for quantitative analysis of PHCs in soil. This benchmark prescribes several analytical approaches depending upon the analyte considered.

The light hydrocarbon fraction, F1, is analyzed by "purge and trap" gas chromatography with flame ionization detection (GC-FID) (CCME 2001b). In this method, hydro-

Table 2.3: North American classification systems for PHCs in soil

USTPHCWG (Gustafson et al. 1997)		CCME (CCME 2001a)	
Carbon Number		Fraction Name	Carbon Number
Aliphatic	Cyclic		
5 - 6	Benzene	B	Benzene
6 - 8	Toluene	T	Toluene
8 - 10	8 - 10	E	Ethybenzene
10 - 12	10 - 12	X	m,n,p -Xylenes
12 - 16	12 - 16	F1	6 - 10
16 - 35	16 - 21	F2	10 - 16
	21 - 35	F3	16 - 35
		F4	35 - 50+[a]

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[a] by various methods

carbons are extracted from soil by shaking in methanol for one hour. The methanol is transfered to a vial suitable for connection to the gas chromatograph. On the chromatograph, a carrier gas is bubbled through the solvent, to purge it of extracted volatiles. The gas is then passed through a sorbant cartridge, or directly onto an appropriate column where the volatile analytes are concentrated, or trapped (Fowlis 1995). The column is then heated through an appropriate temperature program.

Heavier hydrocarbons, F2 and up, are first extracted in a soxhlet apparatus using a 1:1 hexane:acetone solution for 18 to 24 hours (CCME 2001b). The soxhlet is a common piece of laboratory glassware for chemistry applications. The complete assembly provides for a receiving chamber at the base, an upper chamber above the base with two connections to the lower chamber and a cooling tower at the top. When the soxhlet is first set up, the extracting solvent is placed in the lower chamber, and the sample to be extracted is placed in a filter in the upper chamber. The solvent is gently warmed, but not boiled, to increase the evaporation rate. The volatilized solvent rises through the upper chamber and into the cooling tower where it is condensed. This condensate drips into the upper chamber and mixes with the sample. When the upper chamber has accumulated enough solvent, a siphon is developed which drains the upper chamber back into the lower chamber. This process of flushing, or reflux, into the lower chamber continues for 16 to 24 hours (CCME 2001b). Eventually all extractable hydrocarbons have accumulated in the lower chamber. The contents of this lower chamber, known as the extract, are then passed through a column containing sodium sulphate (CCME 2001b) to remove any water molecules that might be included in the extract. The volume of extract is reduced by evaporating most of the remaining solvent in a roto-evaporator. The remaining extract is then passed through a column of #60 to #200 mesh silica gel (CCME 2001b) to remove polar compounds. The column is rinsed with 1:1 hexane:dichloromethane and the volume is again reduced (CCME 2001b). This process of cleaning the sample by passing it through the silica gel is optional (CCME 2001b), but was included to reduce the interference of other organic compounds present in the tarball material. The extract is then transferred to a vial for GC-FID analysis.

According to the CCME Benchmark Method, alternative methods must be applied if there is evidence that not all hydrocarbons have eluted by the end of the C34 to C50 window (CCME 2001b). This evidence is usually the GC trace, which should return to baseline. If the trace has not returned to baseline, two options are available. These two alternatives are high temperature gas chromatography (F4-HTGC) or gravimetric analysis (F4G). The CCME agreement states that each jurisdiction is free to accept whatever method is deemed appropriate. The province of Alberta allows HTGC as well as gravimetric determination of F4 hydrocarbons in contaminated soil (Alberta Environment 2007).

High temperature gas chromatography (HTGC) is capable of analyzing to approximately C90 (Swyngedouw 2010). This is appropriate for most hydrocarbon applications, including crude oil contamination. The gravimetric method uses the same sample preparation procedure, however, in place of chromatographic analysis, solvent is simply evaporated in a fume hood and the residue is weighed using a micro balance. The results are reported as F4G. The resulting hydrocarbon concentrations would be expected to contain most of F2 through to the heaviest molecular weight hydrocarbons. In the case of tarballs, this is expected to include bitumen molecules well over C100 (Peramanu et al. 1999).

However, it has been found in recent hydrocarbon analyses that under HTGC conditions the trace does not return to baseline for tarball samples. Thus F4-HTGC values should not be considered to accurately represent concentrations of all hydrocarbons heavier than C34 F4-HTGC, but rather a window from C34 to about C90. F4-HTGC values are presented with other hydrocarbon data for informational purposes. This may foster discussion regarding the application of HTGC to environmental analyses of tarball and other bitumen materials.

2.5 Contaminant Transport - Hydrocarbon Mobility

Mass transport in groundwater has been the subject of academic and practical study for several decades. Much of the theoretical framework is well established. The intent of this section is not to completely review the research to date, as this is the subject of several textbooks [notably Freeze and Cherry (1979), Domenico and Schwartz (1998), and Fetter (1980), among others]f. The intent here is to provide an overview of mass transport mechanisms and how they might relate to the problem at hand.

2.5.1 Mass Transport Processes

Mass transport begins at the point of contamination, or source. Here chemical or biological elements are released into the environment at levels exceeding existing conditions, known as background. Sources may be natural, as in the case of subterranean salt solution, or anthropogenic, for example at the release from wastewater treatment plants. Where the substance contacts groundwater, it may spread underground by means of advection, diffusion and/or dispersion (Freeze and Cherry 1979; Domenico and Schwartz 1998).

Advection - Advection is movement by groundwater flow. This is equivalent to the average linear groundwater velocity (Freeze and Cherry 1979). Total energy, termed 'head', drives the movement of groundwater through porous formations. Under fully saturated conditions, this energy may take the form of pressure, velocity or elevation. As the water moves, it carries dissolved and/or suspended materials with it. Displacements are dependent upon hydraulic gradient and material properties, primarily those associated with porosity. In the case of unsaturated flow, pressure becomes negative, creating a suction throughout the porewater. Displacement again depends upon the hydraulic gradient and porosity, but is reduced by the limited cross sectional area available for water movement. Advection in groundwater is essentially a unidirectional phenomenon, causing displacement in the direction of flow. However this flow direction is subject to change in both space and time.

In cover systems, such as those found in the Athabasca Oil Sands region, advection is generally downward, from the soil surface to the bottom of the cover and on. If hydrocarbons are present in the cover soil they may dissolve into the water and pass through the cover into the underlying material. If no other processes interfere, the hydrocarbons will eventually reach groundwater reservoirs, where the hydrocarbons may accumulate or in turn flow toward the Athabasca River. In the case of a sloping cover water may travel downslope more easily in the cover soils (Domenico and Schwartz 1998), creating a "channel" of porewater. If this were to occur, greater hydrocarbon concentrations might be expected in the leachate water as a result of exposure to significantly more hydrocarbons while travelling the length of the cover as opposed to the thickness.

Diffusion - Molecular diffusion occurs through all media, but is especially effective in liquids and gases. In these fluids, particles will self equilibrate by spreading from high to low concentration due to the concentration gradient. Diffusion acts independently of the movement of groundwater. Thus due to diffusion, contaminants are often detected in advance of strictly advective transport (Domenico and Schwartz 1998; Fetter 1980). In conditions of very slow groundwater movement at long periods of time, diffusion will dominate (Freeze and Cherry 1979). Diffusion is a homogeneous, isotropic, three dimensional process and therefore acts in all directions in homogeneous, isotropic saturated soil.

Diffusion also occurs across physical phases. Thus the hydrocarbons present in the soil might also be expected to migrate to the vapour phase. At high levels of saturation, the vapour phase may be predominantly disconnected, thereby isolating these volatilized hydrocarbons. At low levels of saturation, as expected in field conditions, the vapour phase will be connected throughout much of the soil profile, allowing volatilized hydrocarbons to migrate to the surface and enter the atmosphere.

Diffusion of hydrocarbons within the soil water and vapour might be expected in soil covers constructed with tarball material. This will spread dissolved hydrocarbons over a larger area than simple point contacts. The effect is likely to dilute hydrocarbon concentrations in the soil water or gas fluxes.

Dispersion - Dispersion represents the mechanical mixing of a solute as water passes around individual mineral grains in the soil matrix (Freeze and Cherry 1979). Larger pore spaces act as larger channels which carry a greater volume. Thus some solute is inhibited by the soil structure while other may be carried forward ahead of the net advective transport. Dispersion behaves much the same as diffusion. In engineering practice, the two are often combined mathematically in the form of hydrodynamic dispersion (Domenico and Schwartz 1998).

However, dispersion is not isotropic. Dispersion parallel to the direction of flow (longitudinal) is distinctly different from dispersion across the direction of flow (lateral) (Freeze and Cherry 1979; Domenico and Schwartz 1998). This longitudinal dispersion is often the most significant concern in contaminant transport analyses, and has been found to be scale dependent. Measurements taken farther apart indicate greater levels of dispersivity. This is attributed to various scale dependent physical effects (Domenico and Schwartz 1998). At the smallest level, dispersion is caused by the tortuous flowpath around soil grains. At the mid-level, the effects of lamination within a geological formation will promote physical mixing across the layers. Likewise at the largest scale, the stratification of geologic formations also contributes to a physical mixing. Any one of these effects may dominate depending upon the regional geology and the scope of the groundwater investigation.

Although dispersion is likely to occur in the movement of these contaminants, it's effects are likely not significant from an engineering standpoint. Where quanitifiable, these effects will likely be considered in combination with diffusion as hydrodynamic dispersion.

2.5.2 Mechanisms Altering Mass Transport

The transport of solutes through soil provides the opportunity for interactions with various other components of the soil system. These might include other solutes, matrix materials and/or soil organisms. This may result in changes to solute chemistry, solute adsorption onto the soil solids or solute loss due to degradation or decay. This is generally referred to as phase partitioning, which is understood to occur along the flowpath.

SORPTION - Sorption represents the chemical and electrostatic processes that cause the solute to cling to the soil grains (Domenico and Schwartz 1998). This brings the solute out of solution, reducing contaminant concentrations. Some sorption processes are reversible, like physical adsorption caused by Van der Waals forces, but others are not, such as surface chemical reactions. Reversible processes delay the arrival of the contaminant with respect to the advective front (Freeze and Cherry 1979). In theory, irreversible processes could completely sequester contaminants by removing them from solution.

To understand the potential impacts of sorption processes on hydrocarbon mobility, something must first be understood about the solubility of hydrocarbons in water. Hydrocarbons with the lowest carbon number are the most likely to dissolve in water. Solubility declines significantly with increasing carbon number, however detectable levels of hydrocarbons are present in water well into the F3 range of the CCME guidelines (Gustafson et al. 1997). Hydrocarbons of heavier molecular weight are essentially insoluble. This means that only a small portion of tarball hydrocarbons will show any tendency to dissolve in water. This tendency to dissolve will be countered by a greater preference for remaining sorbed with the tarball material. Even those hydrocarbons that do dissolve might be largely removed from solution if they encounter other tarball material while moving through the soil.

Essentially, the tarballs might be expected to act as a hydrocarbon sponge, holding even those more mobile fractions in place. This would result in aqueous hydrocarbon concentrations below those expected based on tarball concentrations. The presence of F1 hydrocarbons in the tarballs suggests that this is the case.

Reaction - Chemical reaction, either in solution or between solute and soil mineral, will alter or sequester contaminant species as they move through the soil matrix. Reactions that occur relatively quickly with respect to groundwater flow will reach equilibrium conditions. In this case, relatively simple equilibrium models can be applied to predict the evolution of groundwater chemistry.

Hydrocarbons are seldom subject to chemical reaction in groundwater. Hydrocarbon reactions typically require a catalyst or elevated temperature or pressure, which are not present in groundwater settings.

Decay and Biodegradation - Other chemical processes, not necessarily the result of chemical reactions, also result in the modification of a particular compound. For example, radioactive decay transforms heavier elements into lighter ones with the emission of radiation. The breaking up of organic compounds by microbial activity is known as biodegradation. Biodegradation occurs as biotransformation, which alters the existing compound, or mineralization, which reduces organic compounds to mineral compounds such as CO_2 or H_2O. Although the stoichiometry of each reaction will depend upon the specific hydrocarbons involved, an approximation for heavy hydrocarbons using a diesel molecule has been employed by Zytner et al. (2001). The equation is given as follows:

$$C_{16}H_{34} + 24.5O_2 \longrightarrow 17H_2O + 16CO_2 \tag{2.1}$$

Degradation occurs as various microbes take in carbon and produce their energy by the reaction of organic compounds with other chemicals. Biodegradation occurs most readily in the presence of oxygen (aerobic) but can also be stimulated by various other chemicals, such as nitrogen or sulphur. These various decay processes decrease exponentially, meaning that as concentration decreases, the rate of elimination also declines. This allows the use of a first order exponential decay model.

Biodegradation is expected to occur with tarball materials, primarily as biotransformation, although some mineralization will also occur. Biotransformation does not lead to the complete elimination of hydrocarbons because microbes do not simply attack one molecule and reduce it to it's consitutent elements. Instead they are most likely to break simple bonds, fracturing large, complex molecules into several smaller compounds. These small components are more mobile and more soluble, making them relatively more likely to be detected in this study.

Chapter 3

Methods and Materials

3.1 Introduction

This study was carried out under two broad objectives. These were; first to identify the PHC composition of the tarball materials, and second, to determine the tarball PHC leaching and biodegradation potential.

It was recognized at the beginning of this study that tarball PHC composition was poorly understood. Tarball PHC composition is critical within the regulatory framework for reclamation planning and to understanding the leaching and biodegradation behaviour of tarballs. To address this gap in knowledge, tarball PHC concentrations were assessed from samples collected during four separate field investigations at three mine sites. The tarball samples were analyzed for PHCs according to the CCME benchmark method. The results were presented using the Canadian industry standard CCME four fraction plus BTEX system.

The primary focus of this study was to determine and assess the potential impacts to the environment of incorporating tarball materials in reclamation covers. Of particular interest were the leaching and biodegradation characteristics of the tarballs. To this end, a custom designed soil column leaching study was carried out in the Geoenvironmental Lab at the University of Saskatchewan in Saskatoon, Canada. The column study consisted of six soil columns packed with clean native sand and tarball material. The columns were assembled on the basis of two triplicates segregated on the basis of the depth at which the tarball material was recovered below ground surface. That is to say, three columns were assembled using tarballs recovered from the top metre of the native soil profile and three columns were assembled using tarballs recovered from below the top metre of the native soil profile. The columns assembled with tarballs recovered from the top metre are identified as “Shallow” or “S” columns. The columns assembled with tarballs recovered from below one metre are identified as “Deep” or “D” columns.The The volume of tarballs placed in the column was intended to be representative of a wost case reclamation scenario as identified by Paragon (2006).

All PHC migration and degradation pathways were monitored to determine PHC fate. The columns were leached under unsaturated conditions to simulate the mechanisms acting on a reclamation cover as closely as possible. Leachate was monitored for PHCs, total carbon and total organic carbon. Respiration of the soil column was monitored for oxygen, carbon dioxide, methane and PHCs to determine volatilization and approximate PHC degradation. The PHC concentration of the tarballs was determined at the beginning and end of the mobility study to develop a carbon budget.

This Chapter describes the materials and methods applied to determine the tarball PHC composition, leaching potential and biodegradation potential.

3.2 Tarball Soil and Petroleum Hydrocarbon Characterization

Several field studies were carried out in order to collect tarball samples for PHC analysis. Field studies were conducted at Syncrude’s Aurora North Mine and Suncor’s (formerly Petro-Canada’s) Fort Hills mine site. A cursory visit to Shell’s (formerly Albian Sands’) Muskeg River mine was carried out in order to collect tarball samples from formerly saturated soils for comparison. Tarball samples were collected and either shipped directly to Exova Labs or returned to the University of Saskatchewan for processing and subsequent laboratory analysis. The physical characteristics of each tarball sample were noted during fieldwork, such as depth below ground surface and the in-situ manifestation (ball, block or band). On two of the field studies, adjoining soil samples were also collected for subsequent laboratory analysis. Field and laboratory methods for the PHC characterization study are presented in this section.

3.2.1 Sampling Procedures

Prior to carrying out the fieldwork, on-site personnel from the lease holder identified areas known to have tarball accumulations. These areas were then scouted to select appropriate study areas. An appropriate study area typically consisted of the following:

- a soil profile with significant tarball accumulation,
- the opportunity to collect multiple samples from multiple depths, and
- an exposed vertical face (typically available in road sand pits or other cut areas).

After a soil profile had been selected, exposed soil was removed by an excavator or hand shovel to reveal fresh soils behind. Hydrocarbon samples were taken according to best practices as discussed in Section 3.3. Vertical profiles were recorded for each sampling location for future reference. The profiles included layers of tarball affectedness and visual estimates of the area affected. The approximate depth below ground surface and the type of in-situ manifestation were also recorded. The manifestations were identified as one of three broad categories as described below.

- Ball - any discrete accumulation of bitumen having a somewhat spherical shape. Tarballs categorized as balls ranged from a few centimetres to several metres in diameter.
- Band - repeated long and thin horizontal layers of alternately tarball and bitumen free sand. Each bitumen impregnated layer in these accumulations was typically only a few millimetres in thickness, however the entire accumulation might consist of several centimetres.
- Layer - relatively extensive and thick accumulations of bitumen, typically tens of centimetres thick and extending up to tens of metres horizontally.

Samples of apparently bitumen free adjoining soils were collected from above and below the hydrocarbon samples during two field visits. The bitumen free soil samples were stored in sealable sandwich bags and kept at 4 °C until they could be analyzed.

3.2.2 Tarball Bitumen Removal

Hydrocarbon samples were analyzed for all hydrocarbon fractions according to the procedures outlined in Sections 3.4 and 2.4.2. Prior to grain-size analysis, bitumen was removed from tarball samples according to a modified proprietary procedure supplied by Syncrude Canada Limited. In this method samples were shaken in Dichloromethane (DCM), then centrifuged and decanted. The process is repeated, typically three to five times, until the solvent remains visibly clean after shaking.

3.2.3 Grain-size Methods

Several soil parameters were measured for each washed tarball and adjoining soil sample. The parameters are given in Table 3.1. These parameters were used to compare tarball and adjacent soil properties. Several parameters were also investigated for relationships between F3 and F4G content in tarball samples.

Table 3.1: Tarball soil characteristics studied

Symbol	Item	Units	Formula
Θ	volumetric moisture content	v/v	$\frac{\text{volume of water}}{\text{volume of voids}}$
D_{50}	median grain-size	mm	
D_{10}	characteristic grain-size	mm	
C_u	uniformity coefficient		$\frac{D_{60}}{D_{10}}$
C_c	coefficient of gradation		$\frac{D_{30}^2}{D_{60}*D_{10}}$
	silt and clay content	%	passing the # 200 sieve

Where D_{60}, D_{30}, and D_{10} are the soil particle diameters at which 60%, 30%, and 10% of soil particles are finer by mass. In this study, ASTM $D422 - 63$ methods were applied.

3.3 Laboratory Analysis for Petroleum Hydrocarbons

Best practices for laboratory analysis of hydrocarbons were followed throughout this study. Hydrocarbon analyses were conducted on both soil and water samples. Samples were collected in pre-cleaned glass jars with teflon lined lids. Headspace was minimized within the jars. Every precaution was taken to maintain the sample between 0 and 4 °C between sampling and arrival at the laboratory.

The one exception to these practices were the tarballs collected for the laboratory experiment. These were collected frozen at the end of February, 2008 and maintained frozen until they could be packed in the soil columns in mid April, 2008. The tarballs were stored in five gallon High Density Polyethylene (HPDE) pails. A matrix of crushed tarball material was provided for support and also to minimize headspace within the pail to reduce the possibility of losing the volatile fraction.

3.4 Hydrocarbon Analyses

Chromatographic analyses of non-volatile hydrocarbons were conducted as an interlaboratory study between Exova Labs (Exova) in Calgary, Alberta (formerly Bodycote, previously Norwest) and Environment Canada's (EC) National Hydrology Research Centre (NHRC) Labs in Saskatoon, Saskatchewan. Work at Exova was overseen by Dr. Chris Swyngedouw and at EC by Dr. John Headley. This approach was selected in order to develop an understanding of the inter-laboratory repeatability of tarball PHC analyses. In the F2 to F4G range, approximately half of tarball samples were analyzed at Exova and half at NHRC. Due to equipment limitations at NHRC, all volatile analyses (BTEX and F1) were conducted at Exova.

Hydrocarbon analysis in soil was conducted according to the CCME benchmark method discussed in Section 2.4.2. A brief summary of the method highlighting particular modifications is provided for each analyte below.

3.4.1 Volatile Hydrocarbons - F1

Volatile hydrocarbons were analyzed only at Exova Labs in Calgary. Samples from the field were packed into pre-cleaned 250 or 500 mL jars with minimal headspace. PHC samples taken from tarballs in the laboratory were preserved on methanol. All samples were shipped in ice to Exova labs. These samples were extracted by shaking in methanol for one hour. The methanol was then transferred to a vial for gas chromatography. The purge and trap method was used for analysis. This consisted of bubbling a carrier gas through the methanol to volatilize the analytes, which are then carried into the column and trapped by sorbtion.

Volatiles were analyzed on an Agilent 7890 gas chromatograph. The system was equipped with a CombiPal system and dual column analysis for simultaneous Flame Ionization Detection (FID) and Mass Spectrometry (MS). The columns were an HP-1MS 30 metres long with 0.25 mm inner diameter and a DB-1 30 metres long with 0.32 mm inner diameter. The system was operated with 7:1 split injection at 200 °C. GC runtime was 30 minutes with a detector temperature of 250 °C. This system was used to analyze from C6 to C10, plus selected aromatic hydrocarbons, Benzene, Toluene, Ethylbenzene and n, m, p - Xylenes.

3.4.2 Non-Volatiles at Environment Canada Labs - F2 and F3

Non-volatiles in the F2 and F3 range were extracted in a soxhlet apparatus using a 1:1 hexane:acetone mixture, as described in Section 2.4.2. After extraction, the solution was passed through a column of dried sodium sulphate to remove any water present. The volume was reduced and the solvent was passed through a column of activated silica gel to remove polar compounds that might cause false detections. The volume was again reduced and transfered to an appropriate vial for chromatographic analysis.

The F2 and F3 fractions were analyzed on a Hewlett Packard 5890 standard gas chromatograph with a cool on-column injector. The column was an MXT-1, 30 metres long with 0.53 mm inner diameter. The maximum oven temperature was 265 °C and the detector temperature was 295 °C. The program began with an isothermal period to remove the solvent and was 50 minutes long in total. The system was capable of analyzing carbon numbers from C10 to about C43. Gravimetric methods were required to analyze for F4. At NHRC, concerns regarding the operability of the instrument under the influence of the sticky bitumen led to the adoption of a 2.5 gram soil sample instead of 5.0 grams as indicated in the CCME method.

3.4.3 Non-volatiles at Exova Labs - F2 and F3

Sample extractions were performed as described in Section 3.4.2. Exova labs used an Agilent 7890 high temperature gas chromatograph in splitless injection mode. The column was an Agilent J&W DB1HT, 30 metres long with 0.32 mm inner diameter. The length was reduced to 10 metres by Exova. The maximum temperature was 400 °C and the detector temperature was 425 °C. This system is capable of analyzing carbon numbers from C10 to C90, however the system is calibrated only to C60. Most Exova data also includes F4G values for comparison.

3.4.4 Heavy Hydrocarbons - F4 by Gravimetric Methods

Sample extractions were performed as described in Section 3.4.2. Gravimetric quantification of the F4 fraction was carried out on most samples in this study to address several concerns. The baseline trend of tarball samples in the HTGC system at Exova Labs indicated that not all of the sample had eluted at the end of the temperature program. Additionally, this also meant that the sample had continued to elute beyond the calibration of the instrument, which may have led to inconsistent integration methods for various samples taken in previous field monitoring and investigations. There were also equipment limitations at Environment Canada which prohibited high temperature analysis at that facility.

Gravimetric samples analyzed at Environment Canada labs were split from the non-volatile extracts. These extracts, as indicated in Section 3.4.2, were taken from a soil sample of 2.5 grams in place of 5.0 grams as indicated by the CCME.

As discussed in Section 2.4.2, the F4G fraction contains most hydrocarbons from F2 through to the heaviest molecular weight present in the sample. Thus the gravimetric method can be used to quantify the heavy fractions, but can also serve as an approximate check on chromatographic methods. This check provided a valuable insight into the composition of tarball hydrocarbons, ultimately showing that a significant portion of hydrocarbons were going undetected by gas chromatography alone.

3.4.5 Hydrocarbon Analyses in Water

Extraction and analysis of hydrocarbons in water was conducted according to Alberta Reference Method A108.0. This method was provided by Exova as their preferred method. Extractions and analyses were performed at Environment Canada Labs in Saskatoon.

The extraction method consisted of shaking the complete water sample with 50 mL of DCM in a separatory funnel. The solvent was then drained through a column of sodium sulphate to remove any dissolved water. This process was repeated twice, for a total of three extractions from the sample water. The volume of the extract was reduced on a roto-evaporator then transferred to a vial for gas chromatography. Extracts were analyzed by the same GC and methods presented in Section 3.4.2.

This method indicates a sample volume of one litre. Although sample volumes sometimes varried, most samples were between 250 and 275 mL. The reduction in sample volume was required due to experimental constraints on the volume of leachate available at reasonably frequent intervals. Through consultation with Exova labs it was determined that these volumes were sufficient for laboratory analysis.

3.5 Tarball PHC Leaching and Mobility Study

3.5.1 Introduction

A leaching and mobility study was conducted to address several questions regarding tarball behaviour in reclamation soil covers. The experiment was designed to assess the potential for PHC leaching to groundwater, tarball biodegradation, and a preliminary assessment of impacts to the soil moisture regime.

3.5.2 Column Design

Teflon lined steel columns were designed and constructed at the University of Saskatchewan machine shops. The columns were 0.30 m in diameter and 1.0 m tall. In order to reduce any sorbtive or catalytic effects all interior surfaces were teflon lined, glass, or stainless steel to the greatest extent possible. The columns were equipped with a glass lid that provided for a glass access tube down the centre, as shown in Figure 3.1. The access tube allowed the use of a SenTek Diviner 2000, capacitance moisture probe (SenTek Pty Ltd., Stepney, South Australia). A Columbus Instruments Micro-Oxymax Respirometer (Columbus Instruments, Columbus, Ohio) was connected to the column headspace for automated monitoring of Oxygen, Carbon Dioxide and Methane gases. A photograph of the columns set up in the lab is provided in Figure **??**

Beginning at the base, the soil columns consisted of a 10 cm reservoir of coarse silica sand (Oglebay Norton, Colorado Silica Sand, Colorado Springs, Colorado). The sand was autoclaved prior to placement in the columns to prevent the addition of external microbes. This sand created a capillary break that held the soil water in tension to separate the simulated cover from the collection reservoir. The break also allowed for the collection and sampling of leachate water, up to a total volume of about one litre. Teflon tubing for leachate sampling was connected via the bottom plate of the column, below the reservoir.

A 60 cm layer of a synthesized tarball-affected soil was placed above the reservoir. This soil was synthesized from tarballs and a clean native sand. The clean native sand was taken from the same vicinity as the tarball samples, but from a layer of containing no tarballs. The clean native sand was analysed to confirm the absence of detectable hydrocarbons.

The tarballs were placed in the column in a state representative of field conditions after reclamation. The author observed reclamation operations and noted that the tarballs remain essentially intact during excavation. It was only those accumulations cut through by the excavator bucket that were broken apart. Consequently, great care was taken to ensure that the tarballs were not broken apart during transportation or when the columns were packed.

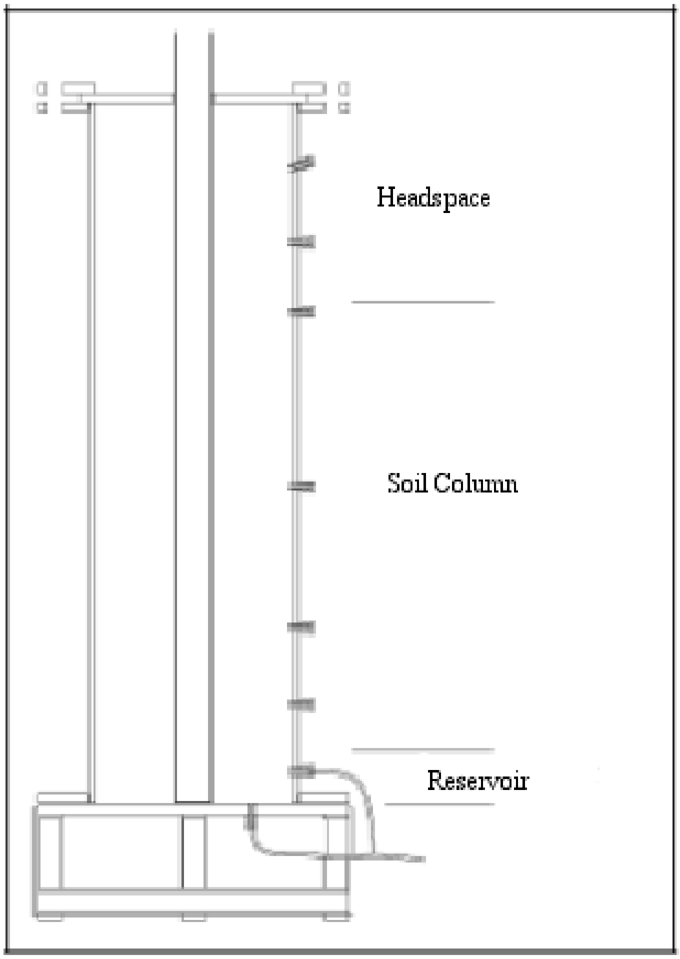

Figure 3.1: Schematic soil column cross section

Sand and tarballs were packed into the columns in four layers. Each layer was approximately 0.17 m in thickness when placed loose. Each of the four layers received 25 blows of a standard proctor hammer to simulate the disturbance associated with large scale excavation and placement of the material (ie. bulldozer tracks, etc). The total mass of each material added to each column was determined. Additionally, a detailed hydrocarbon sampling program was undertaken when the columns were assembled. Thus the initial geotechnical properties and petroleum hydrocarbon content of the soil was established for each column. The completed soil columns consisted of about 35 % tarball material by volume on average, clean sand making up the balance. This composition is representative of the most heavily affected tarball soils observed in the study area (Paragon 2006).

The remaining volume of the column, about 30 cm in height, provided a headspace atmosphere for sampling of respired and volatilized gases.

It is important to note that no organic amendments were added to the mineral soil or placed on top of the tarball affected soil. In the case of reclamation covers, this material will be present. It is likely to have some effects on the behaviour of the system, primarily as a result of providing additional microbial biomass to contribute to biodegradation and limiting oxygen diffusion into the subsoil.

3.5.3 Flow Regime

The columns were operated under unsaturated conditions, using a low flow peristaltic pump to provide small doses of water four times daily. Determining an appropriate dosing rate presented a typical case of competing design objectives. This study was not able to replicate field conditions exactly because of the balance required between between maintaining unsaturated conditions and providing adequate volumes of leachate for hydrocarbon analysis.

For the purposes of this study, the average annual precipitation at Fort McMurray (458 mm/year) was taken as an annual flow rate for the columns. This represents significantly greater infiltration than would be expected in the field.

Estimates of infiltration can vary widely, and it is well beyond the scope of this study to determine average annual infiltration in the Athabasca Oil Sands Region. However, as a point of reference, Alberta Environment assumes infiltration of 60 mm/year in developing contaminated soil guidelines (Alberta Environment 2007). This value is based on 10% of average annual precipitation at the location of highest precipitation in Alberta, which is Edson, near Edmonton.

Based on the assumption of ten percent infiltration, net percolation through the column represents about ten times estimated annual infiltration in the field. This flowrate provided adequate water volumes for hydrocarbon sampling at intervals as frequent as four to five days. This is considered an acceptable, but less than ideal, holding time for the analysis of hydrocarbons in water. Increasing the rate of infiltration in the column would shorten this time, but would represent a clearly unrealistic flow condition; reducing the rate of infiltration would lead to unjustifiable retention times in the experimental reservoir.

The water used was dechlorinated Saskatoon tap-water dosed at a rate of 460 mm/year. This dosing was equivalent to 1.3 mm/day, or 90 mL/day in the 0.30 m diameter column. The water was dosed four times per day in increments of 22.5 mL.

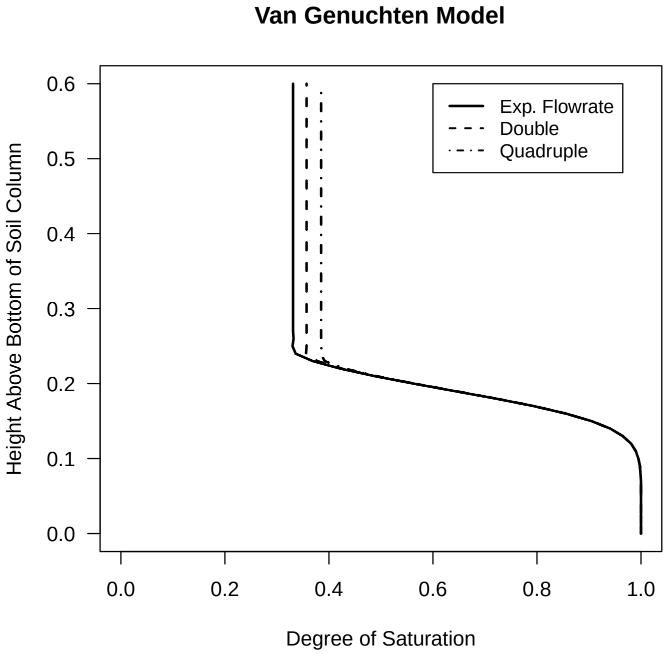

Figure 3.2: Soil moisture content prediction for experimental conditions

Microbial activity and gas flux can be greatly inhibited at high levels of saturation. It was necessary to confirm that such a condition would not develop in this experiment. Using the method of van Genuchten (1980), a model of volumetric water content was prepared for this soil. To establish the Van Genuchten parameters, one full scale column was assembled. This column contained only the clean sand packed at an average density of 1460 kg/m^3. It was subjected to two cycles of saturation and drainage to determine drainable porosity. Readings were taken after drainage had nearly stopped to determine the van Genuchten parameters for the soil. Volumetric water contents were determined using a Sen-Tek Diviner 2000 capacitance probe (which is described in Section 3.5.4) in the glass tube. This provided a direct measurement of volumetric water content across the height of the column. The model was calibrated to the experimental data by inspection; simply adjusting the parameters until the volumetric water content curve matched the observed data points as best as possible. Assumed parameters required for the model were; saturated volumetric water content $\Theta_s = 0.37$, and residual volumetric water content $\Theta_r = 0.04$. The resulting van Genuchten parameters for this model were; $\alpha = 0.55$ and, $n = 7.0$. These model parameters were then used to estimate column saturation for multiple flow rates.

The model was used to predict the degree of saturation within the column under experimental conditions using an assumed saturated hydraulic conductivity of $k_s = 10^{-4}$ m/s. The results of this model for several flow rates are presented in Figure 3.2. An estimate of 33% saturation was considered appropriate for the soil under experimental flow conditions. However, because the columns were to be packed with air dried sand, it was necessary to increase the rate of flow during the initial period of the experiment. During this time, water was dosed at four times the experimental rate. According to the model predictions, this would result in 40% saturation under a steady state condition. Under both conditions, the volumetric water content was considered adequate to maintain predominantly aerobic conditions in the soil column. The presence of water begins to affect the movement of soil gases at low water contents, however, significant limitations, particularly in sands, require a relatively high degree of saturation. While some impact on soil gas movement is expected in the columns, significant impacts are considered unlikely. Model predictions of moisture content are given in Figure 3.2.

During normal operation the columns were expected to retain approximately 5 litres of water, providing a complete volume change every 56 days, or approximately 2 months. Leachate water was analyzed for chromatographable hydrocarbons, total carbon and total organic carbon.

3.5.4 Diviner 2000 Water Content Sensor

Volumetric water content within the test columns was monitored by a SenTek Diviner 2000 system. This instrument operates by taking measurements from two horizontal coils, one above the other. When supplied with a current, the coils generate a magnetic field, with a range of influence about 10 cm high and extending radially into the soil. If an alternating current is applied the magnetic field alternates. Polar water molecules in the adjoining soil have a damping effect on the frequency of the alternating current. This is a result of the capacitance of the moist soil. The more water, the greater the capacitance and the more the frequency is reduced, however, it is important to note that this represents an 'average' over the 10 centimetres of influence. The resulting change in frequency can be correlated to volumetric water content. This is achieved by a default calibration equation provided by the manufacturer, or by developing a soil specific calibration equation.

Calibration equations were developed for both the moisture test column and the experimental columns. These equations were developed by taking a reading with the Diviner immediately prior to disassembling the column. Then multiple soil samples were taken at several elevations - corresponding to different water contents on the moisture retention function discussed in Section 3.5.3. The water contents were determined and correlated with the Diviner readings. The Diviner system was used to monitor the moisture regime within the experimental columns. This provided a check to ensure that the column moisture regime developed as intended. It also provided a useful observation of column moisture retention under dynamic flux, which is discussed in Section 5.3.1.

For this study, moisture content profiles have been refined by taking a reading every five centimetres along the soil column. The vertical centre of the probe was taken as the location of each reading. Moisture content at the very top of the column were not presented. Water was released to the soil at three discrete points on the surface. Consequently, some distance was required for the water to distribute itself evenly over the soil cross section. This was demonstrated in that water content readings that included the top five centimetres of the soil column were found to be lower than the rest of the column height. Consequently, water content readings that included the top five centimetres of the column are not presented. Readings at the bottom of the column are also artificially low. At the bottom of the soil column, the reading represents an average over the 10 centimetres in which saturation increases to nearly 100%.

3.5.5 Respirometer

Soil respiration was used as an indicator of microbial degradation during this experiment. This requires the assumption that all soil respiration is associated with microbial degradation of tarball hydrocarbons. Although it is not possible to take direct measurements of only tarball respiration, the columns were packed with only tarball material and a very clean native sand. Any background measurements would be minimal and consistent across all six columns.

Respiration was monitored by a Columbus Instruments Micro-Oxymax automated respirometer (Columbus Instruments, Columbus, OH). The Micro-Oxymax was used to monitor Oxygen (O_2), Carbon Dioxide (CO_2) and Methane (CH_4). The system software provided fully automated data storage, conversion of units and tracking of cumulative respiration. Measurements were taken four times daily. The Micro-Oxymax was connected directly to each soil column via a multi-port manifold. This allowed the system to remain closed, with no input or release of headspace gases during measurement.

In order to maintain headspace gas concentrations at or near atmospheric conditions, the Micro-Oxymax was programmed to exchange the headspace gases with ambient air. In the course of the experiment, headspace gases were exchanged approximately every 25 days. At this frequency, Oxygen and Carbon Dioxide concentrations in the headspace gases deviated from ambient by less than one percent.

3.5.6 Additional Headspace Gas Analyses

Screening for other microbial processes was conducted by measuring for several other headspace gases. These were Ammonia (NH_4), Hydrogen Sulphide (H_2S), Nitrogen Oxides (NO_X), and Sulphur Oxides (SO_X). These measurements were taken via a sampling port located on the front of the columns. Measurements were made using Draeger sampling tubes (Dräger Safety AG & Co. KGaA, Lübeck, Germany). Using this system, measurements are taken by drawing a known quantity of air through a glass tube packed with reactive compounds on a granular substrate. The reactive compounds change colour on contact with the gas to be analyzed, drawing a line of colour change into the tube. Approximate concentrations are determined by reading the mark of discolouration. These methods are commonly used for health and safety monitoring. The manufacturer indicates that measurements are accurate to ± 25 %, the Draeger tubes are reliable for a determining the presence or absence of a given gas. This was the primary objective for these measurements.

3.5.7 Carbon Analyses

Carbon analyses were conducted throughout the experiment to monitor leaching of organic materials. Since hydrocarbon analyses select primarily non-polar organic materials, total carbon and total organic carbon were investigated to provide context for hydrocarbon concentrations in the leachate. The mobility of polar organic matter is significantly different from that of hydrocarbons. The presence of these compounds in the water could possibly limit the ability of the water to absorb hydrocarbons, thereby reducing hydrocarbon mobility.

To the fullest extent possible, carbon analyses were conducted on samples drawn at the same time as those taken for hydrocarbon analyses. Carbon analyses were conducted at the University of Saskatchewan on unfiltered samples using a Tekmar-Dohrmann Phoenix 8000 UV/persulphate analyzer (Tekmar-Dohrmann, Cincinnati, Ohio). A check of filtered samples indicated minimal change in carbon readings.

CHAPTER 4

PHC CHARACTERIZATION

4.1 Introduction

Chapter 4 presents an assessment of the hydrocarbon composition of the tarball materials and outlines several attempts to understand the nature and origin of the tarball material. The amount of hydrocarbon and the composition by CCME fraction were determined. Grain-size information was collected for both tarball and adjacent soil samples. Potential relationships between hydrocarbon content and grain-size information were investigated for potential use in field screening. Grain-size parameters of tarball samples and adjoining soils were examined to identify the relationship between the soils.

4.2 Tarball PHC Concentrations

This study represents the first rigorous analysis of tarball PHC content and composition. This information is critical to assessing potential environmental impacts. A thorough understanding of these impacts can then inform regulatory decisions regarding the potential use of these materials in reclamation. The study of hydrocarbon concentrations also provided an opportunity to validate the CCME PHC methods used throughout this and other studies of naturally occuring heavy hydrocarbons in near-surface soils.

4.2.1 Complete Dataset

Hydrocarbon analyses were conducted on 276 tarball samples. Metadata for this dataset is provided in Table 4.1. A data summary is provided in Table 4.2 and in Figure 4.1.

Figure 4.1 summarizes the results for all samples above detection limits. Median, quartile and outlier hydrocarbon concentrations are presented as bold lines, normal lines and open circles respectively. This same dataset is presented in Table 4.2 under the heading of "Detections Only." This approach gives a general picture of the values encountered, but does not represent overall hydrocarbon concentrations in the field. This is particularly true for the lighter fractions; for example Table 4.1 indicates that the F1 figures are based on just 13 values out of 168 analyses. In order to present more 'typical' values of hydrocarbon composition, the headings of "All Values" and "Excluding Outliers" in Table 4.2 are calculated using a value of zero for non-detects.

Table 4.1: Summary of tarball PHC samples analyzed

Fraction	Carbon Number	Number of Detections	Number of Samples Analyzed	Number of Outliers	Lab		Nominal Detection Limit
					Exova	EC	
F1	C6 to C10	13	168	3	168	–	20
F2	C10 to C16	68	276	10	91	185	20
F3	C16 to C34	272	276	15	91	185	30
F4-HTGC	C34 to C50+	147	147	11	91	0	30
F4G	C34 to C50+	220	220	4	91	129	500

A further complication is added by the case of "rich cores." During hydrocarbon sampling, typical tarballs were found to be dry, brittle and exhibit little or no odour. However, occasional tarball samples were found to contain a core of "richer" bitumen. This core was soft and plastic at autumn temperatures of about 5 to 10°C and typically exhibited a significant odour. These cores were in stark contrast to the outer layer surrounding the core, which resembled most other tarball samples. These cores were sampled when encountered and are included in the complete data set. In Figure 4.1, as outliers, and Table 4.2 under the heading of "All Values."

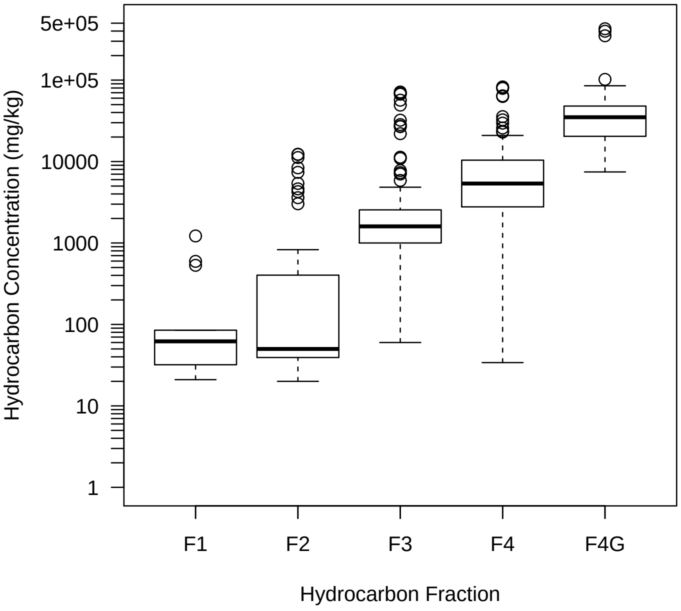

Figure 4.1: Tarball PHCs by fraction

Table 4.2: Hydrocarbon data mean and standard deviation values

Fraction	Regulatory Guidelines[b] (mg/kg)	Detections Only Mean (mg/kg)	Detections Only S.D.[c] (mg/kg)	All Values[a] Mean (mg/kg)	All Values[a] S.D. (mg/kg)	Excluding Outliers Mean (mg/kg)	Excluding Outliers S.D. (mg/kg)
F1	210	219	375	17	112	3	13
F2	150	1,200	2,880	354	1,650	37	125
F3	310	3,470	9,040	3,450	9,015	1,730	1,120
F4-HTGC	2,800	9,740	13,900	9,740	14,800	6,070	5,220
F4G	2,800	39,900	45,000	39,900	45,000	34,700	16,700

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[a] Non-detects as zeros

[b] As established by Alberta Environment for coarse grained soils in a natural environment.

[c] S.D. = Standard Deviation

Including these samples in the calculation of 'typical' hydrocarbon concentrations presents several problems. From a statistical perspective, the samples collected from rich cores cannot be considered random, as they were specifically targeted for sampling when encountered. If a particular layer or tarball was found to have a rich core, then in most cases a sample was collected from this specific location, even though the rich area itself often represented only a small fraction of the total PHC accumulation. Furthermore, the context for including these values in average PHC estimates was not investigated - for example, the frequency of occurrence, volume with respect to total tarball volume, etc. were not quantified in this study. The number of samples taken from these rich cores cannot be considered random, because it was not by chance that these samples were collected. Consequently, the data have been compiled neglecting the outlier concentrations. This is given in Table 4.2 under the heading of "Excluding Outliers". This modification brings the mean hydrocarbon concentration values much closer in line with values from any one particular tarball encountered in the field. For example, the median F3 concentration for all samples was 1,600 mg/kg, which is much closer to the mean excluding outliers than the mean including outliers.

This provides two paradigms for the same data. One in which all samples taken are considered and another in which the bulk of samples are considered with the knowledge that extreme values also occur infrequently. It can be seen that these two paradigms provide a materially different picture of the same data. When non-detects are included as zeros, more representative numbers are seen in the lighter fractions. If outlier concentrations are excluded, values are similar to those found from any one particular tarball

PHC analysis. This is marked by a significant reduction in standard deviation, indicating a much more cohesive data set. Values from the " Excluding Outliers" column will be used throughout the remainder of this thesis. However, it is important to note that hydrocarbon concentrations significantly greater than the mean values discussed in this work are occasionally detected.

4.2.2 Discussion

A general picture of upland tarball hydrocarbons is readily apparent. This picture is presented under the heading of "Excluding Outliers" in Table 4.2 and concurs, in the most part, with expectations. Light hydrocarbons are generally rare, particularly the F1 fraction. Heavy hydrocarbons, F3 and up, are much more abundant. F1 concentrations in a typical tarball are below detectable limits and well below clean soil guidelines. F2 PHCs are present at slightly above detectable limits, but are also well below clean soil guidelines. F3 PHCs are found at nearly six times clean soil guidelines. When F4 is determined by the HTGC method, concentrations are slightly more than double clean soil guidelines, but when the gravimetric method is applied, F4G values are approximately 6 times greater than HTGC values.

This is an interesting distinction between the chromatographable heavy fraction, F4-HTGC, and the gravimetric heavy fraction, F4G. For a typical tarball, the difference represents an order of magnitude. This indicates that the vast majority of tarball hydrocarbons are beyond the upper detection limit of the HTGC system, approximately C90.

The standard deviation of the tarball datasets presented in Table 4.2 indicate high variability in all fractions. Although some variability is expected in naturally occurring materials, this highlighted concerns within the oil sands industry regarding the reliability of the CCME analytical methods when applied to bitumen. These concerns are addressed in Section, 4.2.3. Additionally, several attempts to understand this variability were made in the course of this study. They are outlined in Sections 4.3, 4.4 and 4.5.

The infrequent detection of very high concentrations of light PHCs is a noteworthy finding. Samples collected from the rich cores of tarballs consistently indicated F1 and F2 values of several hundreds or thousands of mg/kg, along with elevated concentrations in heavier fractions. In most cases, these rich cores were sheltered by only a few centimetres of tarball. The cores studied were taken from soils generally conducive to natural biological degradation; relatively dry, sandy soils, below a productive forest and frequently within the top metre of the profile. The texture of the tarballs themselves, as will be seen below, is similar to adjoining soils. It is generally expected that under these conditions F1 and F2 are rapidly mobilized and/or degraded because of their volatility and relatively good solubility and bioavailability. The occurance of very high concentrations of light PHCs indicates that this may not have occurred for all tarballs. It is thought that this indicates an ability for heavier hydrocarbons to shelter lighter fractions, by preserving them, even in surface soils, by an 'onion skin' weathering effect. The mechanics of such an interaction require further study and are potentially of great interest to remediation practitioners in the oil sands industry and beyond.

4.2.3 Chromatographic Method Validation

Quality Assurance and Quality Control measures used during the course of this study are useful in validating the applicability of the CCME analytical methods. The CCME methods were developed primarily to deal with contamination expected from refined petroleum products or crude oil rather than naturally occuring bitumen. There was some concern expressed by the sponsors of the project regarding the repeatability of analyses. In response to these concerns, 15 duplicate pairs, taken from a single tarball sample, were analyzed at NHRC. Duplicates were assessed based on the Relative Percent Difference (RPD). This compares the distance of each duplicate data point, x_1 and x_2, from the mean with the mean value itself, as given by the relationship in Equation 4.1. In GC-FID analyses, 15% is a typical criterion for reproducibility. However when working with environmental media, a more appropriate expectation is 25% due to the heterogeneity of the material itself.

$$RPD = \frac{|x_1 - x_2|}{x_1 + x_2} \times 100\% \tag{4.1}$$

A summary of the RPD data is provided in Table 4.3. Of the 15 duplicate pairs, only one sample had detectable levels of F2. This sample exceeded the 25% criterion. Fractions 3 and 4 exhibited some variability, but on average fell well within criteria. This level of repeatability indicates the applicability of the method given its limitations and the inherent variability of the material.

Table 4.3: CCME PHC method validation results

Fraction	Number of Detections	Number Exceeding 25%	Average RPD	Standard Deviation
F2	1	1	32.4%	–
F3	14	3	15.8%	12.7%
F4G	15	15	9.7%	9.5%

4.2.4 Summary

In this section a general overview of tarball PHC concentrations has been developed. A typical tarball sample contains little or none of the light fractions (F1 and F2) and significant levels of F3 and F4. F3 typically exceeds clean soil guidelines by a factor of 2 to 4 times. When determined using High Temperature Gas Chromatography, the F4 fraction is typically two times the clean soil guidelines, whereas using the gravimetric method the data suggest that F4 exceeds the guideline by an order of magnitude.

The chromatographic methods routinely used in industry and evaluated during this study demonstrate acceptable levels of reproducibility. Tarballs contain significant levels of chromatographable hydrocarbons, but consist primarily of hydrocarbons not detectable by gas chromatography. Instead, the heavy bitumen fraction is most readily detectable by gravimetric analysis.

4.3 Tarball PHC and In-situ Relationships

As discussed in Section 4.2.2, several attempts were made to understand the variability seen in the tarball hydrocarbon samples. It was hypothesized that there might be some relationship between the hydrocarbon content of the tarballs and their physical location and/or the nature of the host materials. Three parameters that were readily quantifiable and might have some relation to hydrocarbon content were selected. Each was studied with respect to the hydrocarbon fractions present. Mean values are compared using a two tailed student-t test. They were:

- depth below ground surface,
- type of in-situ manifestation, and

- depositional environment - as reflected in grain-size of tarball and adjoining material.

Depth below ground surface and the in-situ manifestation are discussed in Sections 4.3.1 and 4.3.2. The depositional environment is addressed in Section 4.4.

4.3.1 Depth Below Ground Surface

The top metre of the soil profile is generally considered by soil scientists to be more chemically and biologically active than deeper regions. There are several reasons for this:

- the activity of plant and animal species living at or below the surface,
- the availability of oxygen from the atmosphere, and
- the gas and moisture fluxes due to precipitation, pressure changes, etc..

It was hypothesized that this activity might lead to enhanced transport and degradation processes operating on tarballs in the top metre. These enhanced processes would be evident in relatively lower hydrocarbon concentrations among tarball samples taken from the top metre. All data points (excluding outliers) which could be analyzed in terms of depth of burial are considered in Table 4.4.

Table 4.4: Tarball hydrocarbon content by depth below ground surface

Sample Set	Number Above / Below 1 Metre	Mean Above / Below 1 Metre F2	F3 mg/kg	F4G	Significant Difference ($p = 0.05$)
Aurora 1	22 / 18	22 / 31	2,280 / 3,150	–	No
Aurora 2	10 / 20	10 / 3	1,500 / 1,600	50,000 / 50,000	No
Fort Hills	14 / 21	17 / 21	1,400 / 1,200	34,000 / 29,000	No
Soil Columns (Aurora)	72 / 72	17 / 25	1,500 / 1,750	35,200 / 32,300	No
All Data		12 / 9	1,420 / 1,520	36,400 / 34,300	No

By comparison of the sample means it is evident that no patterns of hydrocarbon concentration with depth can be distinguished. Although the top metre of soil is more active, the susceptability of tarball hydrocarbons to biodegradation must also be considered. Since tarball hydrocarbons are known to consist primarily of the relatively inert heavy fractions (F3 and F4G), these concentrations have shown little or no change with respect to tarballs at greater depth.

4.3.2 Manifestation Type

It was hypothesized that the physical shape of the tarball might have some relationship to its hydrocarbon concentration. This idea is somewhat intuitive and is also supported by the evidence that thicker manifestations were known to sometimes contain rich cores. It was thought that the availability of the bitumen for degradation might be inhibited at the cores of thicker tarball manifestations, resulting in relatively higher PHC concentrations. It was also considered possible that physical and/or chemical controls on initial concentrations might correlate to tarball shape.

Two sample sets were collected with sufficient information regarding the type of in-situ manifestation. The results are summarized in Table 4.5. Manifestation categories are defined as follows:

- Ball - rounded, isolated accumulation of any size,
- Band - repeating long and thin rows of hydrocarbon impregnated and clean sand, typically a few millimetres in thickness, and
- Layer - expansive accumulations, mostly or completely bitumen impregnated sand, typically tens of centimetres in thickness.

Table 4.5: Tarball hydrocarbon content with in-situ manifestation

Sample Set	Number of Samples from Ball / Band / Layer	Fraction	Mean Ball / Band / Layer (mg/kg)	Significant Difference ($p = 0.05$)
Aurora	12 / 5 / 9	F2	7 / 0 / 3	None
		F3	1,300 / 1,700 / 1,800	None
		F4G	48,000 / 50,000 / 49,000	None
Fort Hills	11 / 16 / 4	F2	35 / 8 / 35	None
		F3	1,000 / 1,200 / 1,600	None
		F4G	32,000 / 27,000 / 41,000	None
All Data	23 / 21 / 13	F2	20 / 6 / 13	None
		F3	1,150 / 1,333 / 1,783	Ball / Layer
		F4G	40,500 / 32,600 / 46,900	Band / Layer

From this data, there are no evident patterns of hydrocarbon concentration with in-situ manifestation. Like depth of burial (Section 4.3.1), the relatively inert nature of the hydrocarbons present are a possible cause of the similarity across the tarball types. In other words, the type of hydrocarbons currently detectable in the tarballs degrade very slowly. Thus samples which may have had differing compositions at deposition may have degraded such that only similar compounds remain. The general absence of volatiles precludes comment on their concentrations at deposition. Clearly no meaningful differences in hydrocarbon composition can be detected at this time, however no conclusion can be extended to the volatile fraction.

4.3.3 Summary

Relationships between tarball PHC contents and depth below ground surface were considered in this Section. No statistical significant differences were found between tarball PHC concentrations of tarballs taken from the top metre of the soil profile as opposed to those taken from below one metre. Based on the overall dataset, significant statistical differences were found between the manifestation types of 'ball' and 'layer' in Fraction 3 and between the types 'band' and 'layer' in Fraction 4G. However, since none of these manifestations were significantly different from the third type considered, the results are not considered particularly meaningful.

4.4 Hydrocarbon Content and Grain-size of Tarball Soils

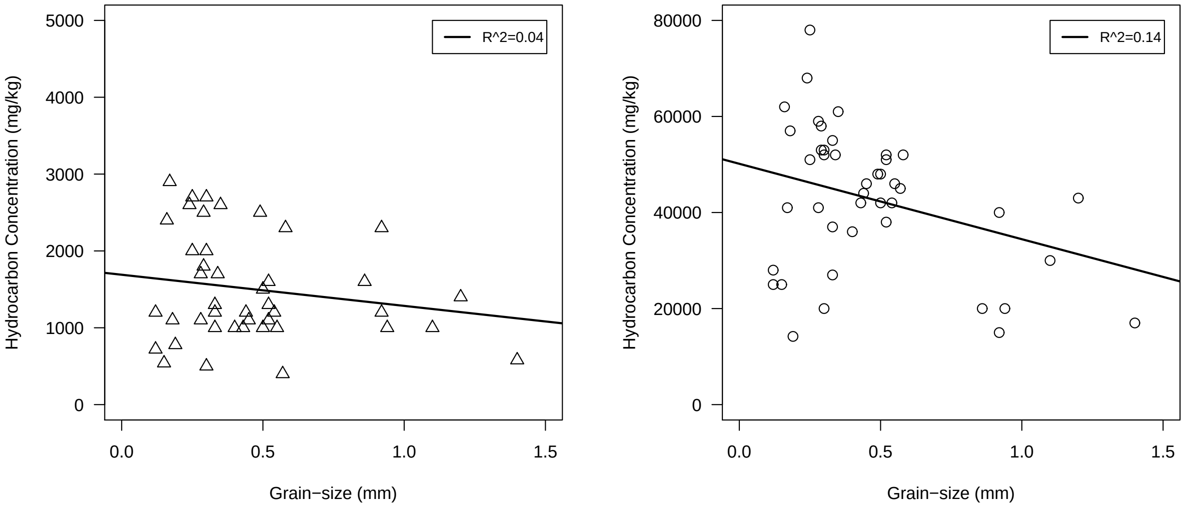
After considerable experience with the tarball materials, the author hypothesized that the grain-size of the mineral component of the tarballs might correlate to hydrocarbon composition. This was considered possible for several reasons. Since tarball soils seem to have the same, or very similar, properties as the host material, perhaps the bitumen was deposited under the same conditions as the surrounding soil, which varies in plan and profile. More turbulent conditions might be expected to deposit hydrocarbons of a different composition than calm conditions as the rolling of the water encourages volatilization of light hydrocarbons. A second possible reason that hydrocarbon concentrations may be linked to grainsize of tarball or host soils is that the various soil hydraulic conductivities might have resulted in increased leaching and degradation rates for tarballs in coarser soils. To test this hypothesis F3 and F4G values were compared with various soil properties. They were:

- median grain-size - which provides an indication of the depositional environment,
- characteristic grain-size - which indicates possible controls on leaching or biodegradation, and
- silt and clay content - which also indicates possible controls on leaching or biodegradation.

Relationships to physical parameters that could be easily determined in the field would be of particular interest to the oil sands industry as this might eventually allow field personnel to perform a simple screening for tarball soils with elevated PHC concentrations. This is significant in a reclamation setting, where limits might be imposed by regulators, or perhaps the industry itself, on soil PHC concentrations.

4.4.1 Median Grain-Size

The median grain-size (D_{50}) represents the particle diameter at which half of the sample, by weight, is of larger diameter and half is of smaller diameter. Hydrocarbon Concentrations are plotted against median grain-size (D_{50}) in Figures 4.2a and 4.2b.



(a) F3 Hydrocarbons with median grain-size

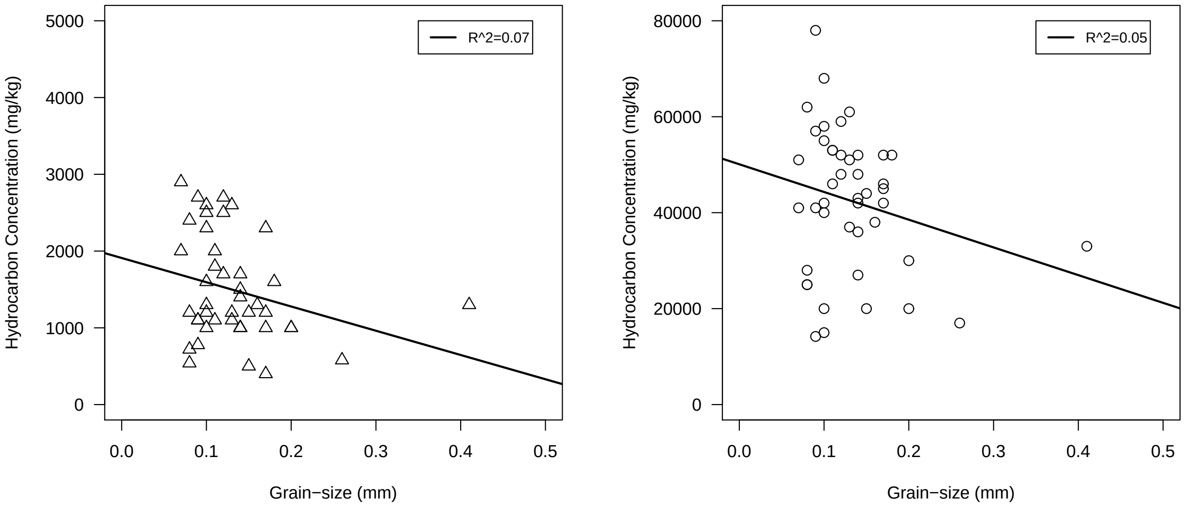
(b) F4G Hydrocarbons with median grain-size

Figure 4.2: Hydrocarbon concentrations by median grain-size

The correlation of F3 hydrocarbons to median grain-size is considered too weak to represent a meaningful relationship. It is noteworthy that a weak relationship exists between F4G hydrocarbons and tarball grain-size. The F4G values for these samples are essentially total hydrocarbon values, which seems to indicate a general trend of lower hydrocarbon deposition, or possibly higher rates of degradation -or both- among tarballs in coarse soils. However, since degradation of heavy PHCs is sufficiently slow that it has very little affect on the very heavy molecular weight hydrocarbons, the latter is an unlikely scenario. Thus it appears that depositional environment had some weak control on the overall intensity of bitumen deposited. Unfortunately the weakness of this relationship gives it little predictive ability in field applications.

4.4.2 Characteristic Grain-size

The characteristic grain-size (D_{10}) of a soil is given by the diameter at which 10% of the particles, by mass, are smaller. This grain-size can often control the hydraulic conductivity and other physical properties of the soil. Given these controls in geotechnical engineering, they author hypothesized that the relationships between hydrocarbon content and D_{10} might more accurately reflect controls at deposition or during subsequent leaching and degradation than D_{50}. Relationships are shown in Figures 4.3a and 4.3b.



(a) F3 Hydrocarbons with characteristic grain-size **(b)** F4G Hydrocarbons with characteristic grain-size

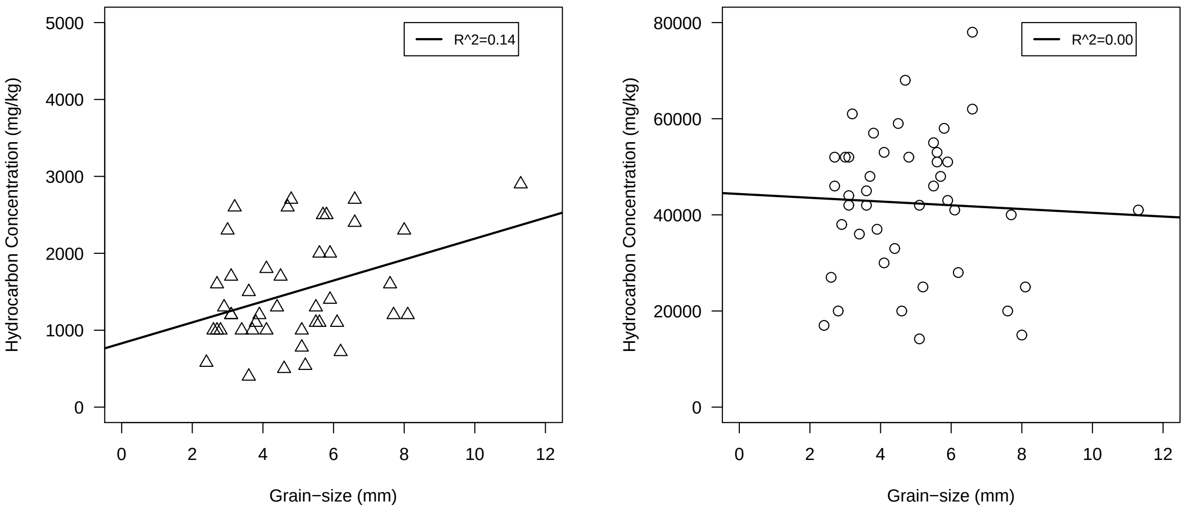
Figure 4.3: Hydrocarbon concentrations by characteristic grain-size

Both Fractions 3 and 4 indicate very weak correlations with characteristic grain-size.

The nearly coincident correlation in both fractions may indicate that some weak control existed. However, the weakness of the correlation makes this a tenuous conclusion at best.

4.4.3 Silt and Clay Content

Silts and clay size particles are defined in the Unified Soil Classification System as any particles passing the #200 sieve (75μm). If present in sufficient quantity these fine particles can limit soil hydraulic conductivity. This may lead to differing leaching and degradation rates among tarballs of differing silt and clay content. F3 and F4G concentrations are presented against total silt and clay content for the tarballs analyzed in Figures 4.4a and 4.4b.



(a) F3 Hydrocarbons with silt and clay content

(b) F4G Hydrocarbons with silt and clay content

Figure 4.4: Hydrocarbon concentrations by silt and clay content

Fraction 3 hydrocarbons are as strongly correlated to silt and clay content as F4G was correlated to median grain-size. Although not a particularly strong correlation, this might indicate slightly different leaching and degradation rates for tarballs with elevated silt and clay contents. This is a somewhat tenuous conclusion given the spread in the data, but seems possible from a qualitative evaluation of the likely mechanisms of weathering and leaching.

4.4.4 Summary

Potential relationships between grain-size parameters and tarball hydrocarbon concentrations have been investigated. Some weak correlations have been identified. None were found to be predictive for field determination of hydrocarbon concentration. Weak correlations and patterns were exhibited as:

- greater overall hydrocarbon content (as F4G) at finer median grain-size,
- generally greater hydrocarbon content (F3 and F4G) with finer characteristic grain-size, and
- greater F3 content at higher silt and clay content.

All other relationships are considered to exhibit no meaningful correlation.

4.5 Hydrocarbon Content and Grain-size of Host Soils

The relationships between the soil physical parameters of tarball and adjoining soils were investigated as a possible window on tarball deposition processes and as potential indicators for field determinations of PHC content. There are two likely theoretical mechanisms of tarball deposition. One hypothesizes a large scale extraction that separated the bitumen from its host material. The bitumen was then carried downstream and deposited on fluvial sediments, likely an existing beach. The alternative is a traction load scenario in which fragments of the McMurray formation were broken away from the exposed face and rolled or carried downstream intact. While it is unlikely that one of these processes acted alone, it is reasonable to expect that one might have dominated the transport and deposition process.

Grain-size comparisons were used to indicate which process was active in tarball deposition. In theory, extracted bitumen would settle and create tarballs with nearly identical grain-size properties as adjoining soil. Tarballs rolled in by traction would be expected to maintain essentially the same grain-size composition as the McMurray formation.

Tarball soils were compared with soil samples taken from above and below the tarball. Comparisons were made with the same categories as hydrocarbon content in Section 4.4, with the addition of uniformity coefficient, coefficient of gradation and water content. They are:

- water content,
- median grain-size,
- characteristic grain-size,
- uniformity coefficient,
- coefficient of gradation, and
- silt and clay content.

Water content was added to these investigations as a preliminary assessment of the impact of tarball hydrocarbons on the soil moisture regime.

4.5.1 Water Content

The impact of tarball hydrocarbons on the overall soil moisture regime remains largely unknown. It has been observed that the area above tarball soils seems to be wetter. This often occurs over the relatively large layers, which act as a pavement to create a zone of elevated water content similar to a perched water table. This study provided an opportunity to quantify the relative water content of tarball and adjoining soils. This is presented in Figure 4.5 and Figure 4.6.

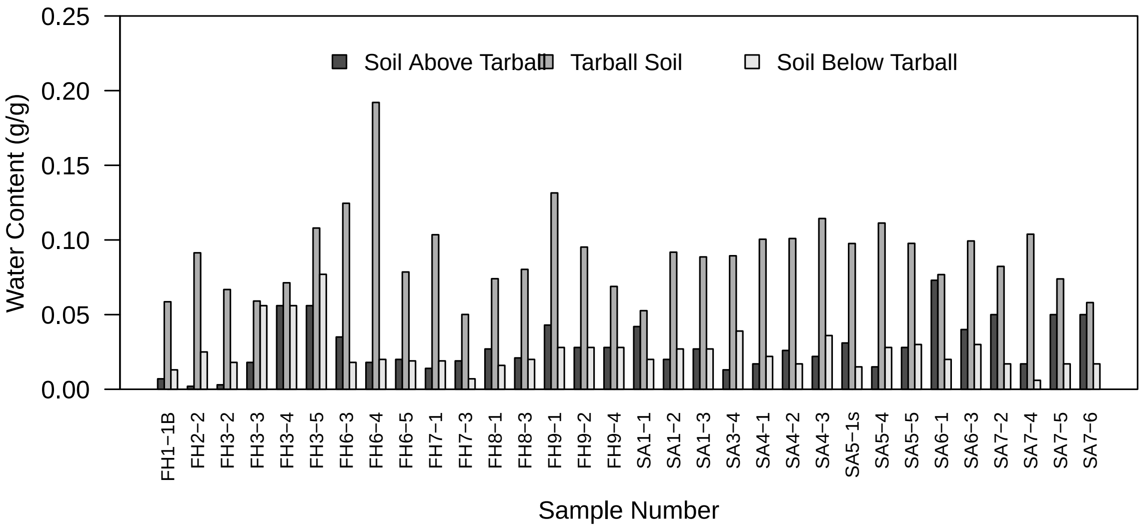


Figure 4.5: Tarball and adjoining soil sample water content data

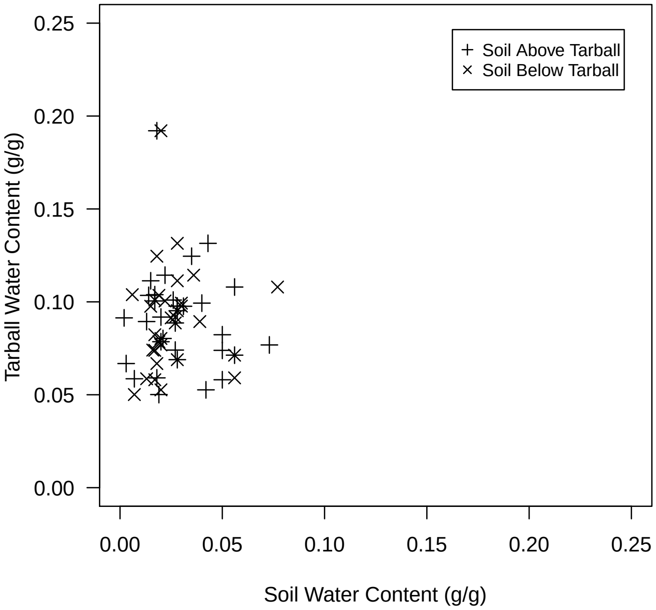


Figure 4.6: Tarball and adjoining soil water content comparison

It is apparent that in most cases tarball water contents are significantly higher than adjoining soils. Mean water content and standard deviation are included in Table 4.6. A paired student t test was carried out between the soil and tarball data. Based on the student t test, for 95% confidence, the tarball moisture contents were significantly different from both adjoining soil groups.

The data indicates that without exception the tarballs retain more moisture than adjoining soils. Water contents are often greater by several multiples. There are several possible mechanisms leading to this phenomenon. The most obvious, and presumably dominant, is the sealing qualities of the bitumen accumulated in void spaces. This likely leads to the perched water table phenomenon discussed above. It is also likely that the bitumen has its own pore space, which would be made up of finer pores than adjoining soil without the bitumen. These pores could hold additional water by the same capillary mechanisms as fine pore space in soil if the bitumen has not developed hydrophobicity. Either of these might be encouraged by the various hydrophilic/hydrophobic nature of an individual tarball. Hydrophobic pores may also trap and hold water, whereas hydrophilic tarballs may actually absorb water into the bitumen matrix itself.

Table 4.6: Tarball and adjoining soil water content summary

Soil	Moisture Content	Standard Deviation	Significant Difference[a] compared to Tarball
Soil Above	3.03	1.84	Yes
Tarball Soil	9.64	3.37	–
Soil Below	2.58	1.48	Yes

---

[a] paired t-test, n=33, p=0.05

Anecdotal evidence from field personnel who have worked with tarball materials suggests that most tarball accumulations are hydrophilic, while some others are hydrophobic. When the tarballs were removed from the soil column study discussed in Chapter 5, they were found to be wet throughout and also wetter than the adjoining soils. This is a noteworthy finding as it is contrary to the expectation of hydrophobicity encountered in many cases of hydrocarbon contamination.

The hydrophilic properties may be due to the advanced state of weathering of the tarballs. It may also be due to the nature of the McMurray formation bitumen, which is known as 'wet' bitumen for its thin coating of water between the sand grains and bitumen. The cause and occurrence of hydrophobicity are beyond the scope of this project, but the observed hydrophilic behaviour has both scientific and industrial importance. The relatively greater quantities of water stored by the tarballs is likely to be beneficial to the establishment of vegetation, by providing a reservoir of water to be drawn by the plants during periods of dryness. By definition, this mechanism would also inhibit deep infiltration of water by intercepting its downward migration and storing it until it is drawn by evapotranspiration. This effect may be expected to reduce infiltration to waste piles and ultimately total hydrocarbon loading to deep groundwater.

4.5.2 Median Grain-size

The median grain-size (D_{50}) provides one measure by which to characterize a soil sample. In this instance a similarity of median grain-size between two soil samples would provide an indication that extracted bitumen was deposited onto existing soils, rather than rolled into place. Median grain-size values for the tarball samples are shown in Figure 4.7 and Figure 4.9a.

Mean D_{50} and standard deviations are included in Table 4.7. A paired student t-

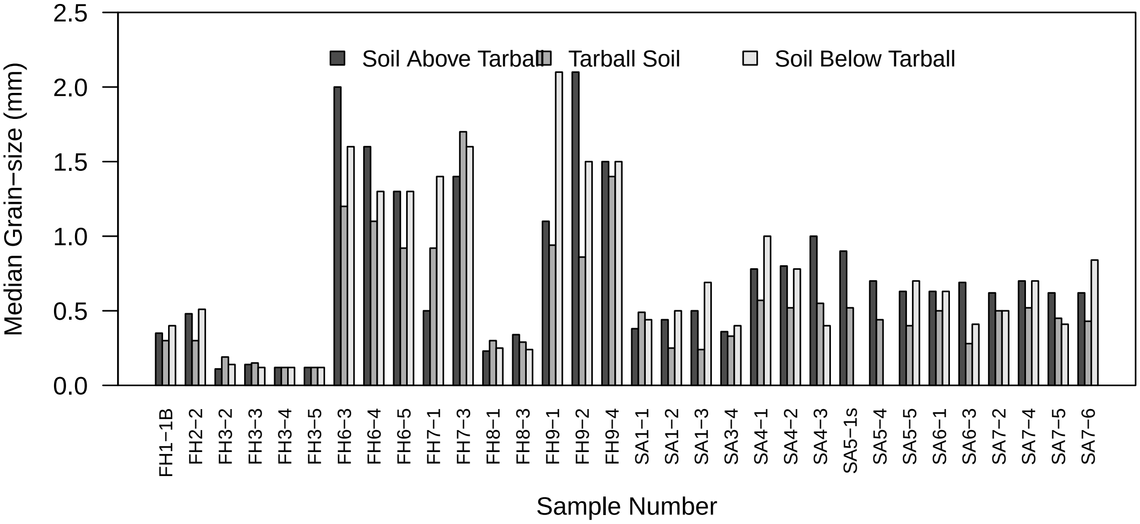


Figure 4.7: Tarball and adjoining soil median grain-size data

test was carried out between the soil and tarball data. Based on the student t test, for 95% confidence, the tarball median grain-sizes were significantly different from both adjoining soil groups. There appears to be a slight trend of tarball soils being finer at D_{50} than host soils. This is best illustrated in Figure 4.9a. A finer D_{50} usually indicates a finer soil texture overall. However the differences between tarball and adjoining soils seems to be driven not by a shift in texture, but a relative enrichment of the silt and clay fraction in tarball soils. See Section 4.5.6. This suggests that the tarball soils are similar to native soils, but have experienced some change in texture associated with the deposition of bitumen.

Table 4.7: Tarball and adjoining soil median grain-size summary

Soil	Median Grain-size	Standard Deviation	Significant Difference[a] compared to Tarball
Soil Above	0.74	0.51	Yes
Tarball Soil	0.56	0.38	–
Soil Below	0.71	0.55	Yes

---

[a] paired t-test, n=32, p=0.05

4.5.3 Characteristic Grain-size

Differences in characteristic grain-size (D_{10}) would indicate potentially differing soil conductivities and response to moisture dynamics. A relatively finer D_{10} could indicate a finer soil texture, or as discussed above, simply an enrichment of silts and clays. This would also provide a means to differentiate between the redeposition of extracted bitumen and the deposition of oil sand chunks as discussed in Section 4.5. Characteristic grain-size data are presented in Figure 4.8 and Figure 4.9b.

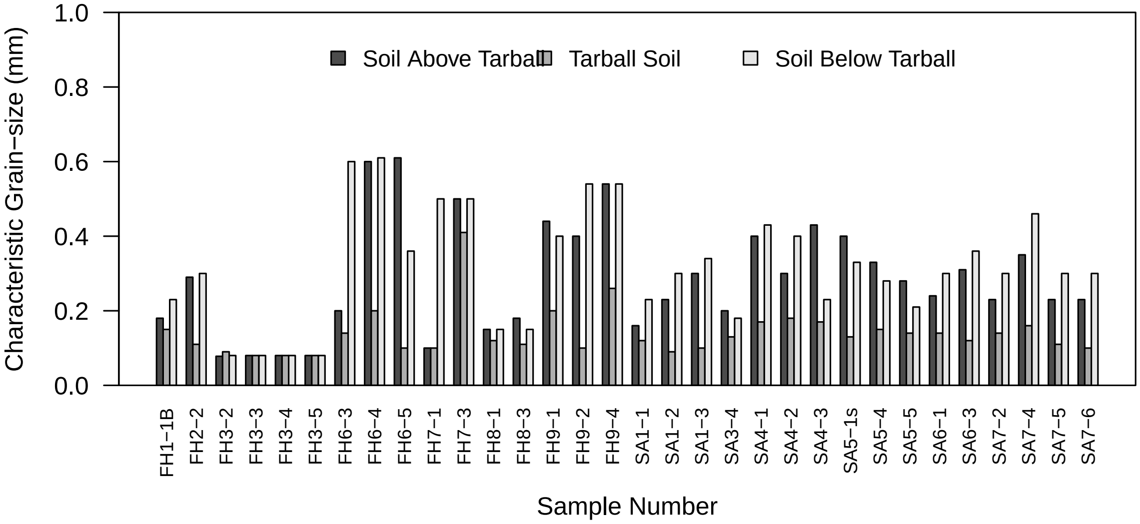
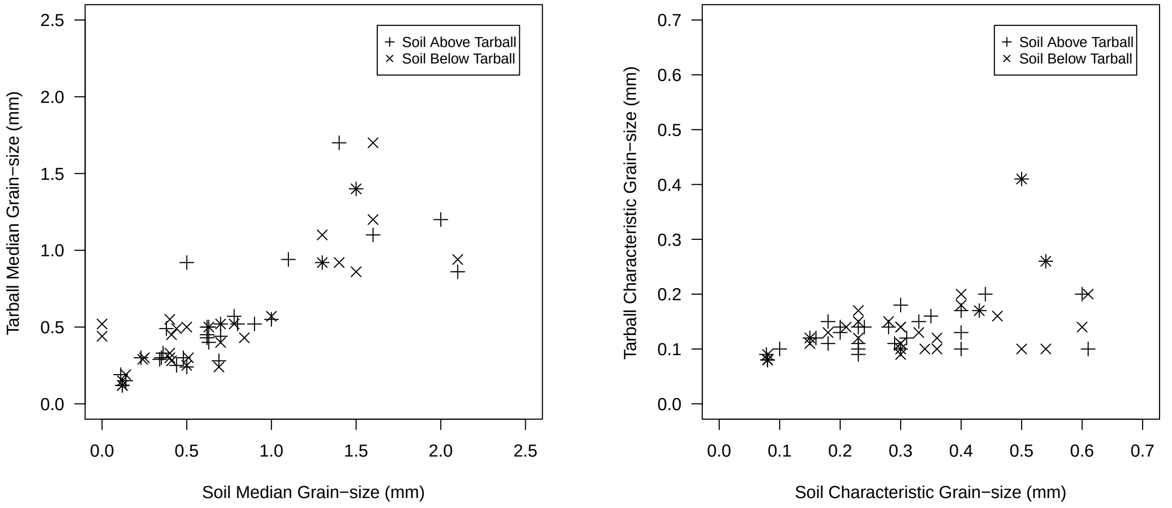


Figure 4.8: Tarball and adjoining soil characteristic grain-size data

Mean characteristic grain-size and standard deviation are included in Table 4.8. A paired student t test was carried out between the soil and tarball data. Based on the student t test, for 95% confidence, the tarball characteristic grain-sizes were significantly different from both adjoining soil groups. The characteristic grain-size of the tarball samples is consistently at or below that of the adjoining soil. In several cases the difference is quite large. This can be seen in the data summary provided in Table 4.8. Figure 4.9b suggests that D_{10} for the tarball soils occurs over a relatively narrow band from about 0.1 to 0.2 mm diameter. This suggests that most tarballs would behave in a similar manner with regard to characteristics governed by D_{10}. This would indicate relatively higher wa-



(a) Tarball and adjoining soil median grain-size comparison

(b) Tarball and adjoining soil characteristic grain-size comparison

Figure 4.9: Median grain-size and characteristic grain-size comparisons

ter content at field capacity and lower hydraulic conductivities. Tarball soils have been shown to retain more water than adjoining soils in Section 4.5.1. The added water content is likely attributable to the combined effects of the relatively finer tarball soils and the sealing characteristics of the bitumen. The relative significance of each mechanism is beyond the scope of this study. Future research into the question of tarball moisture retention is recommended.

As with D_{50}, the differences in the D_{10} data are attributable to a relative increase in silt and clay content (Section 4.5.6). From this data it appears as though the bitumen impregnated existing soils, bringing with it a load of fine particles. This would be consistent with industry experience, where the separation of fine particles from the bitumen has proven to be a significant challenge.

Table 4.8: Tarball and adjoining soil characteristic grain-size summary

Soil	Characteristic Grain-size	Standard Deviation	Significant Difference[a] compared to Tarball
Soil Above	0.29	0.15	Yes
Tarball Soil	0.14	0.06	–
Soil Below	0.32	0.15	Yes

---

[a] paired t-test, n=32, p=0.05

It is interesting to note that there seem to be no consistent patterns in terms of characteristic grain-size before (below) and after (above) tarball deposition. It might have been expected that tarball deposition would occur after a pulse of increased flow. This does not appear to be the case. The conclusion is corroborated by a review of the median grain-size data, Figure 4.7.

4.5.4 Uniformity Coefficient

The Uniformity Coefficient provides a measure of the range of grain sizes in a soil sample. The uniformity coefficient (C_u), given in Equation 4.2, provides a measure of the shape of the particle size distribution. In this equation, D_{60}, and D_{10} represent the particle diameters at which 60%, and 10% of the soil is finer.

$$C_u = \frac{D_{60}}{D_{10}} \tag{4.2}$$

Sands with C_u greater than 6 may be considered to be well graded, having particles ranging several orders of magnitude in diameter. The behaviour of well graded soils tends to be defined by the characteristic grain-size, whereas for poorly graded soils the characteristic grain-size and median grain-size are often representative of each other. Differences in soil composition between tarball and adjoining soils are likely to be identified under this parameter. The data are illustrated in Figure 4.10 and Figure 4.12a.

Mean Uniformity Coefficient and standard deviation are included in Table 4.9. A paired student t-test was carried out between the soil and tarball data. Based on the student t-test, for 95% confidence, the tarball uniformity coefficients were significantly different from both adjoining soil groups. Most of the samples investigated have C_u values in the range of 2 to 4, approaching the criterion for well graded sands. Occasional samples have large C_u values indicating a non-uniform (well graded) soil. It is apparent that tarball C_us are slightly greater than those of adjoining soils. Tarball C_us edge into the partially graded zone around 4. The data are summarized in Table 4.9.

Figure 4.10 and Figure 4.12a both illustrate that, in general, tarball soils are slightly less uniform than adjoining soils. This is likely attributable to the addition of fine particles caused by bitumen deposition onto an existing soil matrix as discussed in Section 4.5.4. The extra fines reduce the value of D_{10}, which increases C_u.

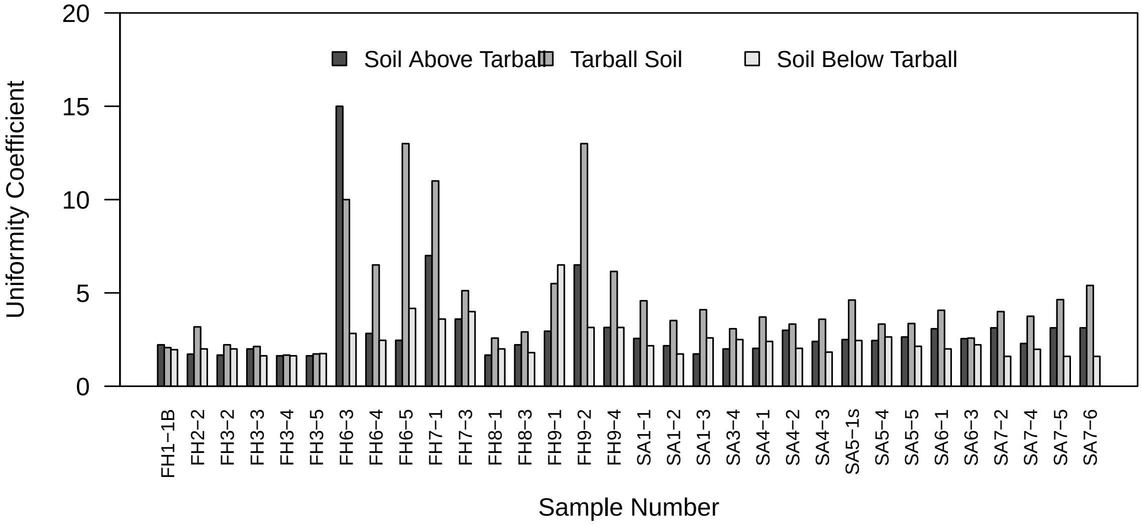


Figure 4.10: Tarball and adjoining soil uniformity coefficient data

Table 4.9: Tarball and adjoining soil uniformity coefficient summary

Soil	Uniformity Coefficient	Standard Deviation	Significant Difference[a] compared to Tarball
Soil Above	3.10	2.44	Yes
Tarball Soil	4.70	2.95	–
Soil Below	2.44	0.99	Yes

---

[a] paired t-test, n=32, p=0.05

4.5.5 Coefficient of Gradation

As with the Uniformity Coefficient (Section 4.5.4), the Coefficient of Gradation provides a means of determining the range of grain sizes in a soil sample. Coefficient of Gradation data are presented in Figure 4.11. The coefficient of gradation (C_c) is given in Equation 4.3. In this equation, D_{60}, D_{30} and D_{10} represent the particle diameters at which 60%, 30% and 10% of the soil is finer.

$$C_c = \frac{D_{30}^2}{D_{60} * D_{10}} \tag{4.3}$$

Soils with C_c between 1 and 3 are considered to be well graded, having particles ranging several orders of magnitude in diameter. The behaviour of well graded soils tends to be defined by the characteristic grain-size, whereas for poorly graded soils the characteristic grain-size and median grain-size are often representative of each other.

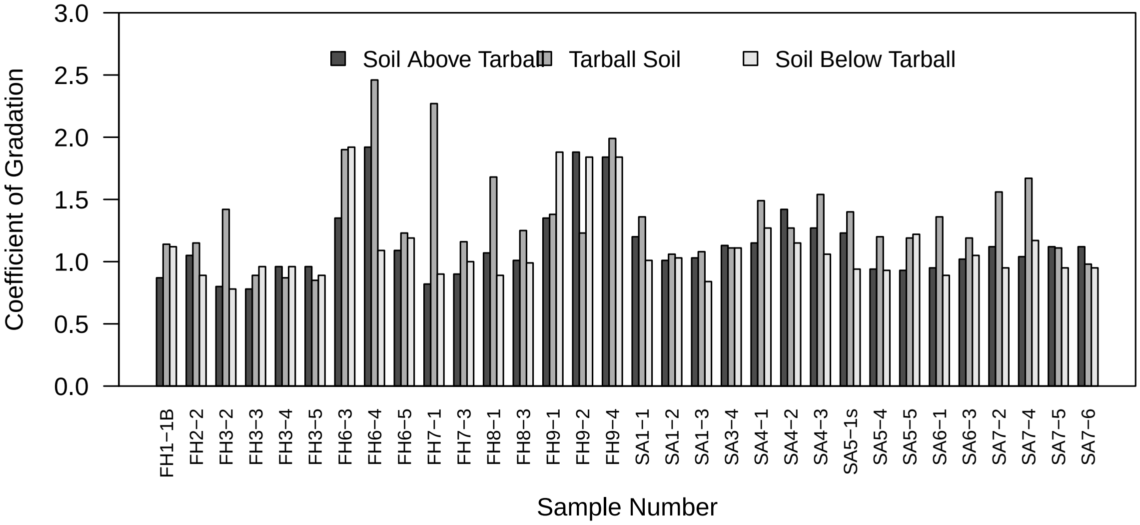


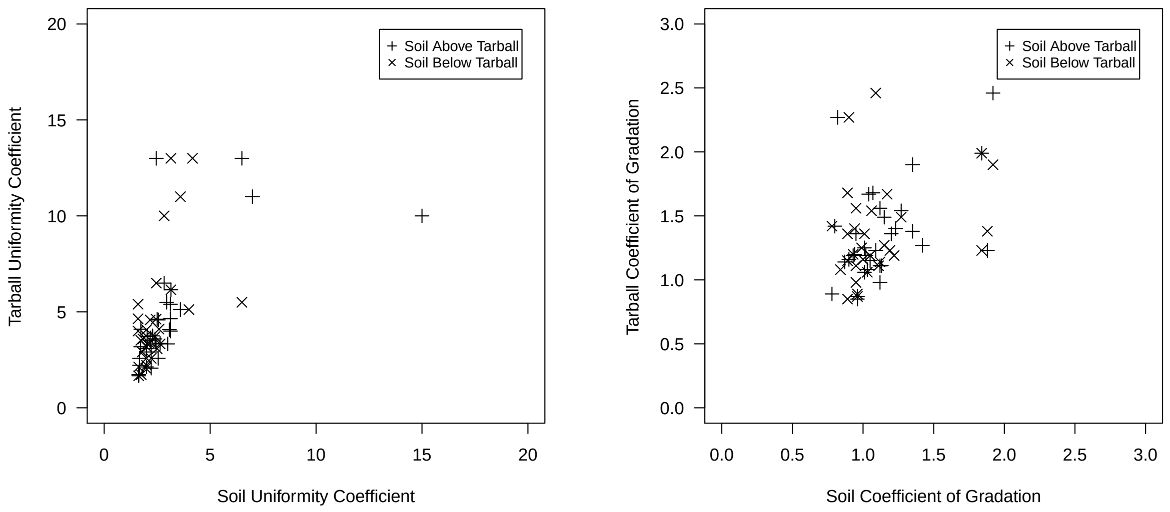
Figure 4.11: Tarball and adjoining soil coefficient of gradation data

Mean Coefficient of Gradation and standard deviation are included in Table 4.10. A paired student t-test was carried out between the soil and tarball data. Based on the student t-test, for 95% confidence, the tarball Coefficients of Gradation were significantly different from both adjoining soil groups. Coefficients of Gradation generally range from about 1 to 2, placing them within the range of well graded soils. There is a general pattern of slightly higher C_cs in tarball soils compared to adjoining soils. This indicates a slightly better gradation of the tarball soils compared to those adjoining. A summary is provided in Table 4.10.

As with the Uniformity Coefficient (Section 4.5.4), the Coefficient of Gradation also indicates the addition of fine particles by bitumen deposition on an existing soil matrix. The extra fines reduce the value of D_{10}, which increases C_c.

4.5.6 Silt and Clay Content

Silt and Clay size contents in sandy soils provide a measure of the conditions at deposition. Extended periods of calm will deposit more fines into a soil matrix than a



(a) Tarball and adjoining soil uniformity coefficient comparison

(b) Tarball and adjoining soil coefficient of gradation comparison

Figure 4.12: Coefficients of uniformity and gradation comparison

Table 4.10: Tarball and adjoining soil coefficient of gradation summary

Soil	Coefficient of Gradation	Standard Deviation	Significant Difference[a] compared to Tarball
Soil Above	1.14	0.28	Yes
Tarball Soil	1.36	0.37	
Soil Below	1.11	0.31	Yes

---

[a] paired t-test, n=32, p=0.05

consistent flow. Also, as mentioned several places above, silt and clay content may give an indication as to the mechanics of bitumen deposition. High silt and clay contents could indicate deposition of intact chunks of the McMurray formation. Low silt and clay contents would indicate bitumen extraction and deposition on an existing matrix. Silt and clay contents are presented in Figure 4.13 and Figure 4.14.

Mean silt and clay content and standard deviation are included in Table 4.9. A paired student t-test was carried out between the soil and tarball data. Based on the student t test, for 95% confidence, the tarball silt and clay contents were significantly different from both adjoining soil groups. All but a few samples have much greater silt and clay contents in the tarball soils than adjoining materials. Tarball silts and clays range between 4% and 8% while adjoining soils are typically less than 2%. It is clear that tarball soils

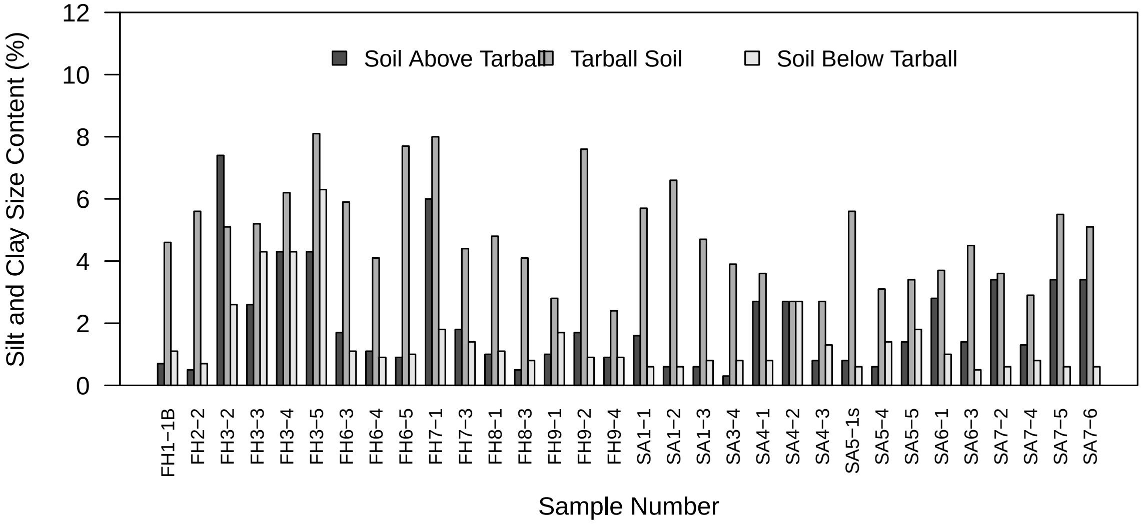


Figure 4.13: Tarball and adjoining soil silt and clay content data

contain significantly more fines than adjoining soils. This is further demonstrated in Table 4.11.

Table 4.11: Tarball and adjoining soil silt and clay content summary

Soil	Silt and Clay Content	Standard Deviation	Significant Difference[a] compared to Tarball
Soil Above	2.01	1.66	Yes
Tarball Soil	4.81	1.58	–
Soil Below	1.45	1.28	Yes

---

[a] paired t-test, n=32, p=0.05

Tarball soils clearly contain more silt and clay than adjoining soils. However, the silt and clay content is well below that of one sample of Lean Oil Sand (LOS) taken from the Syncrude Aurora LOS Dump. This sample was found to contain 26% silt and clay. As discussed in Section 2.1.2, the McMurray formation represents a complex deltaic system of mudstone channels in a fine sand deposit. Consequently, most of the McMurray formation contains some quantity of silt and clay. Some portions of the McMurray formation contain considerable quantities of silt and clay. The sample collected from the LOS dump should be considered a relatively high fines content with regard to the formation as a whole, but an average to lower fine content for those finer portions of the

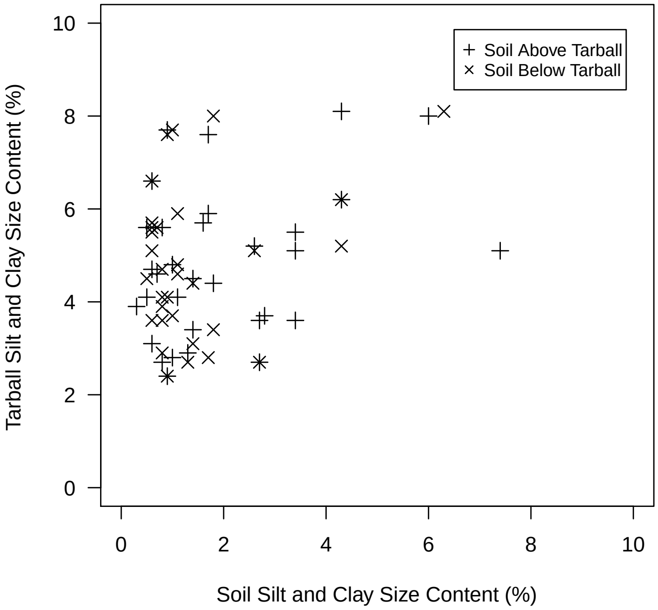


Figure 4.14: Tarball and adjoining soil silt and clay content comparison

formation.

It seems that deposition of intact chunks is an unlikely mechanism for tarball deposition. Instead the evidence suggests an incomplete extraction. In this model, bitumen would have been extracted from the sands of the McMurray formation. The extracted bitumen contains a small fraction of silt and clay. Subsequent deposition on a fluvial sand matrix results tarballs and adjoining soils with a very similar grain-size fingerprint, with the exception of the noted increase in the silt and clay fraction. This is suggested as the likely mode of tarball deposition.

4.5.7 Summary

Several meaningful relationships between tarball and adjoining soils have been identified. These provide insights into the effects of tarballs on the soil moisture regime, tarball soil composition and evidence of the mechanisms at work in tarball deposition. They are:

- tarballs retain three times more moisture, on average, than adjoining soils,
- tarballs contain approximately twice as much silt and clay as adjoining soils, resulting in a significantly smaller D_{10}

- adjoining soils were found to be significantly different from tarball soils in all properties considered.

Based on the observations regarding silt and clay contents it is thought that tarballs were deposited as extracted bitumen on existing river or beach sand, carrying with them a small portion of fines from the McMurray formation.

4.6 Conclusions

This chapter has assessed the hydrocarbon composition of the tarball material from several perspectives. Hydrocarbon composition has been analyzed in terms of quantity and molecular weight distribution. Relationships between hydrocarbon content and tarball manifestation, as well as several tarball soil characteristics were investigated. Relationships between tarball soils and adjacent non-hydrocarbon affected soils were assessed for potential insight into the nature of tarball deposition.

Key findings may be summarized as follows:

- A typical tarball hydrocarbon fingerprint consists primarily of F3 and F4 hydrocarbons at levels several multiples greater than clean soil guidelines. Fractions 1 and 2 are seldom detected. If present, these fractions are typically detected at levels below clean soil guidelines.
- Infrequent exceptions to this hydrocarbon fingerprint are sometimes detected at the core of thicker (>30 cm) tarballs. These 'rich cores' have been found to contain hydrocarbon concentrations approaching ore grade, with all hydrocarbon fractions present at concentrations orders of magnitude greater than 'typical tarball' levels.
- The CCME benchmark method for the analysis of hydrocarbons in soil was found to produce somewhat high but acceptable levels of variability in the analysis of tarball affected soils.
- Predictive relationships between grain-size characterstics and hydrocarbon content were not identified in this study. However, general trends of relatively greater hydrocarbon concentrations at decreasing median grain-size and decreasing characteristic grain-size point to either greater overall hydrocarbon deposition at lower flow conditions or relatively decreased weathering at smaller grain-size.

- Tarball soils have significantly greater silt and clay contents than adjoining non-hydrocarbon affected soils.
- It is proposed that the formation of tarballs occurred primarily as a partial extraction, transport and deposition process.

Chapter 5

Hydrocarbon Mobility Study

5.1 Introduction

A column study was conducted to evaluate the potential for hydrocarbon mobility from, and biodegradability within, a soil cover containing tarballs. The columns simulate a non-vegetated soil cover. Water was regularly added to the surface of the soil and leachate was sampled at regular intervals and analyzed for hydrocarbons. Soil respiration of oxygen, carbon dioxide and methane was monitored using an automated respirometer. Target compounds in the vapour phase were also monitored using air sampling tubes. The water content of the soil within the columns was monitored using a SenTek Diviner 2000 system. The columns, as assembled, are described in Section 5.2. The moisture regime within the column is documented in Section 5.3. Leachate composition and tarball biodegradation potential are discussed in Sections 5.4 and 5.5. A summary of tarball PHC mobility is provided in Section 5.6.

5.2 Soil Column Assembly

Detailed descriptions of the soil column study are given in Chapter 3. The simulated cover soil was composed of clean sand and tarball material. The sand and tarball materials were placed in the column at similar densities and proportions as worst case reclamation conditions. Three columns were assembled using only tarballs collected from the top metre of the soil profile and three using only tarballs collected from below one metre. These are referred to as Surface and Deep tarball columns, respectively.

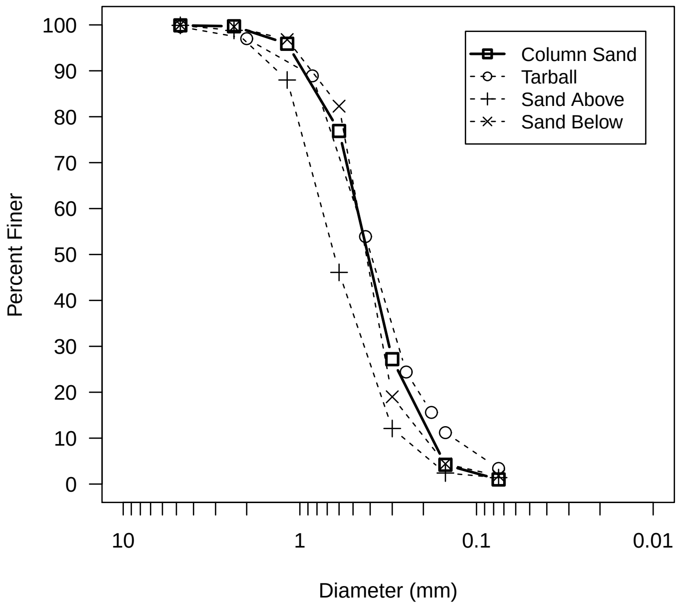


Figure 5.1: Column and tarball sand grain-size distribution

5.2.1 Properties of Column Study Soil

The soil matrix was composed of a sandy soil taken from an area adjoining tarball manifestations. This sand was analyzed for PHCs. No PHCs were detected. Grain-size properties are summarized in Table 5.1. Grain-size distributions for this soil, a typical tarball and it's adjoining soils are presented in Figure 5.1.

The clean soil used in this experiment is a uniform medium sand (SP) with similar grain-size characteristics to typical tarball soils. This soil was air-dried prior to packing the columns. The gravimetric water content after air drying was approximately 2%. The mean water content of 72 tarball samples was determined. These samples were also analyzed for hydrocarbon content as discussed below in Section 5.2.2. The mean gravimetric water content of the tarballs was found to be approximately 9%. The average measured water contents of both sand and tarball were used to determine the initial water content of the soil/tarball mixture placed in the columns. The columns were packed as recorded in Table 5.2.

During packing the total mass of soil and tarball placed in each column was determined. This allowed for the calculation of an overall soil density, as given in Table 5.2.

When the columns were disassembled, an investigation was made into the relative contributions of the sand and tarballs to the overall density. Undisturbed samples of the sandy soil were taken by ring sampler to determine dry density and water content. An average tarball density was calculated, then verified by back calculating the known sand density as follows:

1. Knowing the mass and density of sand placed in each column, the volume occupied by that sand was determined.
2. This in turn was used to determine the volume occupied by the tarballs.
3. An average tarball density (mineral plus bitumen) could then be determined from the known mass of tarball in that column.
4. To verify the resulting tarball densities, the corresponding sand density for each column was determined from the mass of sand placed and the calculated tarball density.

Table 5.1: Soil properties of clean sand matrix

Item	Symbol	Value	Units
Median Grain-size	D_{50}	0.40	mm
Characteristic Grain-size	D_{10}	0.20	mm
Uniformity Coefficient	C_u	2.3	
Coefficient of Gradation	C_c	0.9	

Table 5.2: Column contents as measured during placement

	Dry Mass Placed (kg)			Overall Density	Water Included (L)		
Column	Sand	Tarball	Total	(kg/m^3)	Sand	Tarball	Total
S-1[a]	47.9	25.4	73.3	1710	1.0	2.3	3.3
S-2	44.7	27.3	72.0	1710	0.9	2.5	3.4
S-3	46.9	23.3	70.2	1620	0.9	2.1	3.0
D-1[b]	47.5	23.9	71.4	1680	1.0	2.2	3.2
D-2	46.4	23.5	69.9	1630	0.9	2.1	3.0
D-3	46.1	25.0	71.1	1660	0.9	2.2	3.1
Total	278.5	148.4	427.0	1670 (mean)			
Ratio	65%	35%	100%				

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[a] 'S' denotes tarballs from top metre in-situ

[b] 'D' denotes tarballs from more than one metre below ground surface

The calculated tarball densities and back-calculated sand densities are given in Table 5.3. For the purposes of this discussion, sand densities are determined as the dry mass of mineral soil divided by the volume occupied by the mineral soil. Tarball densities are determined as the dry mass of mineral soil and bitumen divided by the volume occupied. The mean value for calculated tarball density was 1950 kg/m^3. A detailed explanation of the procedure used to develop these values is given below. In general, calculated tarball densities were found to be within the range of several tarball samples measured in the lab. The back-calculated sand densities were generally found to be in good agreement with the measured sand densities. The exception to this agreement was column D-1, which is readily explained by the presence of a large tarball found to contain a large stone at its core. This increased the average tarball density within the column, leading to an elevated sand density from the check calculation.

In total 15 soil samples were taken from the column sand matrix using a ring sampler. These samples were taken from four columns and used to determine water content and dry density. Water content is discussed below in Section 5.3. Density values were found to be very consistent, with a mean dry density of 1540 kg/m^3 and a standard deviation of 70 mg/kg (C_v = 4.4%). The void ratio (e) of the samples was found to average 0.72, yielding an average porosity of 0.42.

By fixing the sand properties at these measured values, the volume of sand in each column can be determined (Step 1). An average tarball density is then found by dividing the total mass of tarball by the remaining column volume (Steps 2 and 3). This information is provided in Table 5.3 under the heading 'Using Sand Density of 1550.' In this way, the average tarball density within the columns was found to be 1950 kg/m^3. This number must be applied with caution, as tarballs have been found to exhibit significant heterogeneity. Some samples, typically those greater than about 30 cm in diameter, have even been found to contain cobble sized stones at the centre.

To verify these parameters, the analysis was reversed (Step 4), assuming a tarball density of 1950 mg/kg, and calculating the corresponding sand density from the total mass of sand and the volume not occupied by tarballs. Sand densities determined in this way are presented in Table 5.3 under the heading 'Using Tarball Density of 1950.' Average total densities for each column are presented under the heading 'Overall Density' for comparison in Table 5.2. Given the good agreement in the data, it is clear that the measured and inferred densities provide an accurate measure of the column geotechnical parameters.

Knowing the density of the tarballs and taking an average bitumen content of 5%, the sand density of the tarball material is estimated at 1860 mg/kg. The sand density of the tarballs is clearly greater than the matric 'clean sand' density of the tarball column. Greater density suggests smaller pore spaces. Smaller pore spaces indicate higher matric suctions and a greater water holding capacity of the tarballs than column soils. This is likely to occur in reclamation conditions as well, where cover soils will be placed loosely and no compaction effort is intentionally provided. It is also anticipated that the tarballs are more dense than adjoining soils in the natural environment, but to a lesser degree.

Table 5.3: Column soil properties as placed

Column	Mean Measured Sand Density	Tarball Density Using Sand Density of 1550 kg/m^3	Sand Density Using Tarball Density of 1950 kg/m^3	Volume Fraction Sand	Tarball
S-1	1580	2130	1610	70	30
S-2	1570	2060	1590	67	33
S-3	–	1770	1490	72	28
D-1	1520	2020	1570	71	29
D-2	1490	1820	1510	71	29
D-3	–	1900	1530	70	30
Mean	1540	1950	1550	72	27

5.2.2 Hydrocarbon Analyses

A detailed hydrocarbon sampling program was conducted on the tarball materials used in column packing. Samples were taken directly from the tarballs prior to their placement in the columns. These samples were often taken rom the outer surfaces of the tarballs. This was done to ensure that the tarballs were not disturbed further than that experienced in the field. This has the potential to reduce average hydrocarbon values if a concentration gradient existed at the outer edges of a tarball. Some samples were taken from tarball interiors if the tarball had been previously broken.

The initial hydrocarbon sampling program consisted of 18 samples were taken for volatile (F1) analysis and 72 samples analyzed for non-volatiles (F2, F3, and F4G). All volatile samples were analyzed at Exova Labs. Of the 72 non-volatile samples, half (36) analyzed at Exova and the other half (36) were analyzed at NHRC. The same program was repeated for hydrocarbon analyses during column deconstruction at the end of the experiment. The hydrocarbon sampling program is summarized in Table 5.4.

The volatile samples were intended to demonstrate the near absence of F1 hydrocarbons from the column study. As such, these samples were taken from tarball locations most likely to contain F1. At the start of the experiment, 3 of 18 samples were found to contain F1 hydrocarbons above the detection limit of 4 mg/l. Their concentrations were 5, 10 and 15 mg/kg. At the end of the experiment a further 18 samples were taken for F1 analysis. Of these, none were found to contain F1 above the detectable limits.

The data are presented in Table 5.5. When the Tukey criterion is applied, just one datapoint is considered an outlier in the F4-HTGC and F4G sets respectively. Its omission results in no more than a 1.1% RPD (Relative Percent Difference) of the mean. However, the F3 fraction has five outliers. Their exclusion results in a 5.1% RPD, which is equivalent to a 10% reduction in mean concentration with respect to the complete dataset. Here the data presented include the outliers. This is considered to most accurately represent the hydrocarbon composition of the columns because of the very high number of samples taken – approximately one sample for every kilogram of tarball material placed.

It is noted that the final sampling of hydrocarbons produced greater mean values for most hydrocarbon fractions. This is likely attributable to the sampling methodology. During the initial round of sampling, PHC samples were often taken from the outer surfaces of the tarballs. This approach was required to maintain the tarballs as close to their condition upon excavation as possible. When possible, samples were taken from the inner parts of tarballs that had been broken open during excavation. However, during the final sampling, tarballs were regularly broken open to expose inner materials for sampling. This was carried out in order to provide the most thorough investigation possible of the tarball PHCs within the column.

Table 5.4: Column hydrocarbon sampling plan

	Quantity per Column		Quantity per Sampling Event		Total Number
Data Obtained	Env. Canada	Exova	Initial	Final	of Samples
F1	–	3	18	18	36
F2	6	6	72	72	144
F3	6	6	72	72	144
F4-HTGC	–	6	36	36	72
F4G	6	6	72	72	144

The average hydrocarbon concentrations given in Table 5.6 were calculated using the

Table 5.5: Column tarball hydrocarbon concentrations (mg/kg)

Fraction	Initial Sampling			Final Sampling			Complete Dataset		
	Mean	S.D.[a]	C_v[b]	Mean	S.D.	C_v	Mean	S.D.	C_v
F2	4.2	16.9	4.02	37.4	122	3.26	20.8	88.7	4.26
F3	1,720	713	0.42	2,000	1,450	0.73	1,630	1,200	0.74
F4-HTGC	5,390	3,050	0.57	5,220	2,360	0.45	5,300	2,730	0.52
F4G	25,600	11,800	0.46	41,700	15,500	0.37	33,700	15,900	0.47

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[a] Standard Deviation

[b] Coefficient of Variation

'Complete Dataset' presented in Table 5.5. These provide a representative concentration if the hydrocarbons had been homogenized across all soil. These are calculated as the total quantity of hydrocarbons added to each column divided by the total dry mass of soil added to each column. Range values provided in Table 5.6 indicate the maximum variation of the true mean for a one-tailed, 90% confidence interval about the calculated mean.

Table 5.6: Overall hydrocarbon concentrations (mg/kg)

	Fraction 2		Fraction 3		Fraction 4-HTGC		Fraction 4G	
Column	Mean	Range	Mean	Range	Mean	Range	Mean	Range
S-1	7.2	3.3	565	45	1,840	150	11,900	590
S-2	7.9	3.6	618	49	2,010	160	13,000	650
S-3	7.0	3.2	548	44	1,780	140	11,500	570
D-1	7.0	3.2	546	44	1,770	140	11,500	570
D-2	7.0	3.2	548	44	1,780	140	11,500	570
D-3	7.3	3.3	573	46	1,860	150	12,100	600
Mean	7.2	3.3	566	45	1,840	150	11,900	590
Regulatory Limit[a]	250		310		2,800		2,800	

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[a] As established by Alberta Environment for coarse grained surface soils in a natural environment.

This assessment is informative on the effects of simple dilution. When total hydrocarbons are averaged over the complete soil profile, hydrocarbon concentrations shift much closer to regulatory guidelines than a direct measurement of tarball hydrocarbons. F1 and F2 hydrocarbon concentrations in the column are well below regulatory guidelines. The average F3 hydrocarbon concentration is slightly less than twice the regulatory guideline. The F4 fraction presents a challenge, as the gravimetric method identifies a significantly greater quantity of hydrocarbons than the F4-HTGC method. These represent very heavy molecular weight compounds not detected by gas chromatography.

According to CCME procedures, F4G methods must be applied in this case, yielding F4 concentrations slightly more than 4 times greater than guidelines.

As discussed in Chapter 3 and again in Section 5.2.1, the columns were packed to represent a worst case field scenario. As a worst case scenario, the presence of tarballs at this level would not be expected to present significant environmental concerns given the many expected mitigating influences. These include the effects of preferential sorption within the tarball itself and a hydraulic conductivity that is likely to be much lower than adjoining soils.

5.3 Moisture Regime

Moisture is a critical factor in both the mobility and degradation of PHCs. In reclamation covers in the Athabasca region, soil saturations of 22% to 85% or higher have been identified by Anne Naeth (2011). Water content is critical to industrial reclamation strategies. This is especially true during initial plant establishment, when seeds must draw their entire water demand from a small volume of soil.

Detailed information regarding the moisture regime within the experimental columns is necessary to interpret the experimental data, but also useful to industry in reclamation planning. It had been observed that tarballs retain moisture. This was demonstrated in field studies, as outlined in Section 4.5.1 above. The impacts of the tarballs themselves on the moisture regime of the adjoining soil remains to be established.

Quantities and rates of water added to and removed from the column are recorded in this Section. The resultant flow regime and associated water content monitoring are also discussed. Impacts associated with the presence of tarballs in the soil matrix are also addressed here.

5.3.1 Flow Regime

Water was dosed to all six columns using a low flow peristaltic pump. The pump allowed for up to 14 channels, of which 12 were used. In this way flow to each column was maintained as similar as possible. The amount of water dosed was monitored by the change in mass of the reservoir. A control reservoir was maintained for evaporation. Each column had its own reservoir. The water used was dechlorinated City of Saskatoon tap water. This was used to reflect typical environmental conditions in terms of pH and salt content. A routine analysis of this water is included in Table 5.7. The water had a pH of 7.8 and conductivity of 458 μS/cm at 20 degrees celsius. Hardness, as $CaCO_3$ was 164 mg/L.

Table 5.7: Routine water analysis of leachate water

Cations	Concentration (mg/L)	Anions	Concentration (mg/L)
Sodium	36.5	Chloride	15.0
Potassium	3.5	Hydroxide	0.0
Calcium	30.9	Sulphate	104
Magnesium	21.0	Carbonate	0.0
Iron	0.07	Bicarbonate	152
Manganese	0.0		

The amount of water released from the column was also recorded. The column reservoirs were drained of leachate approximately once per week. Reservoir valves were opened and the total volume of leachate collected in the reservoir was removed. The quantity of water drained was averaged over the time since the previous leachate collection to determine an average flux from the soil column into the reservoir. The total amount of water in each column was thus tracked by direct measurement throughout the experiment.

The dosing of water to the columns was intentionally stopped twice during the course of the experiment. The first pause lasted approximately 25 days. The second lasted 66 days. During this second stoppage, two columns were disassembled 10 days after the dosing of water had been stopped. The remaining four columns were not dosed for approximately 57 days prior to being disassembled at the end of the experiment. These stoppages were conducted to assess the column response to the moisture regime.

Infiltration and leachate collection rates are presented in Figures 5.2 and 5.3. The mean inflow and outflow rates of all six columns are presented in Figure 5.4. Cumulative inflow and outflow are presented in Figures 5.5 and 5.6. The mean values will be referenced most frequently in this text. Knowing the quantities of water added and drained, simple subtraction provides a running balance of water retained within the soil column. This is shown in Figure 5.7. As with inflow and outflow rates, mean values will be referenced most frequently in this text. Mean values are provided in Figure 5.8. The balance begins with the total amount of water added as calculated from the water contents of the sand and tarball soils. These figures show the time period from May 2008 to November 2009.

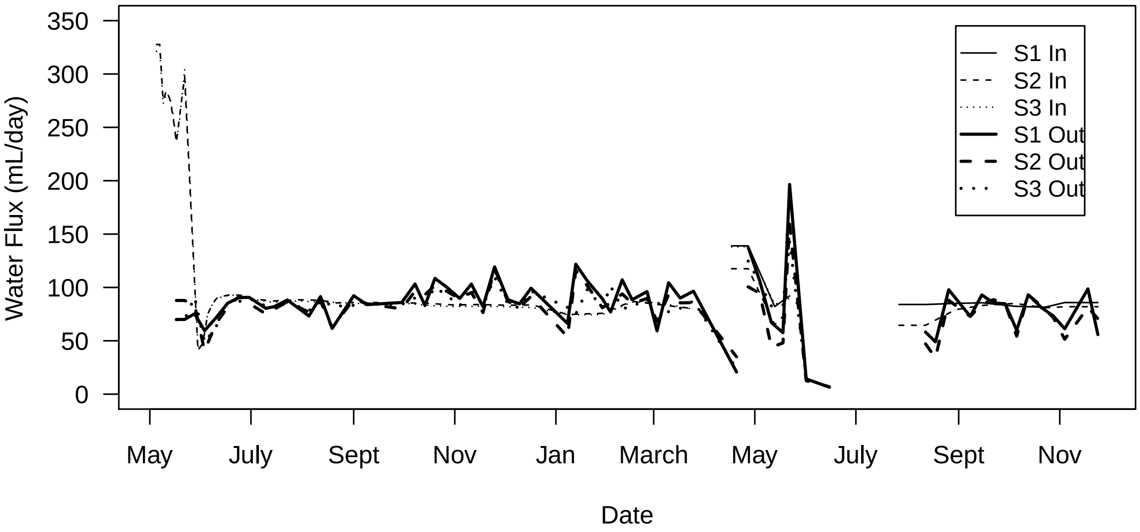


Figure 5.2: Surface tarball columns - water inflow and leaching rates

It is clear that after the initial wetting phase, column leaching rates closely followed the dosing rates. This is marked by the relatively unchanging volume of water retained from May 2008 to February 2009. The drop in total water volume from 5 to 4 litres around April, 2009 resulted from the first stoppage of dosing. After the second stoppage of dosing, the columns again returned to approximately 4 litres of water. This then represents a sort of 'field capacity' for the tarball soils. This 'field capacity' is a measure of the total amount of water retained in the soil column by matric suction. The resulting average degree of saturation for the columns was approximately 23%, although the value is not exactly the water content observed in the unsaturated portion of the column due to the development of a capillary break as discussed in Section 5.3.3.

A general trend of decreasing total water volume is observed from the beginning to the end of the experiment. This is most clearly illustrated in Figure 5.7. This drop may be attributable to a change in the moisture regime throughout the column resulting from the stoppage of leaching. When leaching of the column was first stopped, the column drained to a lower water content. This drainage would redistribute the soil

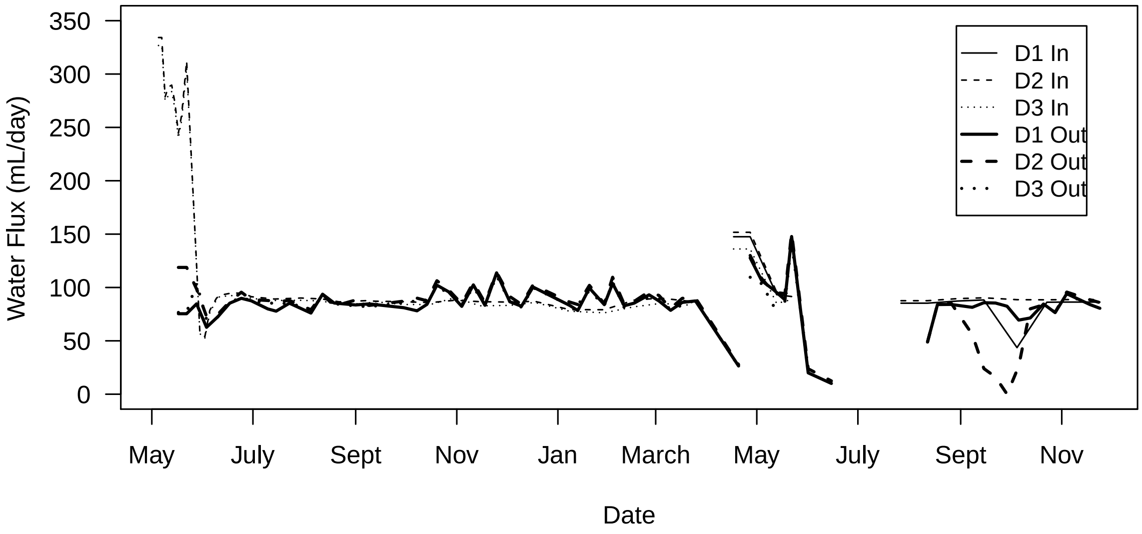


Figure 5.3: Deep tarball columns - water inflow and leaching rates

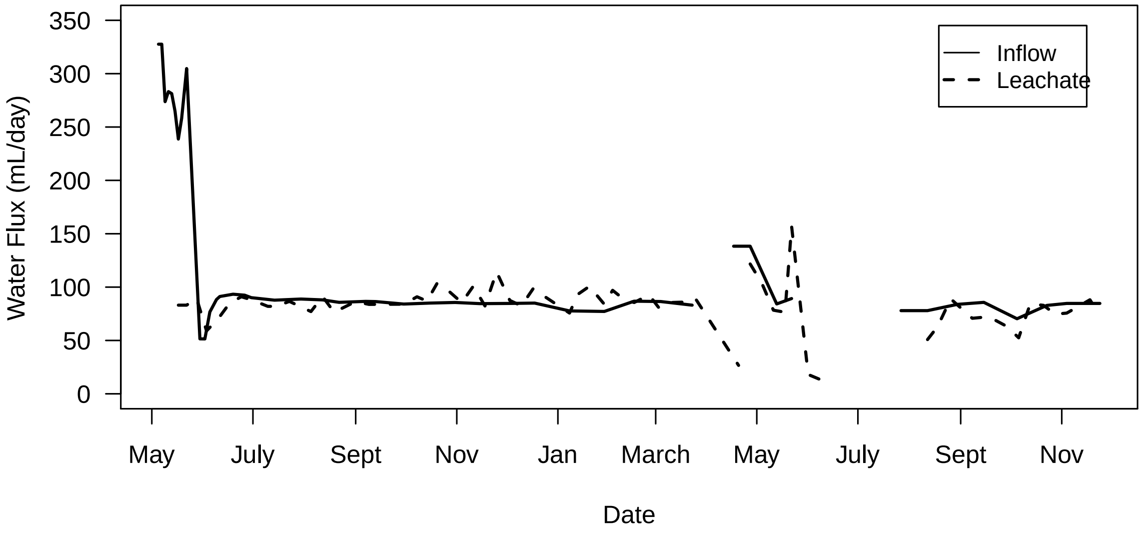


Figure 5.4: Mean column water inflow and leaching rates

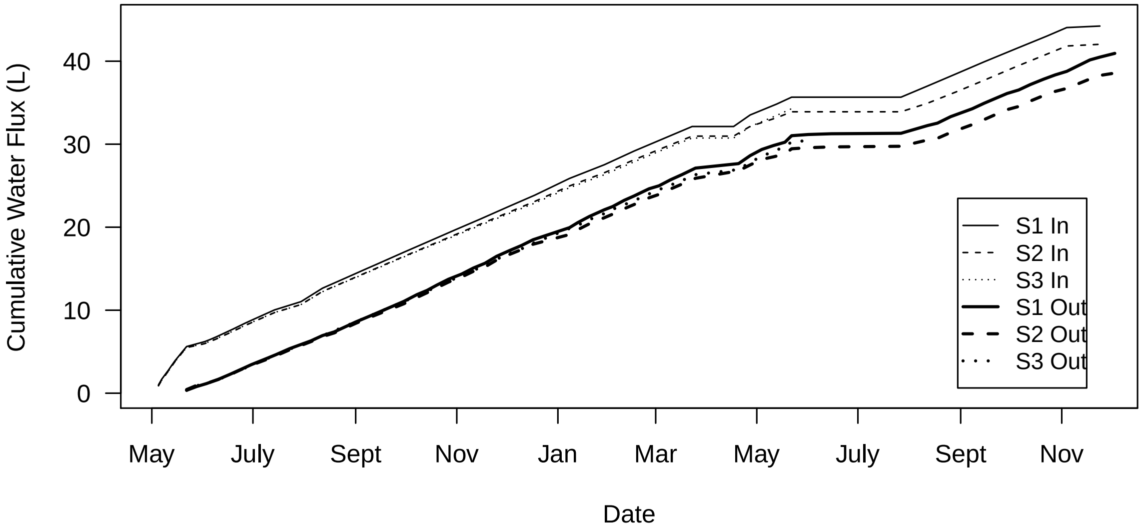


Figure 5.5: Surface tarball columns - cumulative water inflow and leaching

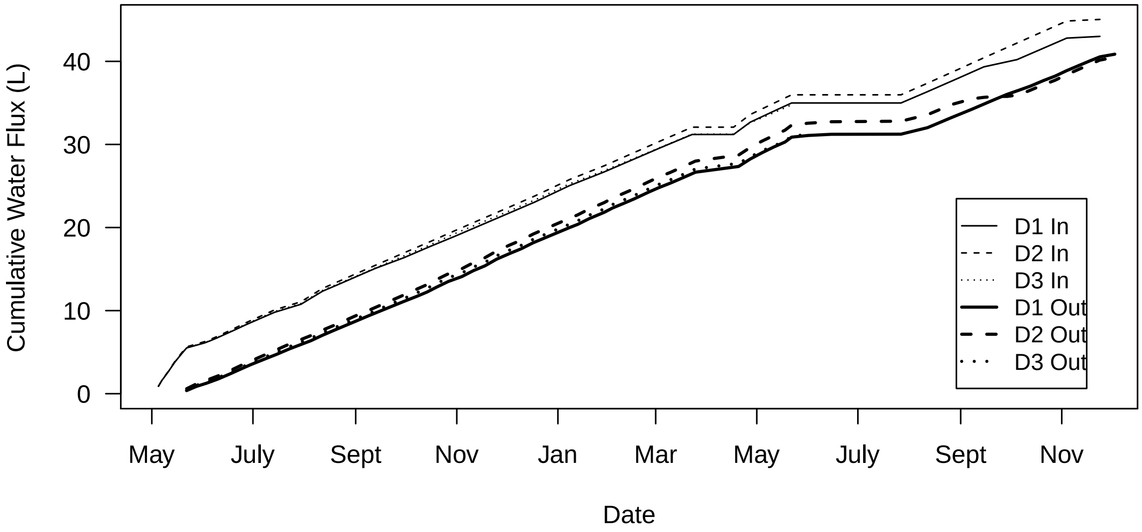


Figure 5.6: Deep tarball columns - cumulative water inflow and leaching

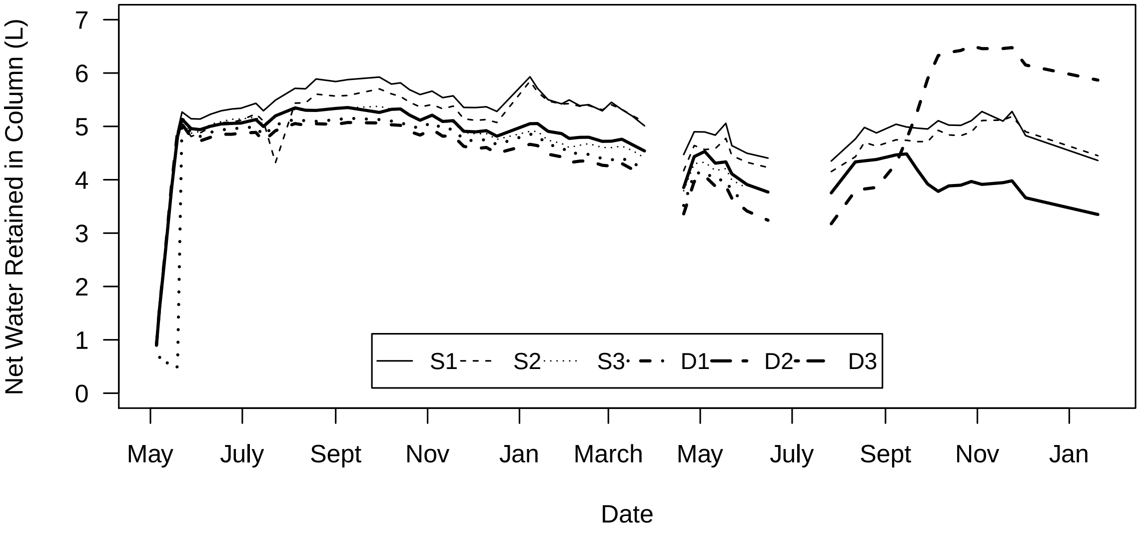


Figure 5.7: Column water retention - all columns

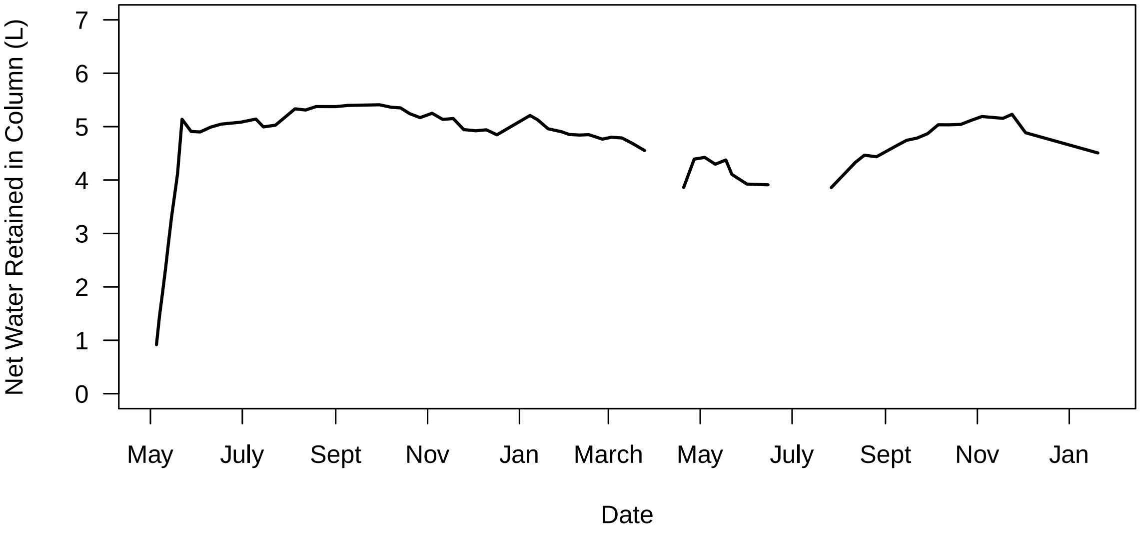
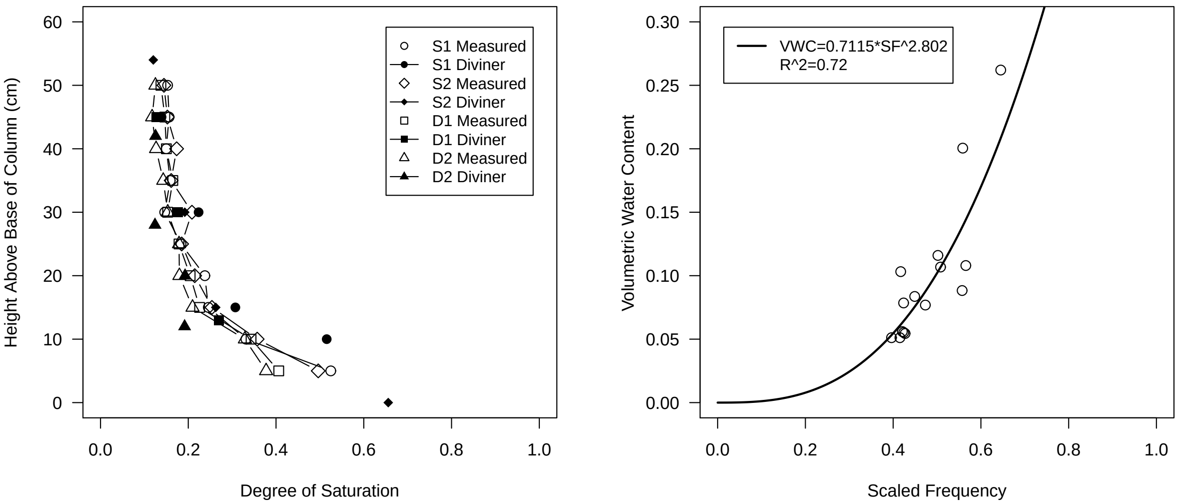


Figure 5.8: Mean column water retention

water and likely alter established flowpaths. When the leaching resumed, a different set of flowpaths would be present, providing more efficient routes to the bottom of the soil column.

5.3.2 Diviner System

Water content within the columns was monitored throughout the experiment using a Sen-Tek Diviner 2000. The Diviner 2000 system requires calibration, which was performed on the basis of 15 gravimetric water content and soil density samples taken from four columns during disassembly. These samples were correlated with Diviner readings from the same depth taken on the same day the columns were disassembled. These profiles and measured water contents are shown in Figure 5.9a. Profiles as measured by the diviner are given in open markers and corresponding water content samples are given by solid markers. The correlation is given graphically in Figure 5.9b. A calibration equation of the same form as that given in the Diviner 2000 manual was found as given in Equation 5.1.



(a) Column moisture profiles measured at disassembly **(b)** Sen-tek Diviner calibration equation with data

Figure 5.9: Development of diviner calibration equation

$$\text{VWC} = 0.7115 \times \text{SF}^{2.802} \tag{5.1}$$

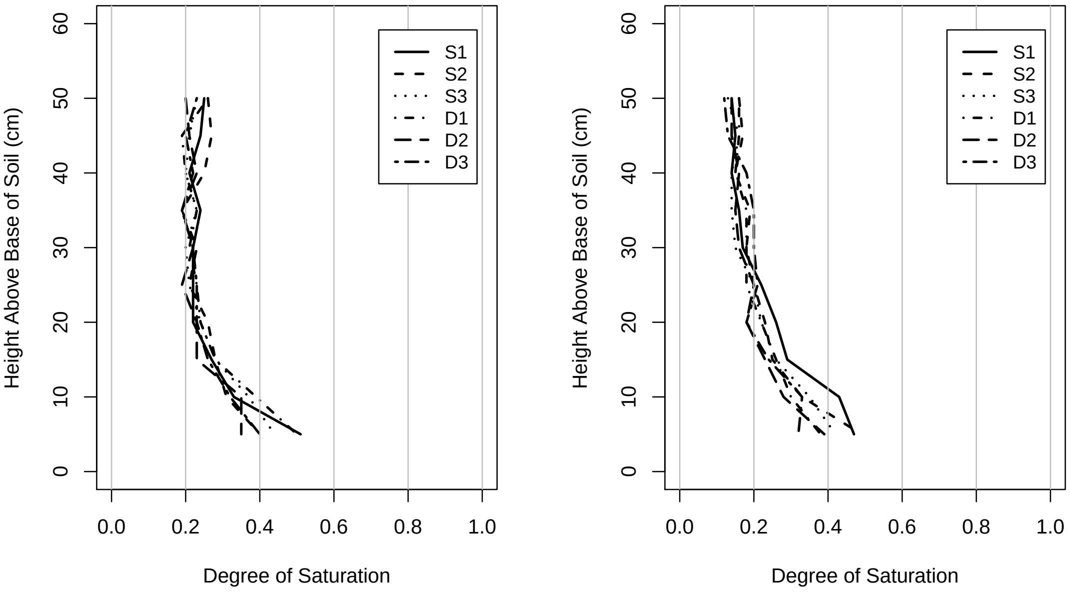
Where VWC is the volumetric water content and SF is the scaled frequency read and recorded by the diviner. It is clear that this equation will likely underestimate volumetric water contents of 0.20 to 0.30. Given the exponential shape of the curve, it may also overestimate VWC at scaled frequencies above 0.8, but no data were acquired in this range. The Van Genuchten model discussed in Chapter 3 predicts a small volume of soil that would be saturated in the 0.8 to 1.0 range. This soil volume represents less than ten centimetres of height in the soil column. Accurate readings in this portion of the column will likely be difficult to achieve.

5.3.3 Column Water Content

Water content profile data can be used at a moment in time to develop a picture of the instantaneous flow conditions and investigate variations between the tarball columns. The data can also be used to illuminate the changes in water content over time at a particular location, including the reaction of the columns to intermittent flow. Water contents at a single point in time will be considered first, followed by water contents over time. In these figures, the capillary break is at 0 cm. The water table is at some depth (negative values) in the coarse sand reservoir below zero.

Typical water content profiles for a given date are presented in Figures 5.10a and 5.10b. The readings in Figure 5.10a were taken in July 2008 after moisture conditions had stabilized early in the experiment. The profiles in Figure 5.10b were taken in April 2009 during the draining phase after the first stoppage of water pumping. The columns show a general agreement at each date, with minor variability throughout each soil column. These relatively small fluctuations in water content likely do not represent increased wetness of the tarballs themselves because the location of the zones of wetness do not appear to be consistent over time. It is also likely that any wetness effects associated with the tarballs are not visible at the resolution of the Diviner as the tarballs are relatively small compared to the volume of sandy soil adjacent to the probe. These fluctuations could result from the tarballs interrupting the moisture regime within the sand matrix or simply instrument variability between readings.

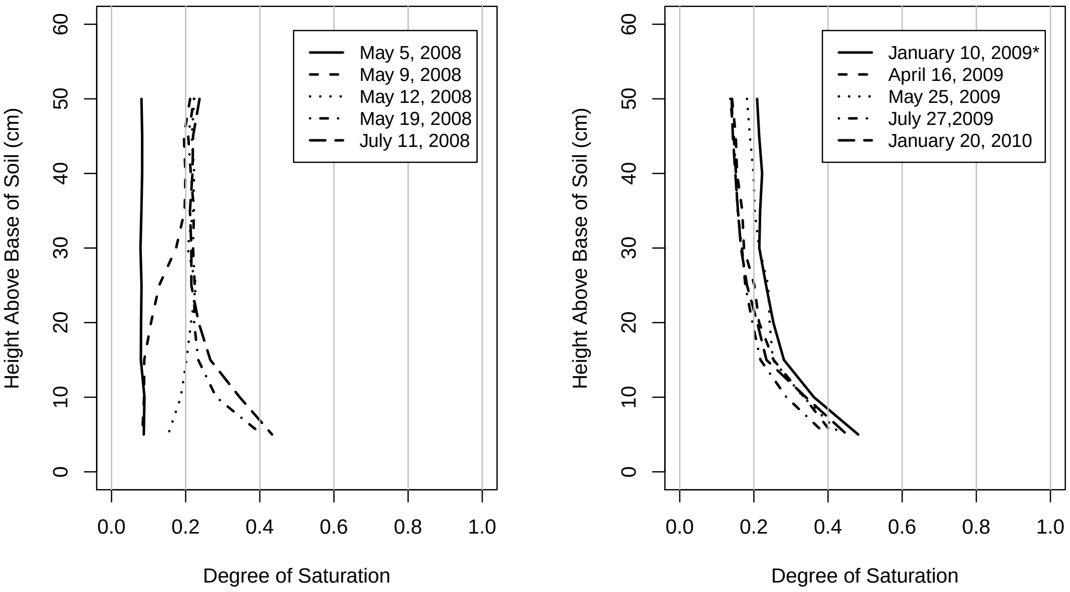
By corollory, the presence of tarballs near the Diviner access tube appears to have no effect on the accuracy of the instrument. This conclusion is reasonable considering that



(a) Column soil water content on July 11, 2008

(b) Column soil water content on April 16, 2009

Figure 5.10: Column soil water content profiles



(a) Soil water content during initial wetting phase

(b) Variations in soil water content during flow variation

Figure 5.11: Selected soil water content profiles

the large bitumen molecules would be very unlikely to exhibit any molecular polarity, even though they may have some internal polar bonds. Non-polar molecules should have no effect on the frequency detected by the Diviner. Additionally, tarball bitumen is predominantly solid, which would restrict any movement of the molecules in response to the alternating magnetic field. Thus producing little or no dampening effect to be detected by the diviner.

Selected water content profiles over time are given in Figures 5.11a and 5.11b. For ease of interpretation, each profile represents an average of all data collected on that date. In Figure 5.11a, averages are on the basis of six columns. In Figure 5.11b, averages are on the basis of four columns with the exception of January, 2009 which is on the basis of six columns. Figure 5.11a traces the development of the soil profile at the beginning of the experiment. Figure 5.11b shows the effect of intermittent flow on volumetric water contents.

The water content profiles indicate typical saturations in the unsaturated zone of approximately 20 to 22% under steady state flow conditions. When flow was stopped, the columns drained to approximately 15% saturation. These values may be higher than typical field conditions. Gravimetric water contents for non-tarball soils identified in this study were typically about 3%.

5.3.4 Summary

Diviner readings appear to be reliable in the presence of tarball material. The total volume of water within the column as computed from Diviner water content readings generally agreed with the known water volumes, except in cases of relatively rapid wetting or drying. Volumetric water contents within the sand as measured with the Diviner were found to be approximately 22% during active flow and settled to approximately 15% when dosing of water was stopped.

5.4 Groundwater Pathway

The primary focus of this column study was the assessment of potential mobility of PHCs from the disturbance of tarball material and its incorporation in reclamation covers. Significant attention was given to the PHC concentration of column leachate. Hydrocarbons were extracted and quantified as outlined in Sections 3.4. In addition to hydrocarbon analyses, Total Carbon and Total Organic Carbon were tracked throughout the experiment. Leachate was also analyzed for napthenic acids.

5.4.1 Leachate Hydrocarbons

Leachate was analyzed for hydrocarbon Fractions 1 through 4. F1 analyses were conducted on 17 sets of samples throughout the experiment. None of these samples were found to contain F1 hydrocarbons above detectable limits.

F2 through F4 hydrocarbons were analyzed 28 times at Environment Canada Labs. Hydrocarbon detections are shown in Figures 5.12 and 5.13. For ease of presentation, concentrations below the detection limit of 0.02 mg/L are shown as zero. Cumulative hydrocarbons leached are shown in Figures 5.14 and 5.15. Cumulative hydrocarbons leached from the columns indicates similar behaviour for most columns, except S-3 which leached one to several multiples of the other columns. This is thought to be associated with one exceptionally large tarball that was placed near the base of this column.

F4 hydrocarbons were not detected in leachate water.

The most noteworthy item in these figures is the scale of hydrocarbon concentrations. These figures range from 0 to 0.6 mg/L. This is well below the permitted hydrocarbon concentrations in groundwater in a natural setting. Alberta Environment limits F2 hydrocarbons to 1.1 mg/L. There is no limit on F3 hydrocarbons because toxicity thresholds are greater than solubility.

Fraction 2 hydrocarbons followed the anticipated leaching pattern from May 2008 to March 2009. Leaching began with high F2 concentrations and tapered off with time. When the dosing of water was stopped near the end of March, F2 hydrocarbons were detected in the water drained from the column. When flow resumed in mid April, hydrocarbon concentrations again dropped below detectable levels. After the second stoppage, which occurred from mid May to late July, F2 concentrations were consistently above detectable limits. Some F2 hydrocarbons were detected in the tarball samples, but generally from within the tarball itself, not at the outer surface. The F2 hydrocarbons detected in this experiment are thought to have resulted from the accumulation of daughter products from biodegradation when water flow was stopped. The daughter products were

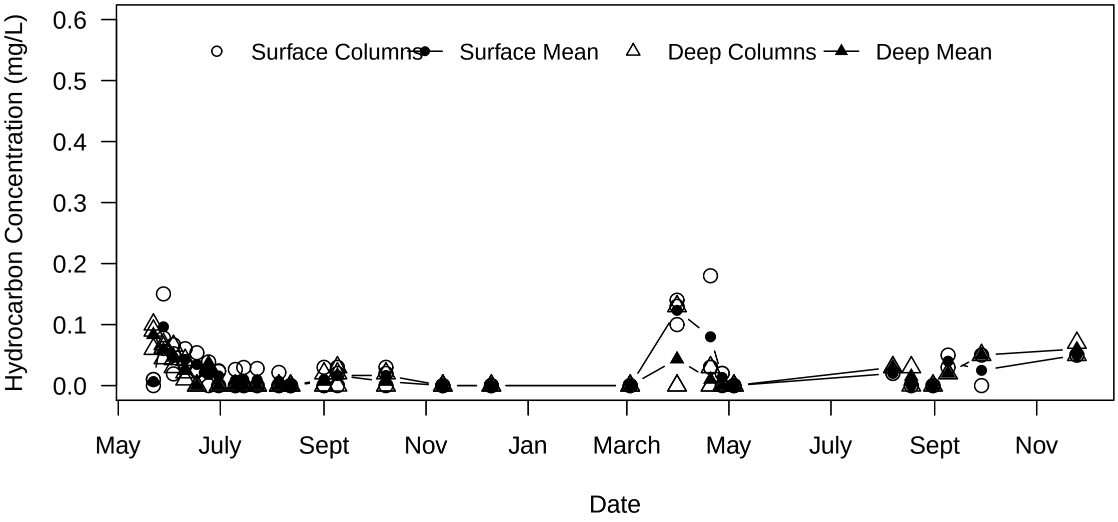


Figure 5.12: F2 hydrocarbon concentrations in leachate water

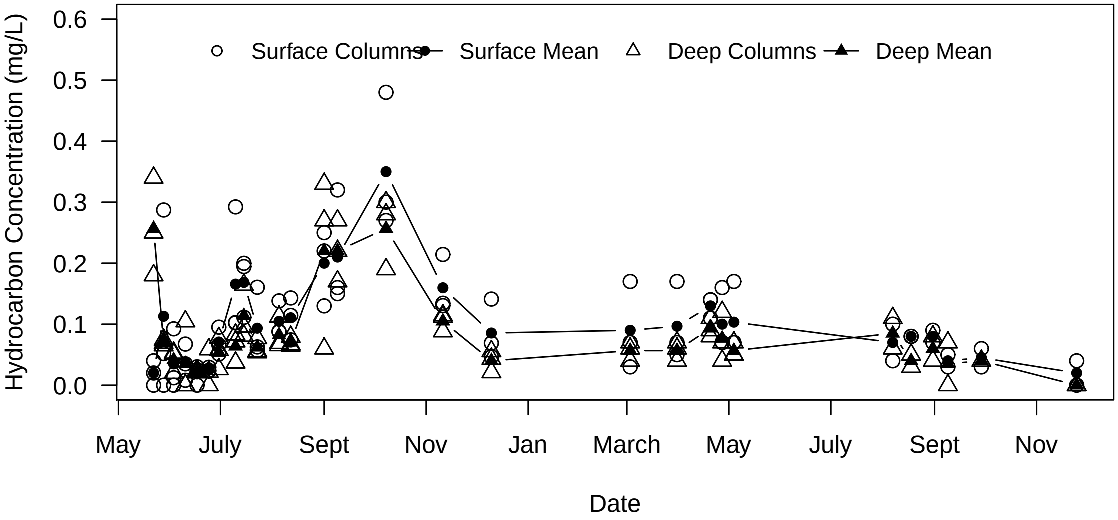


Figure 5.13: F3 hydrocarbon concentrations in leachate water

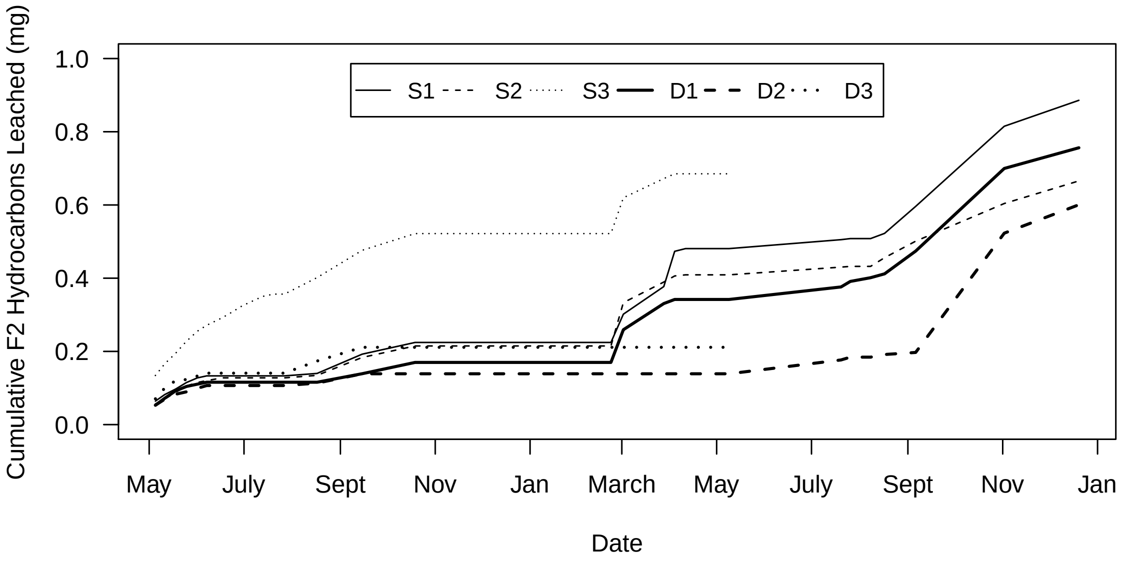


Figure 5.14: Cumulative F2 hydrocarbons leached

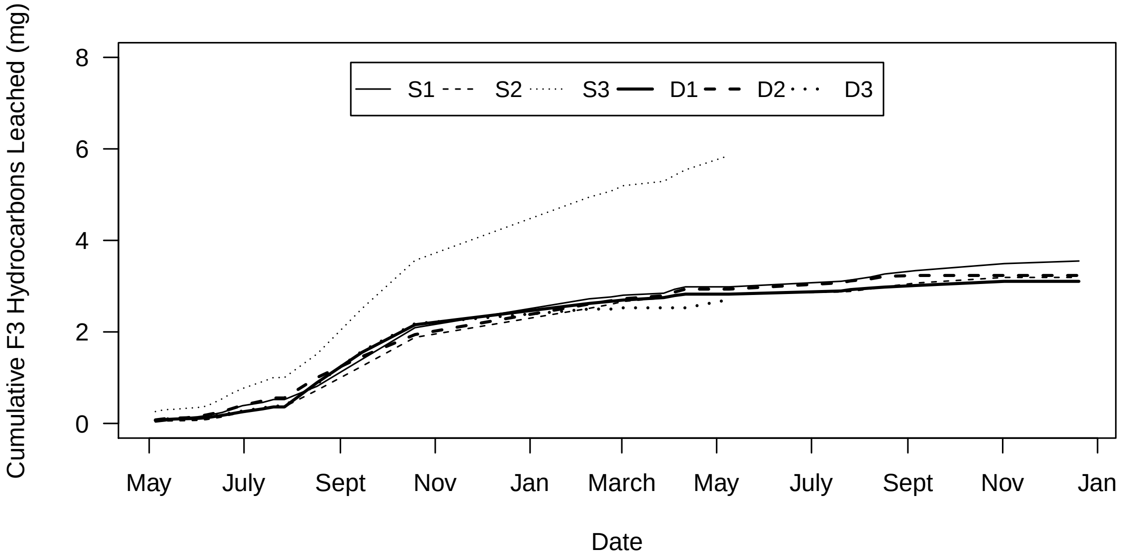


Figure 5.15: Cumulative F3 hydrocarbons leached

subsequently flushed away when the dosing of water resumed.

Fraction 3 hydrocarbon concentrations remained fairly consistent throughout the experiment, above detection limits, as shown in Figure 5.13. The abundance of F3 hydrocarbons in the tarballs and their relatively low solubility make this similar to an infinite source condition. The result is a relatively steady F3 concentration in the leachate. Cumulative hydrocarbon leaching confirms that most columns leached in a similar pattern at similar rates, with the exception of S3.

Two possible explanations are considered for the F2 and F3 concentration differences in the leachate. It may be that in flowing around the tarball material, the soil water failed to dissolve detectable quantities of F2. If this were the case, F3 hydrocarbon concentrations would be expected to behave in the same manner. This was not observed, as can be seen in Figure 5.13. Alternatively, F2 hydrocarbons may not be continuously present at the surface of the tarball in sufficient quantity to produce detectable concentrations in the leachate. The presence of F2 at the surface of the tarball could be the result of F2 within the tarball itself or as a daughter product resulting from the decomposition of larger hydrocarbon molecules. Although diffusion likely does occur within the tarball they are near solid in consistency, so diffusion must be very slow, much slower than the flow of water. Thus it appears likely that the F2 hydrocarbons are daughter products from degradation. The continued decline in leachate concentration under steady state flow indicates that this degradation occurred at a rate slower than the leaching of water. This would also explain the recovery of these concentrations after a period of no flow, as the hydrocarbons have an opportunity to accumulate.

Extrapolating this data to expected field conditions requires a broad understanding of environmental science, as well as judgement and experience. This experiment represents only one level of tarball affectedness, at a particular hydrocarbon concentration, and essentially only one flowrate. A reasonable interpretation of the data suggests that detectable levels of hydrocarbons will leach from areas with heavy tarball accumulations. Concentrations leaching from areas of light accumulation are likely to be below detection limits, and perhaps zero. These hydrocarbons will be within the F2 and F3 range at concentrations well below the F2 regulatory guideline for clean groundwater in a natural environment.

5.4.2 Leachate Total Carbon and Total Organic Carbon

Leachate samples were analyzed for Total Carbon and Total Organic Carbon at 21 dates throughout the course of the experiment. These analyses were conducted at the University of Saskatchewan on a Teckmarr-Dohrmann Phoenix 8000 persulphate analyzer. The results of these analyses are shown in Figures 5.16 and 5.17. Average concentrations of Total Carbon and Total Organic Carbon in the water added to the columns (background) are represented by dashed lines on these graphs.

Leached carbon and organic carbon both follow a typical leaching profile throughout the course of the experiment. The profiles decline gradually from an initial high to concentrations that are just a fraction of the initial rates. Note that total carbon and total organic carbon are plotted on different vertical scales.

Differences are apparent between surface and deep columns for both total carbon and total organic carbon. In total carbon, initial concentrations from the deep columns were slightly greater than those from surface columns. After about a month this pattern reversed, with surface columns releasing carbon at a greater rate than the deep columns throughout the remainder of the experiment. The deep columns began leaching total organic carbon at nearly double the concentrations of surface columns. After about three months the surface and deep columns were leaching at nearly the same rates. These remained at approximately the same rates throughout the experiment.

There are no direct regulations on total carbon and total organic carbon in natural groundwater in Alberta. However these values provide an interesting perspective on the materials leached by the tarballs. Organic carbon is leached at rates an order of magnitude greater than chromatographable hydrocarbon material. Total carbon is leached at several times the rate of organic carbon, although there may be some contribution to total carbon from the sand matrix.

Total carbon and total organic carbon concentrations in the field would be expected to have a less pronounced ‘initial flush,’ due to the relatively lower infiltration rates. The stabilized concentrations might be expected to be somewhat above the concentrations detected in this experiment because infiltration rates will be considerably lower.

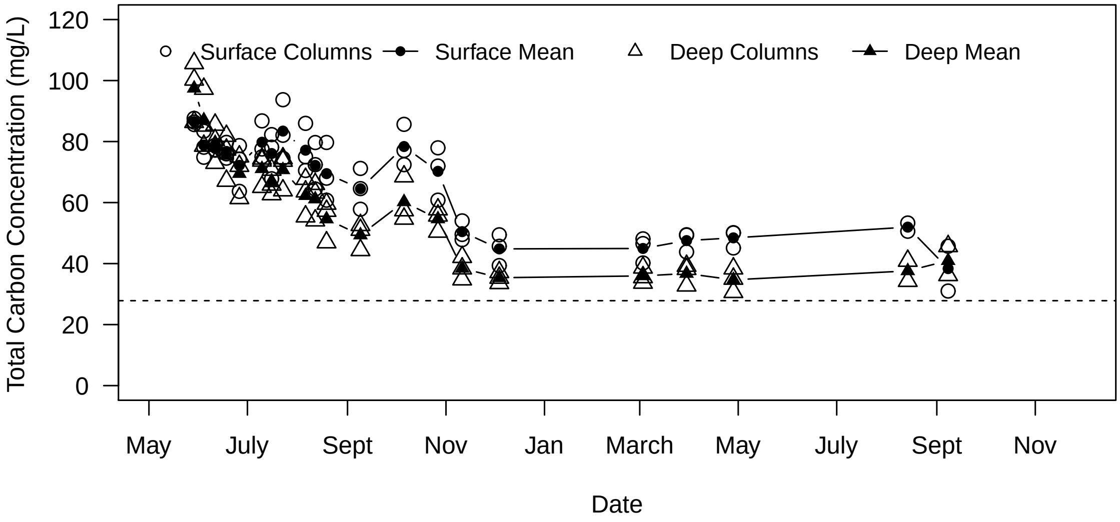


Figure 5.16: Total carbon concentrations in leachate water

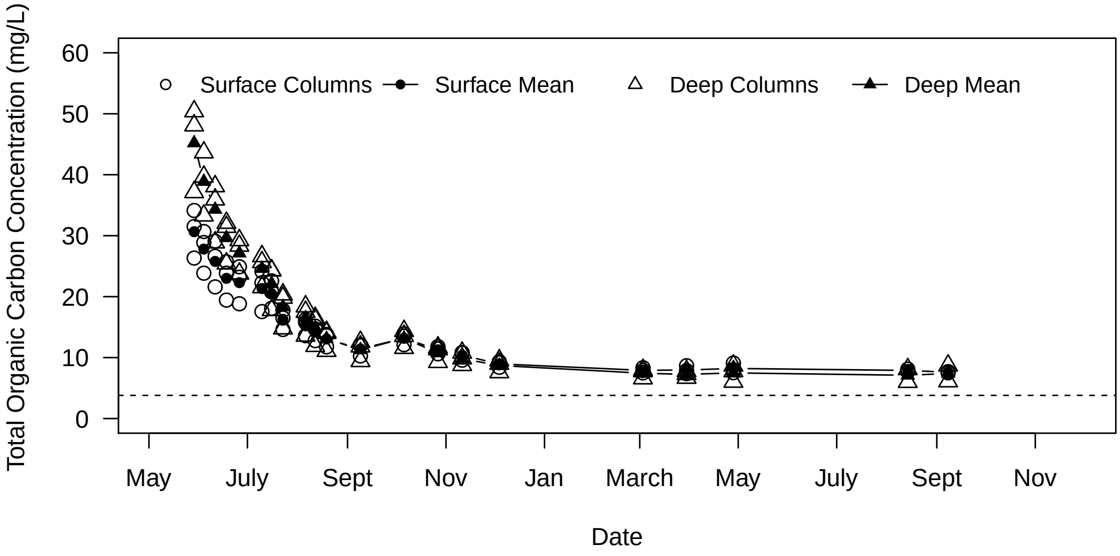


Figure 5.17: Total organic carbon concentrations in leachate water

5.4.3 Leachate Naphthenic Acids

Column leachate was also analyzed for the presence of naphthenic acids. Naphthenic acids are carboxylic acids of cyclic organic molecules. Naphthenic acids were not expected in the leachate. However, given their signficant toxicity, a precautionary scan was conducted. This was done according to procedures under development at the National Hydrology Research Centre of Environment Canada in their labs. Procedures were provided in Chapter 3.

Four samples from August of 2008 were analyzed. Based on the chromatographic fingerprint it was determined that naphthenics were not present at detectable levels in the column leachate.

5.4.4 Summary

The presence of tarballs in the soil column has been shown to cause minor carbon and hydrocarbon impacts to water leaching through the soil column. F1 hydrocarbons were not detected during this experiment. Fractions 2 and 3 were consistently present at detectable levels under an intermittent flow regime. These fractions remained well below the clean water guidelines established for Natural Areas by Alberta Environment. Total organic carbon and total carbon were detected at levels one and two orders of magnitude greater than chromatographable hydrocarbons, respectively. Tarballs taken from the top metre were found to consistently leach more total carbon than those taken from greater depth. Organic carbon leaching rates were nearly the same for the surface and deep tarball columns. Both total carbon and total organic carbon leaching rates declined to low, steady levels after approximately six months. Napthenic acids were not detected in leachate water.

5.5 Biodegradation Potential

Another important component of this study has been an assessment of the biodegradability of tarball materials. Oxygen and Carbon Dioxide concentrations within the column headspace were monitored by an automated system throughout the course of the experiment. Changes in these concentrations are attributed primarily to microbial activity since the columns contained only tarball material and very clean fluvial sands. It is important to note that no microbes were added to the soil column. That is to say, the only microbial biomass present in the column was the population naturally present in the soil and tarball materials. This approach was taken in order to test the tarballs under similar conditions as in the field. Monitoring was also conducted for the release of volatile hydrocarbons from the column and a variety of other gases that might possibly indicate microbial activity.

5.5.1 Respiration Monitoring

Cumulative respiration for the experiment is illustrated in Figures 5.18 and 5.19 and summarized in Table 5.8. These figures all follow the same convention, where individual readings are illustrated by open markers and the mean of all readings in that category (surface or deep) are illustrated by filled markers and connected by a line. Mean values are calculated as weighted averages after two of the columns were disassembled in June so as to maintain the trend of the mean value lines in these figures. If this approach was not taken, the mean value line would suddenly shift after the columns were disassembled. These weighted averages are based upon two thirds from the column which closely traced another and one third for the column which did not follow the other two. Also, the oxygen sensor encountered technical problems near the end of October 2009. For completeness, oxygen readings have been extrapolated using the historical relationship between the oxygen and carbon dioxide values. Data points generated in this way are indicated with a superimposed ‘x’.

It is clear from Table 5.8 that tarballs taken from the top metre of the soil column are more active than tarballs from deeper in the soil profile. This is expected because the top metre of the soil profile is more biologically active than lower depths.

The relationship given by Zytner et al. in Chapter 2 was used to provide an estimate of hydrocarbon degradation by microbial activity. This relationship is given in Equation 5.2. It provides a stoichiometric balance for the complete biodegradation of diesel fuel. Inferred degradation can be determined by applying this relationship to either oxygen consumption or carbon dioxide production. The resulting values are given in Table 5.9, where degradation under the heading oxygen is calculated based upon oxygen

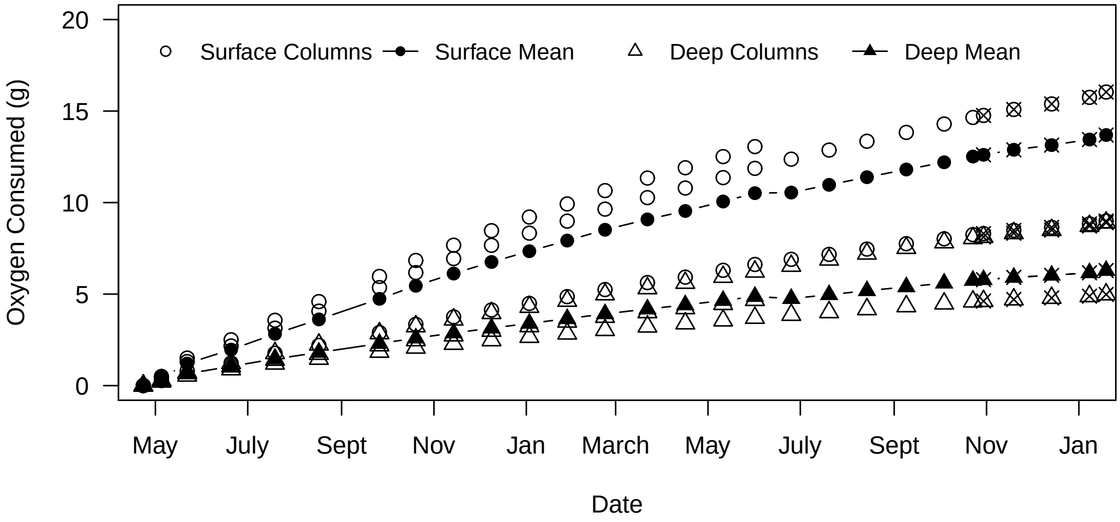


Figure 5.18: Total oxygen consumed - all columns

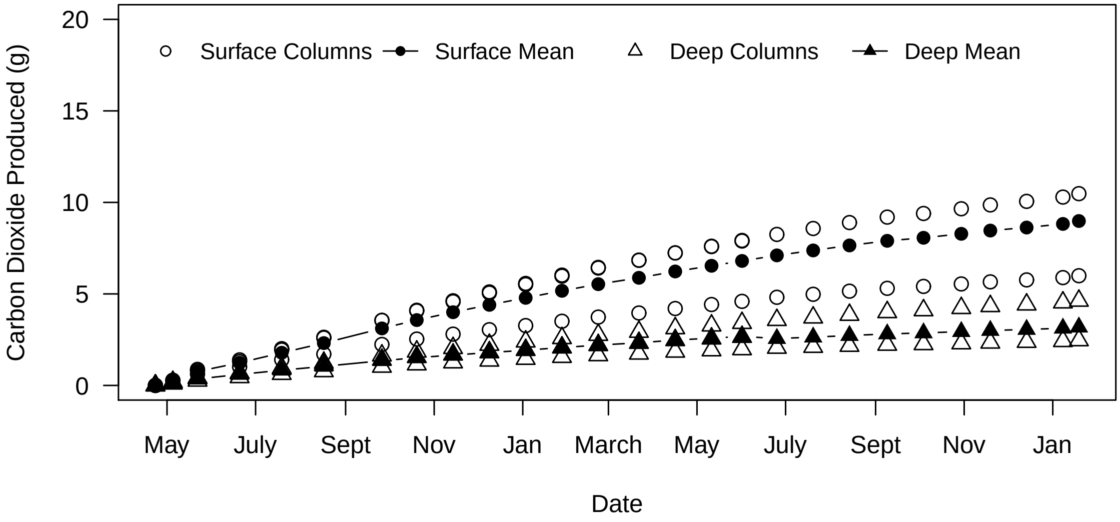


Figure 5.19: Total carbon dioxide produced - all columns

readings and values under the heading carbon dioxide are calculated based upon carbon dioxide readings.

Table 5.8: Cumulative soil respiration

Column	Duration (months)	Oxygen Consumed (g)	Carbon Dioxide Produced (g)	Methane Produced (g)
S-1	21	8.99	5.99	0.01
S-2	21	16.0	10.5	0.02
S-3	13	13.1	7.92	0.02
D-1	21	4.98	2.47	0.01
D-2	21	8.90	4.63	0.02
D-3	13	4.68	2.65	0.01

Table 5.9: Inferred cumulative PHC degradation using Zytner's Diesel molecule model

		Total Degradation (g)		Degradation Rate (g/year)	
Column	Duration (months)	Oxygen	Carbon Dioxide	Oxygen	Carbon Dioxide
S-1	21	2.6	1.9	1.5	1.1
S-2	21	4.6	3.4	2.7	1.9
S-3	13	3.8	2.6	3.4	2.3
D-1	21	1.4	0.8	0.8	0.5
D-2	21	2.6	1.5	1.5	0.9
D-3	13	1.4	0.9	1.2	0.7
S-Mean				2.5	1.8
D-Mean				1.2	0.7

$$C_{16}H_{34} + 24.5O_2 \longrightarrow 17H_2O + 16CO_2 \tag{5.2}$$

These indicate degradation per column ranging from 0.9 g to 4.6 g. This represents a very small proportion of the approximately 860 g of hydrocarbon present in each column. It is concluded that degradation of tarball materials occurs at very slow rates. Assuming this to be a constant rate of degradation acting on tarballs of average hydrocarbon content, it would require between 275 and 650 years to degrade all hydrocarbon material at surface tarball rates and between 675 and 1250 years at deep tarball rates. In a field situation, the time required would be much longer due to several factors. These include periods of:

- lower productivity at unfavourable temperatures,
- no productivity during freezing conditions,

- limitation due to the availability of oxygen and/or accumulation of carbon dioxide, and
- insufficient or excess soil moisture.

These rates are also expected to slow over time as the relatively more biologically available molecules are consumed. The remaining, less biologically available molecules are subsequently consumed at a slower rate.

5.5.2 Volatile Hydrocarbons

Monitoring for volatile hydrocarbons was conducted using Orbo 302 charcoal sorbent tubes as outlined in Chapter 3. The Orbo tubes provide a cumulative measure of hydrocarbons in the headspace gas, extracting all hydrocarbons with each refresh cycle of the respirometer. Volatile hydrocarbons were expected to be minimal because the F1 (volatiles) concentration of the tarballs is virtually zero and slow degradation rates would produce very little in the way of daughter products. Volatile hydrocarbons detected in this experiment are included in Table 5.10

Table 5.10: Hydrocarbons volatilized

Column	Duration (months)	Hydrocarbons (mg) F1	F2	F3	Total
S-1	21	0.23	0.11	0.05	0.39
S-2	21	0.38	0.29	0.08	0.75
S-3	13	0.17	0.24	0.00	0.41
D-1	21	0.36	0.28	0.10	0.74
D-2	21	0.17	0.30	0.10	0.57
D-3	13	0.13	0.26	0.01	0.40

It is clear that minimal volatilization occurred during the course of this experiment, on average just 0.54 mg of approximately 860,000 mg contained in each column.

5.5.3 Monitoring of other Gases

Several other gases were monitored throughout this experiment to determine if biodegradation occurs using electron receptors other than oxygen. To ensure conditions remained predominantly aerobic, methane (CH_4) was monitored using the Micro Oxymax respirometer. These gases were scanned using Draeger gas detection tubes as outlined in Chapter 3. Each of the gases scanned are listed in Table 5.11 along with minimum detectable concentrations. Of these gases, only sulphur dioxide (SO_2) was regularly detected, however at very low levels of about 5 ppm, which represents a total concentration after approximately 30 days of respiration. After four sampling intervals sulphur dioxide also was not detected. Sampling of these gases was discontinued at that time.

Table 5.11: Soil respiration of other gases

Gas	Formula	Minimum Detection Limit in ppm
Ammonia	NH_4	5
Hydrogen sulphide	H_2S	1
Nitrogen oxides	NO_X	2
Sulphur dioxide	SO_2	1

It is clear that under experimental conditions, tarball degradation occurred almost exclusively by oxidation of carbon. Since microbial degradation occurs almost exclusively by the respiration of oxygen and carbon dioxide, this validates the application of such a model to column respiration, as in Section 5.5.1.

5.5.4 Summary

The potential for biodegradation appears minimal on all but a geologic timescale. The most active column was found to degrade at most a fraction of one percent of its hydrocarbon content in a 21 month period. Volatilization of hydrocarbons occurred at rates several orders of magnitude less than degradation, representing virtually no hydrocarbon content in the same time. Microbial activity associated with electron receptors other than carbon was not detected.

5.6 Mass Flux Summary

By way of conclusion, a summary of column activity is provided in Table 5.12. This table is intended to summarize pertinent chemical and physical properties of the column, and its activity in terms of air, water, dissolved carbon and hydrocarbon fluxes.

From this it is clear that tarball hydrocarbons are largely inactive and immobile. Although the tarballs contain significant quantities of hydrocarbon material across several fractions, very minimal leaching or volatilization occurred during this experiment.

Table 5.12: Column study summary

	Units	S-1	S-2	S-3	D-1	D-2	D-3
Duration	(Months)	21	21	13	21	21	13
Mass of Sand	(kg)	47.9	44.7	46.9	47.5	46.4	46.1
Mass of Tarball	(kg)	25.4	27.3	23.3	23.9	23.5	25.0
Total Mass	(kg)	73.3	72.0	70.2	71.4	69.9	71.1
Calculated Sand Density	(kg/m^3)	1610	1590	1490	1570	1510	1530
Calculated Sand Porosity	(kg/m^3)	0.39	0.40	0.44	0.41	0.43	0.42
Volume of Water Leached	(L)	40.9	38.6	30.4	40.9	40.5	31.2
Hydrocarbon Content							
F2	(mg)	331	317	583	262	810	863
F3	(mg)	34,700	38,600	40,160	39,000	56,000	38,900
F4G	(mg)	935,000	995,000	747,000	762,000	986,000	727,000
Total Hydrocarbons							
Leached	(mg)	4.4	3.9	6.5	3.9	3.7	2.9
Volatilized	(mg)	0.4	0.8	0.4	0.7	0.6	0.4
Degraded	(mg)	2,260	4,000	3,160	1,120	2,030	1,100
Other Carbon Leached							
Total Carbon	(mg)	905	1,180	1,110	629	988	721
Total Organic Carbon	(mg)	354	290	303	297	444	347

Leached hydrocarbons, when detected, were a fraction of regulatory guidelines. Meaningful quantities of hydrocarbons were degraded, but this does not represent a negative impact to the environment. By way of comparison, annualized flux rates are presented in Table 5.13. These flux rates were calculated by simply dividing the total quantities leached, volatilized or degraded during the experiment.

Overall flux rates represent a very small proportion of tarball hydrocarbons under experimental conditions. Field conditions are likely to produce similar, or possibly much reduced fluxes. The reduction primarily attributable to the limited supply of soil moisture and the suspension of the water cycle during the freezing months of winter. Leaching rates would also be expected to decline over time as the components are further weathered or progressively leached away. Annual flux rates at these orders of magnitude would be expected to have minimal impact on the natural environment.

5.7 Conclusions

This chapter has presented the results of a soil column leaching study intended to assess the potential for tarball mobility and biodegradation. The columns consisted of approx-

Table 5.13: Annualized flux rates

	S-1	S-2	S-3	D-1	D-2	D-3
Total Hydrocarbons (mg/yr)						
Leached	2.5	2.2	6.0	2.2	2.1	2.7
Volatilized	0.2	0.5	0.4	0.4	0.3	0.4
Degraded	1,290	2,290	2,920	640	1,160	1,020
Other Carbon Leached (mg/year)						
Total Carbon	517	674	1,020	359	565	665
Total Organic Carbon	202	166	280	170	254	320

imately 30% tarball material and 70% clean sand by mass. Hydrocarbon concentrations, as total hydrocarbon content divided by total soil mass ranged from below clean soil guidelines for Fractions 1 and 2 to 2 and 4 times clean soils guidelines for Fractions 3 and 4 respectively. Total hydrocarbons leached, volatilized and degraded over 21 months were less than 1% of initial total hydrocarbons. It is concluded that tarballs present minimal, if any, risk of environmental impacts if incorporated in reclamation covers.

The evolution of the moisture regime within the columns suggests that tarballs have a definite impact on the movement and storage of water within the soil structure. The tarballs were found to retain moisture, and are suspected of interfering with the movement of water through the soil.

Chapter 6

Conclusions

6.1 Overview

This thesis presents a detailed study of the geochemical properties and behaviour of surficial accumulations of bitumen (tarballs) identified in glaciofluvial soils throughout the Athabasca Oil Sands region. A brief literature review indicates a continual awareness of the presence of these materials from the earliest explorations forward. The greatest interest is taken by the early discoverers, who suggest that the abundance and distribution of these materials would make the area ideal for the study of hydrocarbon redistribution by geologic processes. After this initial description, references to "reworked bitumen" are made in passing with little or no discussion as to their nature or abundance. However, the presence of these hydrocarbons among soils to be used for reclamation by oil sands operators have prompted concerns regarding the applicability of tarball affected soils in reclamation settings.

Several topics were addressed in the course of this study, namely:

- in-situ hydrocarbon concentrations,
- potential indicators of hydrocarbon concentration,
- hydrocarbon mobility to the groundwater cycle,
- hydrocarbon biodegradability, and
- additional insight into the genesis of the material.

6.1.1 In-situ Hydrocarbon Concentrations

The hydrocarbon concentrations of tarball materials were analyzed in 276 samples collected over the course of this study. Hydrocarbons were analyzed according to the Canadian Council of Ministers of the Environment Benchmark Method for Petroleum Hydrocarbons in Soil. The data were found to be widely variable, however some general trends were identified. Most tarball accumulations were found to be hard and brittle, difficult to break with the hand, or in some cases simply crumbling apart when picked up. These tarballs had typical hydrocarbon concentrations as given in Table 6.1. However, the cores of large tarballs were occasionally found to contain hydrocarbons at concentrations several orders of magnitude greater than typical tarball accumulations. These 'rich cores' were soft and malleable even at cool autumn temperatures. Their typical hydrocarbon concentrations are also given in Table 6.1.

Table 6.1: Tarball PHC concentrations

Fraction	'Typical' (mg/kg)	Rich Core (mg/kg)
F1	n.d.[a]	100 to 1,000
F2	30	600 to 3,000
F3	600	3,000 to 8,000
F4G	25,000	55,000 to 85,000

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[a] n.d. - not detected

It must be emphasized that this study focuses only on tarballs taken from upland settings. Preliminary evidence suggests that tarballs taken from wetland areas have very different hydrocarbon concentrations and compositions.

6.1.2 Potential Indicators of Hydrocarbon Concentration

It was hypothesized that changes in various soil properties might correlate to hydrocarbon concentration. Tarball hydrocarbon Fractions 3 and 4G were investigated for direct relationships to the following grain-size characteristics:

- median grain-size,
- characteristic grain-size,
- uniformity coefficient,
- coefficient of gradation, and
- silt and clay content.

Very weak correlations, and sometimes none at all, were identified for these parameters. None were considered useful for field screening of hydrocarbon content.

6.1.3 Hydrocarbon Mobility to Groundwater

The mobility of tarball hydrocarbons was found to be near insignificant, leaching only a few milligrams from soils containing several hundred thousand milligrams. It was noted that the leached hydrocarbons consisted in significant proportion of F2 hydrocarbons, suggesting the production of daughter products by microbial activity. This would be consistent with observed soil respiration.

Hydrocarbon concentrations in the leachate increased after periods of relative dryness. This suggests a concentrating effect, where microbial activity produced greater quantities of soluble hydrocarbons than were carried away by the water. Although this seems to suggest that concentrations might climb very high under field conditions of very little water movement, field conditions are also expected to significantly inhibit microbial activity due to variations in temperature, gas concentrations and moisture availability. Thus it is expected that hydrocarbon concentrations observed in the field will not greatly exceed those observed in this study.

6.1.4 Hydrocarbon Biodegradability

Biodegradation is presumed to be associated with the presence of tarball materials. This was observed as both soil respiration and the evolution of daughter products found in leachate. However, total inferred degradation was less than one percent of the total hydrocarbon content of a given column. At observed rates of degradation, if allowed to continue under experimental conditions and if constant over time would require hundreds to thousands of years to degrade all hydrocarbons present in the columns. Degradation in the field would likely take orders of magnitude longer, given the limitations on microbial activity in the field due to variations in temperature, gas concentrations and moisture availability. This is further complicated by the expected decline in the rate of degradation as biologically available hydrocarbons are selectively removed from the system. Thus it appears unlikely that biodegradation will have a significant impact on tarball hydrocarbon concentrations.

6.1.5 Material Genesis

Field observations that tarball soils were not significantly different in grain-size than adjoining soils were confirmed in this study, with the exception of a slight enrichment in the silt and clay fraction of tarball soils. However, the silt and clay content of tarball soils was found to be considerably less than that of a sample of lean oil sand. These observations further support the theory that tarball bitumen was placed by a large scale flood event. It is hypothesized that the bulk of soil material was extracted from the bitumen, except a small portion of the fine particles. This bitumen was later deposited in downstream beach environments, impregnating the existing soil matrix with bitumen and a small component of fine soil particles.

6.2 Recommendations for Future Work

Other avenues for further research were identified throughout the course of this study. These fall into two broad categories depending upon the mechanism or charateristic to be studied;

- Industrial Research - of particular interest in the reclamation of mining areas, and
- Academic Research - of interest to the scientific community, but with little application to industrial reclamation.

6.2.1 Industrial Research

With direct regard to this study, there exists a definite need to confirm the results - specifically the minimal impacts to groundwater - with field scale investigations. The focus of these studies would be hydrocarbon concentrations of in-situ porewater and/or surface water in tarball reclaimed areas. This would incorporate the effects of site specific soil and atmospheric conditions, as well as the spatial variability of tarball material in reclamation soils. Such a study is a prudent next step before tarball soils are applied throughout reclamation.

The mechanisms of moisture retention are hypothesized in this work. However, a detailed study is required to determine the moisture retention behaviour associated with tarball materials and their relative dominance in an unsaturated condition. This detailed understanding would permit the development of appropriate engineering models to quantify and predict moisture availability to plants.

In addition to this study, there exists a definite need to address tarball hydrocarbons from wetland areas. Wetlands formerly made up a significant portion of area under active mining and tarballs from these areas were excluded from the population studied in this work. Initial investigations suggest that wetland tarballs are significantly different from upland tarballs in terms of both hydrocarbon content and fingerprint. There is no reason to expect that the results of this study are applicable to tarballs with a significantly different geologic history.

6.2.2 Academic Research

Under the broader scientific umbrella, this study points to several gaps in scientific knowledge regarding these materials. Specifically, patterns of deposition may be indicative of drainage history through the Clearwater-Lower Athabasca Spillway. Furthermore, the mechanics of bitumen mobilization remain essentially unstudied. The question of naturally occurring hydrocarbon releases in the Athabasca river system would also benefit from a program of study regarding the mobilization (as potentially dissolved, non-aqueous or traction sediments) of bitumen in running surface waters. Perhaps the presence or absence of tarballs may indicate a threshhold velocity which would also shed light on the draining of the CLAS.

REFERENCES

ALBERTA ENVIRONMENT 2007. Alberta tier 1 soil and groundwater remediation guidelines. Technical report, Alberta Environment.

AOSERP 1982. Soils inventory of the Alberta Oil Sands Research Program study area.

BAYROCK, L. A. 1974. Surficial geology, alberta foothills and rocky mountainsa joint project of alberta environment and the alberta research council.

CARRIGY, M. A. 1959. Research Council of Alberta: Geological Division Memoir 1 Geology of the McMurray Formation, volume 3. L. S. Wall, Queen's Printer for Alberta, Edmonton, Canada.

CARRIGY, M. A. 1966. Lithology of the athabasca oil sands. Technical Report 18, Alberta Research Council.

CARRIGY, M. A. AND KRAMERS, J. W. 1973. Guide to the Athabasca oil sands area. Alberta Research Council, Edmonton, Canada.

CCME 2001a. Canada-wide standards for petroleum hydrocarbons (PHC) in soil. Technical report.

CCME 2001b. Reference method for the Canada-Wide Standard for Petroleum hydrocarbons in soil - Tier 1 Method. Canadian Council of Ministers of the Environment Inc., Winnipeg, MB.

CCME 2008. Canada-wide standard for Petroleum hydrocarbons (PHC)in Soil: Technical Supplement.

CEMA 2006. Land Capability Classification System for Forest Ecosystems in the Oil Sands, volume 1. Edmonton, Canada.

CONLY, F. M., CROSLEY, R. W., AND HEADLEY, J. V. 2002. Characterizing sediment sources and natural hydrocarbon inputs in the lower athabasca river, canada. *Journal of Environmental Engineering and Science* 1:187.

DOMENICO, P. A. AND SCHWARTZ, F. W. 1998. Physical and chemical hydrogeology. Wiley, New York.

ELLS, S. C. 1926. Bituminous sands of northern alberta :occurrence and economic possibilities : report on investigations to the end of 1924. Technical Report 632, F.A. Acland Printer to the King's Most Excellent Majesty.

ELLS, S. C. 1932. Investigations of mineral resources and the mining industry, 1931. F.A. Acland Printer to the King's Most Excellent Majesty, Ottawa.

ENVIRONMENT CANADA 2008. Canadian climate normals 1971-2000.

ERCB 2011. Alberta's energy reserves 2010 and supply/demand outlook 2011-2020. Technical Report ST98-2010, Energy Resources Conservation Board.

FETTER, C. W. 1980. Applied hydrogeology. C. E. Merrill, Columbus.

FISHER, T. 2002. Preboreal oscillation caused by a glacial Lake Agassiz flood. *Quaternary science reviews* 21:873.

FISHER, T. G. 2009. Deglaciation ages and meltwater routing in the fort mcmurray region, northeastern alberta and northwestern saskatchewan, canada. *Quaternary science reviews* 28:1608.

Fisher, T. G. and Smith, D. G. 1994. Glacial lake agassiz: its northwest maximum extent and outlet in saskatchewan (emerson phase). *Quaternary science reviews* 13:845.

Flach, P. D. 1984. Oil sands geology - Athabasca deposit north. Technical Report 46, Alberta Research Council.

Fowlis, I. 1995. Gas Chromatography: Analytical Chemistry by Open Learning. Wiley, New York, NY.

Freeze, R. A. and Cherry, J. W. 1979. Groundwater. Prentice-Hall, Englewood Cliffs, N.J.

Green, R. 1970. Bedrock geology of northern alberta.

Gustafson, J. B., Tell, J. G., and Orem, D. 1997. Selection of Representative TPH Fractions based on fate and transport considerations, volume 3. Amherst Scientific Publishers, Amherst, MA.

Hein, F. J. and Cotterill, D. K. 2006. The athabasca oil sands: A regional geological perspective, fort mcmurray area, alberta, canada. *Natural resources research* 15:85.

Lanoue, A. 2009. Personal communication.

Leverington, D. W. 2000. Changes in the bathymetry and volume of glacial lake agassiz between 11,000 and 9300 14c yr b.p. *Quaternary Research* 54:174.

Leverington, D. W., Mann, J. D., and Teller, J. T. 2002. Changes in the bathymetry and volume of glacial lake agassiz between 9200 and 7700 14c yr b.p. *Quaternary Research* 57:244.

M. Fleming, I. Fleming, J. H. J. D. K. P. 2011. Surficial bitumens in the Athabasca oil sands region, Alberta, Canada. *International Journal of Mining, Reclamation and Environment* 2:134.

McPherson, R. A. and Kathol, C. P. 1977. Surficial geology of potential mining areas in the Athabasca oil sands region. Technical Report Open File Report 1977-4, Alberta Research Council.

Mossop, G. D. 1980. Geology of the Athabasca oil sands. *Science* 207:145.

Naeth, M. A. 2011. Vegetation and soil water interactions on a tailings sand storage facility in the Athabasca Oil sands region of Alberta, Canada. *Physics and Chemistry of the Earth* 36:19.

Paragon 2005. Hydrocarbons in natural soils: Literature review. Technical Report Paragon: 05-011.

Paragon 2006. Hydrocarbons in natural oil sands soils: Field survey. Technical Report Paragon: 06-053.

Peramanu, S., Pruden, B. B., and Rahimi, P. 1999. Molecular weight and specific gravity distributions for Athabasca and Cold Lake bitumens and their saturate, aromatic, resin and asphaltene fractions. *Industrial and engineering chemical research* 38:3121.

R. G. Zytner, A. Salb, T. R. B. M. L. and Striver, W. H. 2001. Bioremediation of diesel contaminated soil. *Canadian Journal of Civil Engineering* 28:131.

Rhine, J. L. and Smith, D. G. c1988. The late pleistocene athabasca braid delta of northeastern Alberta, Canada: a paraglacial drainage system affected by aeolian sand supply. Fan deltas:sedimentology and tectonic settings. Blackie, Glasgow.

Smith, D. G. 1993. Glacial lake agassiz: the northwestern outlet and paleoflood. *Geology* 21:9.

Swyngedouw, C. 2010. Personal communication.

Teller, J. T. 2006. Two possible routings for overflow from lake agassiz during the younger dryas. a reply to comment by t. fisher, t. lowell, h. loope on "alternative routing of lake agassiz overflow during the younger dryas: new dates, paleotopography, a re-evaluation". *Quaternary science reviews* 25:1142.

van Genuchten, M. T. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Journal of the Soil Science Society of America* 44:892.

Visser, S. 2008a. Petroleum Hydrocarbons (PHCs) in Lean Oil Sand (LOS): Degradation potential and toxicity to ecological receptors. Technical report.

Visser, S. 2008b. Petroleum Hydrocarbons (PHCs) in Tar Balls: Degradation potential, leaching potential and toxicity to ecological receptors. Technical report.