BIOPILE TREATMENT OF HYDROCARBON CONTAMINATED SOIL OF THE REDWATER OIL PRODUCTION AREA

BY

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In the words of Adam Smith (1776);

“Individuals or corporations acting in their own self-interest can guide society towards common goals”
Biopile Soil Treatment in the Redwater Oil Production Area

Abstract

The Redwater Production Area (RPA) is an established oil field located north of Edmonton in central Alberta. Recent assessments indicate that substantial amounts of hydrocarbon contaminated soil exist in the RPA as a result of the use of flare pits, ecological ponds, product spills and pipeline leaks. Alternative remedial technologies may reduce the quantity, cost, and ultimately the long-term liabilities associated with the current practice of landfill disposal. The purpose of this thesis is to assess the viability of accelerated biopile soil treatment as a remedial methodology in the rehabilitation of contaminated soil in the RPA. The thesis includes a literature search, a bench scale treatability and pilot biopile experiment and concludes with a summary of the viability of biopiling to be employed as part of a multi-year/multi-site remedial initiative. Construction of the Redwater Soil Treatment Facility began in 2008 with treatment and recycling operations commencing in early 2009.
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1 Introduction

Considerable attention has been focused on the effects of point source contamination on human, animal and ecosystem health, as society has begun to realize the long term and far-reaching adverse effects of industrial contaminants (Beck, Wilson, Alcock & Jones, 1995). Environmental protection through remediation and reclamation of industrial sites, many of which were contaminated years before there was widespread concern with environmental deterioration and effects on human health, is now a major concern to government regulators and industry (Alexander, 1995). Spills from petroleum distillates are the most significant common type of contamination that effect soils (Cookson, 1995), and soil and groundwater contamination as a result of the production of oil and gas is a legacy of older operating fields. Ignorance, lack of regulatory guidance and even malicious intent has resulted in literally thousands of contaminated sites. Alberta is home to an estimated 30,000 flare pit sites alone (Amatya, Hettiaratchi & Joshi. 2000).

The Redwater Production Area (RPA), an active oil and gas field, has prohibitive quantities of hydrocarbon contaminated soil at a number of locations that are directly attributed to former storage, transport and handling practices; and, given the mobility potential of hydrocarbons, these sites pose serious environmental threats, especially to nearby groundwater sources (RemedX, 2005). Landfill disposal is a commonplace procedure for contaminated soil resulting from these operations. Aside from the significant direct cost of this approach, there is an inherent realization that the continued use of landfill as the primary remedial method should be minimized for reasons of sustainability, the need for additional urban lands for redevelopment; soil loss issues; and long-term corporate liability since soil will retain its hazardous characteristics, including green house gas production, for literally hundreds of years in a landfill scenario (Mohareb, Warith & Narbaitz, 2004).

Due to increased public, corporate and political awareness, new pressures have been brought to bear on companies to accomplish remediation in a more intelligent, less expensive and more expeditious fashion and consequently, there exists opportunity to explore novel techniques for cleanup. While a percentage of the soil in the RPA is thought to be recalcitrant due to its toxic nature, a considerable portion of soil that exists at the periphery of the recalcitrant material is thought to be potentially treatable through bioremedial methods.
Bioremediation can be defined as the artificial enhancement of microbial activities to diminish contaminant levels in the environment, and refers generally to the process by which organic contaminants are remediated by the action of soil bacteria (Baker & Herson, 1994). Since the constituents of petroleum products are naturally occurring, soil bacteria capable of degrading them, normally into carbon dioxide and water, are typically ubiquitous. In one method of bioremediation, known as biopile, so named because the soil is arranged above ground in a pile fashion, is an ex situ treatment system that employs process controls to expedite the native degradative qualities of the affected soil. The benefits of engineered biopile systems include safe operations, predetermined material balance potential and process control (Von Fahnestock, Wickramanayake, Kratzke & Major, 1998).

1.1 Research Objectives

It is envisioned that bioremediation, and in particular, biopile technology may be an elegant remedial solution for use within the RPA. The intention of this research is to determine the appropriateness of the technology and its applicability to a multiyear, multisite program within the RPA. The objectives of this paper are therefore twofold; first, to establish the specific contamination levels and site conditions of the RPA through the completion of background research, a bench scale treatability program and a pilot study to confirm or refute the validity of bioremedial soil treatment. The second objective will be to determine if the circumstances of the RPA make it suitable for a permanent commercial bioremedial facility. If biopile methods are determined to be a pragmatic remedial option in the RPA, the significance in terms of liability reduction, cost savings and sustainability initiatives could be significant. An adjunct research objective was to establish the functionality and reliability of field instrumentation and methods, as an important aspect of long-term management requirements are simplified and expedited qualitative analytical methods.

1.2 Background

The Redwater pool, located in north-central Alberta, was discovered in 1948. The field is approximately 50 kilometers from the city of Edmonton, with the main producer being ARC Resources Ltd. (ARC), who purchased controlling interest of the oil field from Imperial Oil Ltd. in 2005 (ARC Energy Trust [AET], 2008). A major abandonment and reclamation program for the RPA is being undertaken by ARC. It has been acknowledged that a significant quantity of contaminated soil exists as a result of
historical operations, spills and infrastructure failure, as well as a number of known former flare pits; these are earthen pits, often buried, which have been used to contain liquid wastes and burn off volatile components from the processing of the crude oil (RemedX, 2005). The soils in and around these releases are typically contaminated with high levels of hydrocarbons, metals and/or salts. There are few records available of the types and amounts of flare-pit disposed contaminants, as the release may be decades old and long since buried. Soil contaminants which are water soluble may disperse with groundwater movement and consequentially, these releases may be a long term threat to human and environmental health both on and off site (Nublein, Feicht, Schulte-Hostede & Kettrup 1994; Wang & Bartha, 1990).

1.3 Legislation and Remediation Objectives

For petroleum hydrocarbons in soil, international regulatory guidance on the management of risks from contaminated sites is emerging. In Canada, the Canadian Council of Ministers of the Environment (CCME) provides the risk management framework to guide decision making, application of reference analytical methodologies, derivation of toxicological criteria for contaminants, and criteria that are applied throughout Canada, as required. Alberta has developed its own set of legislation and criteria, based on CCME standards which will be discussed below. Given the evolution of environmental regulations, the rules governing remediation in Alberta are complicated. Regulation is partitioned depending upon the activity and whether it is on private or public lands. The Provincial regulatory agency, Alberta Environment (AENV), has jurisdiction over the legislation and regulations, the approval/review process and the regulatory instrument to terminate or transfer liability. With respect to soil contamination on specified land, the Alberta Tier 1 and Tier II Soil and Groundwater Remediation Guidelines establish generic remediation guidelines for achieving equivalent land capability (Alberta Environment [AENV], 2009). Three management options are provided: Tier 1, Tier 2, and exposure control. Tier 1 remediation guidelines are generic and can be used at most sites without modification. The Tier 2 approach allows for the consideration of specific conditions through the modification of Tier 1 guidelines and/or the removal from consideration of exposure pathways that may not be applicable. Exposure control involves risk management through exposure or administrative controls based on site-specific risk assessment (AENV, 2009).
A second governance system, specific to oil and gas properties, is provided through the Energy and Resources Conservation Board (ERCB). Broadly speaking any oilfield operations, which would include remediation on a site, are guided by the regulations and guidelines of the ERCB, although the criteria and standards of the AENV are utilized. Interestingly, once the contamination moves beyond the fenceline of an oil and gas site (i.e. off site), AENV becomes the lead agency.

The move towards risk-based corrective action has been slow, and while progress has been made in integrating the aspects of analysis, exposure assessment and technology verification, there are gaps. Regulatory systems are not well targeted on risk-critical components; risk assessments do not account for the weathered contaminants encountered at many older sites; and claims of treatment success are still supported by data showing reductions in hydrocarbon load in isolation of a combined reduction in toxicity, chemical mass and risk (American Petroleum Institute, 2001; Hough, et al, 2005).

Caught between stringent criteria to reuse soil, and archaic policies that unwittingly encourage landfilling, many companies do not explore treatment/recycling of contaminated soil as a remedial alternative. There are few incentives for companies to recycle/reuse once contaminated soil: in fact the present governance regime acts as an unstated deterrent. Soil multifunctionality, a common goal, requires that after remediation soil should pose no harm to humans, animals or plants, regardless of the use of the site, the type of soil, the pollutants or the locale (Beinat & Nijkamp, 1997). Didactic policies of this ilk result in cost escalations and thus do not promote soil recycling and limit remedial alternatives. The result is that companies responsible for cleanups often delay remediation rather than trying new technologies because they perceive no economic gain from an accelerated cleanup (National Research Council, 1997).

For this study and future remedial operations in the RPA, the criteria for treatability are the generic criteria applicable to all land-uses, as dictated by AENV criteria management which does allow the use of risk-based corrective action. This is an important factor in remediated soil management in Alberta as there is at least recognition that strict adherence to numerical standards, the demand for soil multifunctionality and an increasing, inadvertent reliance on landfill as a remedial solution, is unsustainable.
1.4 Literature Review

The need to remediate contaminated sites has lead to the development of new technologies that emphasize the detoxification and destruction of the contaminants rather than the conventional approach of landfill disposal. Although bioremediation is viewed by some as an innovative technology, microorganisms have been used for the treatment of waste for decades; the waste water industry utilizes microorganisms to degrade contaminants. What is innovative is the application of bioremediation to the treatment of contaminated soils. While the basic microbiological processes are similar between waste water treatment and soil bioremediation, there are substantive differences. Primary is that soil bioremediation frequently must address multiphase, multi contaminant situations in non homogenous soil matrices. It is because of these additional complexities that an interdisciplinary approach is necessary when considering bioremediation as a soil treatment technique and a review of previous works’ successes and failures is requisite.

1.4.1 Treatability Study Literature

Numerous bioremediation experiments focusing on the biodegradation of hydrocarbons have been conducted at both bench and field scale levels (Brook, Stiver & Zytner, 2001; Coulon, Gourhant & Delille, 2005; Ferguson, Franzmann, Revill, Snape & Rayner, 2003; Gallego, Loredo, Llamas, Vazquez & Sanchez 2001; Riis, Kleinsteuber & Babel, 2003; Zytner, Salb, Brook, Leunissen & Stiver, 2001). These studies are fundamental reading regarding bioremediation and the treatment of petroleum hydrocarbons. While the successes are well documented, bioremediation is not a panacea. The removal of contaminants from soil by organisms is not always a successful exercise as organisms tend to function suitably under only very specific environmental conditions. Works from the literature that are particularly relevant to this study are outlined below.

Balba, Al-Awadhi & Al-Daher (1998), stated that the biotechnology is effective in dealing with petroleum hydrocarbon contamination; however, bioremediation is a site-specific process and feasibility studies are required before full-scale remediation can be successfully applied. The type and scale necessary is specific to the bioremediation approach to be employed during full-scale clean-up operations. The focus of the paper was to highlight the need for the integration of laboratory data to
design of full-scale bioremediation, and the authors provide several microbiological methods which can be used for the feasibility assessment of soil bioremediation.

Respirometry, a keystone of this study, has been applied to studies in hydrocarbon biodegradation research and engineering bioremediation systems. Davis, Johnston, Patterson, Burber & Benett (1998); Fiuza & Vila (2005); Hinchee & Ong (1992); Tabak, Govind, Fu, Yan, Gao & Pfanstiel (1997) and Fu et al. (1996), utilized respirometric data to develop kinetic models of hydrocarbon biodegradation. These authors developed predictive off gas models for biodegradation of hydrocarbons in treatment by applying theoretical base models and fitting them to respirometric data generated by changing certain environmental parameters. While all these studies arrived at a form of numerical determination of hydrocarbon degradation on a site/material specific basis, each author emphasized that the particular nuances and kinetic transformations that may occur during bioremediation will fluctuate, and results will be variable from site to site (Balba et al., 1998).

A bioremediation of crude oil contaminated soils study was carried out in engineered laboratory biopile systems by Benyahia, Abdulkarim, Zekri, Chaalal & Hasanain (1999) that displayed virtually identical trends in respiration rates when indigenous and commercial added bacteria where employed. However, the bioaugmented experiments yielded much greater respiration rates. The benefits of bioaugmentation were demonstrated and it was found that when no nutrients were added to the soil, bacteria tended to catabolize hydrocarbons into carbon dioxide and water, rather than assimilate carbon during cell growth, which can result in incomplete hydrocarbon degradation (Benyahia et al, 1999).

Trindade, Sobral, Rizzo, Leite & Soriano (2004) completed a comparative bioremediation study between weathered and fresh oil contaminated soil samples. They concluded that bacteria from the weathered soil performed better than bacteria from the freshly contaminated soil. They explained this result in terms of the acclimation of bacteria in the weathered samples, and that the low biodegradation efficiencies they measured reflected the treatment difficulty of a weathered soil contaminated with a high crude oil concentration. Moreover they concluded that both soils, which were subjected to bioaugmentation and biostimulation techniques, resulted in biodegradation efficiencies approximately two times higher as the ones without the augmented treatment (Trindade et al., 2004).
Similar genera of petroleum hydrocarbon-degrading microbes appear in contaminated soils across different climactic regions, with the differences being attributable to their adaptation to different environmental conditions. A study by Marquez-Rocha, Olmos-Soto, Rosmo-Hernandez & Muriel-Garcia (2005), isolated hydrocarbon-degrading microbial species from contaminated soils collected in Tabasco, Mexico. Among the determined isolates from the soils, *Pseudomonas* spp. were dominant in numbers, which was a similar result to the studies from cold soil regions. They concluded that the climate and topography of a location determines microorganisms’ ability to adapt to changes in their environment (Marquez-Rocha et al., 2005).

It has been estimated by Atlas (1981), that there are more than 100 species of bacteria and fungi that have evolved to degrade petroleum hydrocarbons. In non-contaminated soil, less than 0.1% of the microbial community consists of hydrocarbon degraders, compared to up to 100% in contaminated systems (Atlas, 1981). Consequently, it is considered preferable to use indigenous microbial populations because of controversy surrounding the use of genetically engineered microorganisms (Leahy & Colwell, 1990; Bossert & Bartha, 1984). Dibble and Bartha (1979) noted that bacterial populations and efficiency of remediation tended to decrease at higher levels of hydrocarbon contamination, suggesting that the soil system becomes more toxic as the hydrocarbon concentration increases.

### 1.4.2 Management Options For Hydrocarbon Contaminated Soil

Over the past few decades, billions of dollars have been spent cleaning up petroleum contaminated sites (United States Environmental Protection Agency [USEPA], 2004). As a result of this investment, several physical, chemical, and biological technologies have been developed to remediate petroleum contaminated soils. In recent years, the emphasis has been on providing on-site remedies that involve in situ technologies, while because of their perceived faults, the development of low cost ex situ processes has not kept pace with the development of in situ technologies. However, in specific applications, such as hydrocarbon remediation, there are compelling advantages for ex situ treatments, excluding soil entombment (Fehmidakhatun, Mesania & Jennings, 2000).

Competing remedial technologies include: landfilling, thermal treatment, solidification, leaching, solvent extraction, soil vapour extraction, bioremediation and a host of combined treatment trains involving one or more of these techniques. While particulars of each method are not discussed here, in
general it can be said that bioremediation is often the least costly technique if successfully applied (USEPA, 2007). Bioremediation employs biological processes, based on the growth of petroleum degrading soil bacteria and fungi to reduce petroleum contamination (Eweis, Ergas, Chang & Schroeder, 1998).

Blackburn and Hafter (1993) and others have evaluated the influence of microbiological techniques for remedial processes, and generally concluded that ex situ techniques allow more opportunities to control or engineer conditions to achieve accelerated remediation as compared to in situ methods. Benefits of ex situ bioremediation include simplified design and operation parameters, cost competitiveness, rapid treatment times as well as the ability to treat and make allowances for many combinations of site and contaminant conditions (Von Fahnestock et al., 1998). Biopile remediation is a recognized ex situ treatment technology which generally consists of removing contaminated soil and placing it within pre-constructed cells above ground with the aim of enhancing conditions for biodegradation within the cells (Li, Cunningham, Pas, Philp, & Anderson, 2003). This technique will be the focus of this study, and will be further discussed below.
2 Regional Setting

Recent environmental assessments indicate significant quantities of contaminated soil exist in the
RPA from the historical use of flare pits, product spills and leaks resulting from thousands of miles of
aging pipelines. The field consists of 128 facilities, 400 oil and gas wells, 40 disposal wells and 225
abandoned wells (AET, 2008). An understanding of the regional and specific setting is necessary for
remedial development and management.

Figure 1. Alberta Central Parkland Region, Sturgeon County (outlined) and the Redwater Area North
West of the City of Edmonton (Alberta Municipal Affairs, 2009)

The RPA lies within three counties, Sturgeon, Strathcona and Thorhild in the Central Parkland
Subregion, part of the Parkland Natural Region (Sturgeon County, 2007). The Central Parkland
Subregion extends in a broad arc up to 200 kilometers wide, north of the Grassland Natural Region and
south of the Boreal Forest Natural Region. Within this subregion, there is a gradual transition from
grassland with groves of aspen in the south to closed aspen forest in the north. Native vegetation is
scarce because most of the land has been cultivated to grow agricultural crops. The majority of the remaining naturally vegetated land is on rougher terrain or poorer soils, with aspen and balsam poplar forests being the two major forest types that occur in the region (Strong & Leggat, 1992). Elevations range from just over 500 metres where the Battle River enters Saskatchewan to around 1100 metres in western portions. Numerous permanent streams, all part of the Saskatchewan River system, cut across the subregion with lakes scattered throughout the subregion as well as a wide variety of permanent wetlands (AENV, 1994).

2.1 Geology, Surficial Sediments and Soils

The Leduc reef at Redwater is the third largest oil reservoir in Canada, with original oil in place reserves of 1.3 billion barrels (Alberta Research Council, 2008). The reef complex has a total area of nearly 600 kilometers, lies 1000 meters below ground level (mbgl), is up to 250 meters thick and had an original oil cap that is 50 meters thick. Oil and gas production in the area is primarily concentrated on the coral limestone reefal Leduc (D-3) member of the Woodland formation of Upper Devonian. Situated on the eastern flank of the Alberta syncline, it is affected by the regional dip to the southwest and the productive zone is along the high northeastern rim (Haskett, 1951).

The near surface geology of the Redwater area is characterized by thin, 5 to 20 meter thick, unconsolidated Quaternary deposits overlying Cretaceous shales, siltstones, sandstones and coals. The uppermost bedrock unit is the Wapiti Formation composed of sandstones and shales (Borneuf, 1973). The bulk of surficial material is till, which underlies more recent deposits. Locally, gravel, sand and silt lenses occur within the till. Surficial topography is undulating; with relief generally less than 3 meters (Borneuf, 1973).

2.2 Hydrogeology Groundwater Use and Quality

The formation water in the Redwater reef is of sodium-chloride type with 107,000 mg/l total dissolved solids. The reef experiences a strong water drive from the underlying highly-permeable Cooking Lake aquifer (Haskett, 1951). The Redwater reef is under the last stages of water flooding for oil production, with concurrent sour water disposal. ARC Resources Ltd. plans to convert the Redwater oil pool to a carbon dioxide tertiary recovery scheme (AET, 2008). The Redwater reef is situated close to large sources of relatively pure carbon dioxide in the Redwater-Fort Saskatchewan-Edmonton region.
A major buried channel runs across the region, which roughly follows the present course of the North Saskatchewan River valley. Course sands and gravels are deposited along the channel forming a high yielding aquifer. Glaciofluvial sheet sand deposits are common in the RPA and aeolian action has modified these areas producing extensive dune fields. The area would be considered high risk for groundwater contamination from hydrocarbon contamination due to the prevalence of the sand and gravel deposits (Hydrogeological Consultants, 1998). Generally, the hydrogeochemistry of waters from surficial aquifers is more variable than for waters from bedrock in the RPA. According to Stein (1976), major ionic constituents include sodium, potassium, calcium, magnesium, carbonate, sulphate and chloride with total dissolved solids varying from less than 500 mg/l to more than 3000 mg/l.
3 Remedial Method Selection

In comparison to more traditional engineering projects, the theoretical basis for the design of environmental remediation projects is relatively weak, typically predicated on a limited number of soil samples and contamination information. Although the understanding of a site may never be perfect because characterization tools, financial resources, and sampling methods have practical limitations, one has an obligation to assemble and document evidence that converges towards a consistent picture of the site. This conceptual model is necessarily multi-disciplinary, in that it encompasses a variety of types of data, and it is important to continually reformulate the site conceptual model as new field efforts provide new information.

The economic and practical pressures created by the remedial requirements of the RPA dictate that field screening, consistent site strategies, generalized processes and a common sense approach are vital. It is contingent that a pragmatic and expedient remediation approach be applied.

3.1 Remedial Management Requirements and Opportunities

In order for remediation in the RPA to proceed, specific management and operational factors need to be considered. One obligation under the corporate remedial strategy is a reduction of liability by shifting the focus from disposal only to select disposal, only where necessary, combined with treatment and soil recycling initiatives where plausible (AET, 2008). The cost of landfill, soil transport and replacement is prohibitive. Soil treatment removes the uncertainty of waste burial and its resultant liabilities, and results in optimized risk reduction. The economics of disposing of vast quantities of contaminated soil are practically untenable and it is probable that landfill prices will continue to increase progressively as landfill space is decreasing (Blair & Hite, 2005).

The previous owner completed extensive site characterization studies in the RPA that included multistage site investigative programs intended to provide an understanding of contamination issues and a course for remedial action. This process, while expensive and time consuming, has provided extensive characterization information to guide a remedial planning perspective, and can support and guide future decisions (RemedX, 2005; Komex, 2001). The advanced understanding of individual sites and contaminant situations across the RPA that is available allows the exploration of proactive solutions without the need for exhaustive site investigation.
Another critical factor in remedial management in the RPA is a comprehension that bioremedial-based methods are not viable in all situations. The extensive site investigations have demonstrated that select locations are contaminated not only by ostensibly treatable hydrocarbons, but also by chloride, high molecular weight hydrocarbons, metals and combinations thereof that are considered recalcitrant. However, despite the presence of these compounds at many sites, often only the uppermost layers of soil are significantly affected by these mixtures. The soils below and horizontal to this mixed material appear generally amenable to bioremedial methods (RemedX, 2005). The heavy hydrocarbons are significantly bound to the upper soil layers while more soluble hydrocarbons have travelled downward and horizontally in the soil profile, following the changes in seasonal groundwater and gravity (USEPA, 1997). RPA sites heavily affected by chloride or heavy metals are not deemed to be prospective bioremediation opportunities.

Low permeability soils are not considered economically viable candidates for bioremedial methods as they are time intensive and cost prohibitive to treat due to poor transmissibility qualities and aeration potential (Interstate Technology & Regulatory Council, 2004). In contrast the soils of the RPA have a high proportion of free flowing sands and gravels which do not tend to agglomerate into large particles (Borneuf, 1973). As coarse-grained soils have low moisture absorption capacities and drain well, they are normally considered to be a good candidate soil type for biological treatment in that the delivery of oxygen, nutrients and water is greatly simplified as compared to clay or silty matrices. Further, the low humus content of the RPA soil material limits hydrocarbon sorption to the soil particles. These soil characteristics point to the positive potential for bioremedial method use in the RPA.

An assortment of technologies is available to treat contaminated soil. Many of these technologies, however, are prohibitively costly, may not result in complete destruction of contamination, or may be inappropriate due to fears that mobilized contaminants will escape containment and contaminate previously uncontaminated soil. The sheer volume of contaminated soil and affected sites in the RPA make individualized in situ methods of soil treatment or soil disposal untenable in terms of economic and logistic realities. Former oil and gas sites lend themselves to multi-site remedial planning (USEPA, 1999). Multi-site planning provides the proponent the opportunity to address environmental conditions under a single, cooperative, mutually beneficial, area wide arrangement. Similarities in the configuration and the
contaminants at the sites of interest provide opportunities to apply innovative, yet simple approaches that can benefit from economies of scale. The RPA appears to provide an ideal opportunity to apply tools and technologies from a multi-site remedial planning perspective that can expedite site characterization and remediation.

Although research suggests that petroleum can often be bioremediated relatively quickly (Eweis et al., 1998), the extent and the rate of biodegradation are known to be affected by many factors and successful implementation requires preliminary information. Effective biotreatment can be less cost intensive than other remedial methods, but it can also be scientifically intense, and satisfactory results are not guaranteed. The optimization and control of microbial and system interactions requires the amalgamation of a number of scientific and engineering disciplines, and each case will be somewhat unique in that each site may exhibit some dissimilar characteristics. In spite of these potential drawbacks, the use of bioremedial methods appears to be well suited to the specific conditions of the RPA. The sand-silt nature of the soil, the availability of company owned land, the amenable nature of the contaminants, the realization that recalcitrant components cannot be treated, site proximity, soil recycling opportunities, financial considerations, and the desire for proactive remediation by the operating company all suggest that accelerated aerobic bioremedial methods may be a practical alternative to landfill disposal for hydrocarbon contaminated soils.

3.2 Why Biopile?

In a prepared bed biopile system, the contaminated soil is either moved from its original site to a prepared area, which has been designed to enhance remediation and prevent movement of contaminants from the site; or the soil is initially removed from the site to a storage area while the original location is prepared for use, and then the soil is returned to the prepared bed, where the treatment is accomplished. Biopiles are constructed by forming the excavated contaminated soils into piles or cells above ground with the aim of enhancing conditions for biodegradation.

Soils are rarely contaminated by a single source pollutant. Often one finds a mixture of contaminants that may not be remediated with a single process. The most commonly applied processes (soil vapor extraction, groundwater pump-and-treat and even bioremediation) all can leave behind residual contamination. The obvious approach to overcome this problem is to apply a sequence of
remediation schemes with each in turn addressing the portion of the problem for which it is best suited. This is both difficult to perform in situ and a distinct advantage to biopile techniques as any conventional in situ remediation scheme such as bioremediation or soil vapor extraction can be applied to the ex situ soil pile. The creation of an encapsulated soil pile contains the contaminated soil and provides a means of controlling any discharges produced during treatment. Since the biopile is essentially a closed system, process operational control is greatly simplified and aggressive methods of remediation can be considered. If the pile is constructed for process flexibility, it is simple to design an installation that makes sequencing the remediation processes convenient and inexpensive. As example, a possible adjunct of the proposed biopile system would be to use composting technology.

Biostimulation and bioaugmentation of biopiles is an alluring method of microbial bioremediation as it is not only effective, but also low cost and causes minimal environment impact (Kaplan and Kitts, 2004). Although the excavation process may be expensive, seeking an ex situ solution can have several advantages. Since the pile remains encapsulated until satisfactory results are attained, the performance of the treatment process can be more easily monitored, and unsuccessful processes may be abandoned with little environmental risk. In addition, gradual, long term remediation techniques can be used to provide low cost, low risk remediation that would not be feasible in situ. This is similar to using in situ natural attenuation, but allows for superior mass transport control while the process proceeds. Also, since wastes are removed from their original locations, much of the original site can be quickly recovered. As stated by USEPA (1999), this can be a compelling advantage for redeveloping Brownfields, or in situations where one site can host the remediation for several similar sites, and thus is an appropriate arrangement to consider for soil treatment and reuse in the RPA.
4 Bioremediation Using Biopile Techniques

Soil bacteria can degrade petroleum hydrocarbons, especially under aerobic conditions; however, biodegradation of petroleum hydrocarbons can be limited by various environmental factors, including temperature, moisture, nutrient availability, salinity, and pH (Alexander, 1999). Artificial adjustments of any of these key factors can optimize the enhancement of the hydrocarbon degrading activity of soil microorganisms. By enhancing the conditions within the biopile, degradation rates and the degree of degradation can be increased. In particular, natural and forced aeration can be used to enhance soil venting in order to provide oxygen for the bioreaction in the pile (Admassu & Korus, 1998; LaGrega & Buckingham, 1994).

The design of an above ground soil pile is relatively simple. A low permeability liner, typically constructed of high-density polyethylene or other synthetic materials, is laid down to contain liquid drainage. A network of slotted pipes connected to a manifold system is placed on the liner. For a soil vapour extraction application, the manifold is connected to the vacuum end of a blower to create a negative pressure in the perforated pipes. The negative air pressure at the base of the above ground soil pile will cause air to be drawn through the soils and into the pipes. Extracted soil vapors can be trapped or destroyed using applicable emission control equipment. For soil venting applications, air can be extracted or injected and biological activity can be further promoted in a soil pile treatment system by the addition of water, nutrients, and/or heat. Supplemental moisture can be supplied to the soil by irrigation or sprinklers and a leachate collection and recycle system needs to be added to the biopile system.

4.1 Requirements for Biopile Remediation

Several environmental parameters affect the rate and extent of biodegradation. For any bioremediation system it is important to obtain the correct balance between water, nutrients and air (Ferguson et al., 2003). In different combinations these factors can affect the process substantively. Development of bioremediation technologies strives to optimize these conditions to ensure good petroleum degrading microbial activity. In many cases the optimal conditions are compromises between the ideal conditions for the different microbial species present in the community (Cookson, 1995).

Biostimulation increases the activity of the indigenous microbial population by adding nutrients and/or a terminal electron acceptor. In rare cases, indigenous microbes capable of biodegrading the
contaminants may not be available at the site. To overcome this problem, the degradation potential can be increased through bioaugmentation which is the addition of exogenous hydrocarbon degrading microbial strains (Trinidade et al., 2002). The chemical structures of the contaminants present in the soils proposed for treatment by biopiles are important in determining the rate at which biodegradation will occur. Although nearly all constituents in petroleum products are biodegradable, the more complex the molecular structure of the constituent, the more difficult and less rapid is biological treatment (Atlas & Bartha, 1993).

Most low molecular-weight aliphatic and monoaromatic constituents are more easily biodegraded than higher molecular weight aliphatic or polyaromatic organic constituents. The rate of biodegradation is related to the type of hydrocarbons present with $n$-alkanes being the most degradable and PAH and asphaltenes the least degradable (Huesemann, 1995; Van Hamme, Singh & Ward, 2003). The inability of microbial enzymes to break multiple cyclic and aromatic ring structures limits the degradation of some compounds, and may result in only partially degraded products as microbes remove linear side chains from branched and cyclic molecules (LaGrega et al, 1994). The presence of very high concentrations of petroleum organics or heavy metals in site soils can be toxic or inhibit the growth and reproduction of the bacteria responsible for biodegradation in biopiles. General guidelines for biopile technology recommend that concentration levels of total petroleum hydrocarbons should not exceed 50,000 mg kg$^{-1}$ and toxic metal concentrations should be below 2500 mg kg$^{-1}$ (Von Fahnestock et al., 1998). Specific biopile process requirements are outlined in the following sections of the chapter.

4.1.1 Hydrocarbon Degrading Microorganisms and Energy Source

Soil normally contains large numbers of diverse microorganisms including bacteria, algae, fungi, and protozoa. Contaminated soils contain degradative species from these various groups and consequently by enhancing their environmental conditions, these microbes can be effective in degrading hydrocarbon mixtures in soils. In well drained soils, which are most appropriate for biopiles, and are consistent with the soil type in the RPA, these organisms are generally aerobic (Atlas, 1991). Of these organisms, bacteria are the most numerous and biochemically active group, particularly at low oxygen levels (Leahy & Colwell, 1990). Individually, microbial species are capable of utilizing only a limited range of hydrocarbons (Alexander, 1999). Most bacterial enzymatic reactions are highly specific with respect to
what they catalyze and in the substrates they allow. Aerobic bacteria produce a class of enzymes known as oxygenases to more easily degrade hydrocarbons. The monooxygenase and dioxygenase enzyme subclasses present in many bacteria possess a broad substrate specificity which allows them to catalyze reactions with compounds other than their growth substrate (Loftabad, 2000). Atlas & Bartha (1993) defined cometabolism as a process, which occurs when an organism growing on a particular substrate that also metabolizes a second substrate it is unable to utilize as a sole nutrient or energy source. The secondary metabolite then serves as the supply of carbon for another organism present in the mixed bioculture of the soil. Bioremediation within a mixed, rich culture such as a soil can take advantage of the capability of such enzymes to degrade difficult substances. Generally, microbial consortia suitable for achieving effective remediation will be indigenous to the contaminated soil (Margesin et al., 1999).

The metabolic processes used by bacteria to produce energy require a terminal electron acceptor (TEA) to enzymatically oxidize the carbon source to carbon dioxide. Bacteria that use organic compounds such as petroleum as their source of carbon are heterotrophic (Adoki & Orugbani, 2007). Bacteria that use oxygen as their TEA are aerobic; those that use a compound other than oxygen are anaerobic; and those that can utilize both oxygen and other compounds as TEA’s are facultative. Biopile applications aimed at the remediation of petroleum products utilize bacteria that are both aerobic (facultative) and heterotrophic (Adoki et al., 2007).

Bacteria require a carbon source for cell growth and an energy source to sustain the metabolic functions required for growth; in many cases the petroleum itself can fulfill both functions. While hydrocarbons are an excellent source of carbon and energy for microbes, they are incomplete foods since they do not contain significant concentrations of other nutrients (such as nitrogen and phosphorus) that are required for microbial growth (Prince, Clark & Lee, 2002). The input of large quantities of organic carbon sources into an area tends to result in a rapid depletion of available inorganic nutrients (Margesin, Zimmerbauer & Schinner, 1999), and limited biodegradation. Thus, biostimulation (nutrient addition) can often be used to maximize bioremediation effectiveness (Trindade et al., 2002).

4.1.2 Bioavailability

The bioavailability of hydrocarbon contaminants, that is, how available a compound is for uptake and degradation, is affected by the physiochemical properties of the compound, as well as the various
physical and chemical properties of the soil environment. The characteristics that determine a compound’s distribution between the vapor, liquid, solid and adsorbed phases are characteristics that determine the availability of this compound for uptake and degradation (Cunningham & Ow, 1996).

Volatilization can be responsible for the movement of gaseous-phase xenobiotics from the soil water to the atmosphere (Alexander, 1999). Vapor pressure determines the extent and speed of volatilization of a chemical, with increased vapor pressure resulting in increased volatilization. Along with vapor pressure and water solubility, adsorption rate also has an effect on a chemical’s tendency to volatilize. Contaminants held tightly in the soil as a result of covalent bonding will be less likely to desorb, which could facilitate volatilization (Cunningham et al., 1996). Increased volatilization rates can result in decreased biodegradation due to the contaminant’s limited residence time in the soil, but more rapid remediation, in general.

A similarly important factor influencing bioavailability is sorption. Once in the soil, a contaminant can bind to the organic and inorganic soil fractions through sorption forces, at which point the contaminant may become unavailable for uptake and microbial breakdown (Alexander, 1999). In general, high organic carbon content usually leads to increased adsorption while lower concentrations of organic matter in the soil can mean less area for sorption of hydrocarbons. Soil humus is an important sorbent material for organic compounds. Along with organic decomposition, humus can be synthesized through chemical reactions of low molecular weight monomeric molecules (amino acids, lipids) that have been formed by the degradation of larger molecules such as proteins (Tremblay, Kohl, Rice & Gagne, 2004).

The partitioning of an organic compound is directly related to its water solubility, often described by the octanol-water coefficient (Chiou, 2002), is another important factor in the bioavailability of a substance. The octanol-water coefficient refers to the ratio between the equilibrium concentrations of a chemical dissolved in octanol and water, which indicates the affinity of the chemical for organic as opposed to aqueous phases. Organic contaminants that are hydrophobic in nature will tend to sorb with increased strength to humic molecules of increased aromaticity. Increased aromaticity translates to a greater number of carbon-carbon double bonds within the molecule, and therefore increased strength of the van der Waals forces, considerably increasing in hydrophobicity and reducing the bioavailability of the contaminant to bacteria residing in aqueous media (Klavins, Serzane & Eglite 2000).
Large hydrocarbon compounds partition off quickly onto humic substances as well as soil particles, after which they may undergo further incorporation into the humus, and as a result, they tend to be persistent contaminants in the soil. As the residence times of these compounds in the soil lengthens, they become even more resistant to desorption and degradation (Tremblay et al., 2004). This process is commonly referred to as weathering or aging of the compounds (Cunningham et al., 1996). As contaminants age and become more distributed into isolated micropores within the soil, they tend to become less available for biodegradation. If an organic molecule becomes sorbed to the soil, the overall bioavailability for a microorganism depends on how readily the molecule will desorb back into solution. In addition, the more aged a residue becomes, the more resistant it will be to desorption and microbial degradation, although microbes may utilize humic substances as a nutrient source and consequently release tightly sorbed contaminants in the process (Hsu & Bartha, 1976). This phenomenon is typified by the near surface soils at historic spills or flare pits in the RPA, which are near asphaltene in nature with the contaminants tightly bound to the humic surface soil.

The amount and type of clay in a soil can also affect the bioavailability of organic contaminants (Riser-Roberts, 1998). Clay particles have a high surface area in comparison to other soil particles, and therefore possess a greater area for adsorption of xenobiotics. The small particle size of clay also can lead to decreased diffusion of contaminants due to increased tortuosity, and therefore lower bioavailability (Cunningham et al., 1996). In soils with low clay and organic matter concentrations, as in the RPA soil varietals, the bioavailability of contaminants may be increased. Carmichael, Christman & Pfaender (1997) found that sandy soils had greater hydrocarbon degradation rates than clayey soils.

### 4.1.3 Oxygen

Oxygen plays a vital role in bioremediation processes, particularly for hydrocarbons as it is the terminal electron acceptor for bacteria during aerobic biodegradation processes, and as such is often an important rate limiting parameter for degradation. Although microorganisms can biodegrade hydrocarbons under both aerobic and anaerobic conditions, organic constituents have a more rapid rate of biodegradation under aerobic conditions, as compared to anaerobic conditions (Atlas, 1981) and thus aerobic conditions are considered to be more important for the bioremediation of petroleum products.

The general process of aerobic biodegradation is summarized in the following equation (Cookson, 1995):
Bacteria + Organics + \( \text{O}_2 \) + Nutrients $\rightarrow$ \( \text{CO}_2 \) + \( \text{H}_2\text{O} \) + Biomass + Byproducts + Energy

(1)

In reference to this study, the organics in the Equation 1 are hydrocarbons. Aerobic biodegradation of hydrocarbons involves the incorporation of oxygen by microbial cells via oxygenase enzymes to break the hydrocarbon bonds (Suthersan, 1997). Therefore, consistent aeration is beneficial in stimulating the complete biodegradation of petroleum products and is certainly a potentially limiting factor to the process.

4.1.4 Moisture

Water is crucial for biological activity of any form. Soil microorganisms are especially affected by water content, which can vary among soils. Soil water controls several factors in the soil besides providing water to organisms, including soil aeration, nutrient concentration, nutrient availability, and soil solution pH. Peak microbial activity is observed near a soil’s field capacity; that is, near the point where the soil micropores are filled with water and the soil macropores are aerated (Paul & Clark, 2006).

In general, soils should be moist but not wet or soaked. Biodegradation of contaminants in soil systems is optimal at a soil moisture content of between 30 and 80 percent of field capacity (Dibble & Bartha, 1979; Riser-Roberts, 1992). Field capacities typically range from 5 to 40 percent of the total weight depending on the soil texture. Therefore, a moisture level of 50 percent field capacity might range from 2.5 to 20 percent total moisture by weight (Baker et al., 1994). Periodically, moisture must be added to a biopile because soils may become dry as a result of evaporation, which is increased during aeration operations. Excessive soil moisture, however, restricts the movement of air through the subsurface thereby reducing the availability of oxygen which is essential for aerobic bacterial metabolic processes.

4.1.5 Nutrients

Nutrient availability is the most common limiting factor in the bioremediation of petroleum hydrocarbon contaminated soils (Van Hamme et al., 2003). Organic contaminants typically provide an adequate supply of carbon to promote biological degradation in soils, but the availability of other essential nutrients such as nitrogen, phosphorus, or potassium may be insufficient for optimum treatment. Microorganisms require inorganic nutrients such as nitrogen and phosphorus to support cell growth and sustain biodegradation processes. Nutrients may be available in sufficient quantities in the site soils but,
more frequently, nutrients need to be added to the biopile soils to maintain bacterial populations (Walworth & Reynolds, 1995).

The effectiveness of bioremediation in general, is contingent upon available nutrients for use by plants and microorganisms. Nitrogen (N) and phosphorus are the nutrients that most frequently limit bioremediation (Riser-Roberts, 1998). The addition of petroleum products to the soil can widen the carbon to nitrogen ratio, therefore limiting the available N for degradation processes. Microbes that are able to metabolize hydrocarbons quickly will immobilize the mineral N that is available, leaving unfavorable conditions for other microorganisms and growing plants (Frick, Farrell & Germida, 2000). Stimulation of microbial degrading activity is often successfully accomplished by addition of inorganic and/or organic nutrients, particularly in the form of N (Riser-Roberts, 1998).

Certain sources of N have been shown to successfully enhance biodegradation of certain types of hydrocarbon pollution (Brook et al., 2001). An example is the use of ammonium chloride as the primary source of N to enhance the biodegradation of diesel fuel (Brook et al., 2001; Ferguson et al., 2003). The recommended carbon to nitrogen ratios for soil hydrocarbon bioremediation vary greatly and range from at least 200:1 to 10:1 (Atlas & Bartha R, 1992; Morgan & Watkinson, 1989). The typical carbon, nitrogen, phosphorus ratio necessary for biodegradation falls in the range of 100:10:1 to 100:1:0.5, depending on the specific constituents and microorganisms involved in the biodegradation process. Phosphorous is also a frequently limiting factor because of its low solubility and low bioavailability. Phosphorus is necessary for building nucleic acids and cell functions, and since organic phosphorous is found mainly in humus, its availability in the sandy soil of the RPA may be limited (Jinyan et al., 2007).

4.1.6 Temperature

Soil temperature can significantly affect microbial activity, and is dependent on the climate of the geographic location among other factors. Temperature also affects the chemical and physical nature of the petroleum hydrocarbons in soil (Whyte & Golan, 2001). Increases in soil temperature can increase bioavailability of hydrocarbons by increasing their solubility and diffusion rates by decreasing their viscosity. Generally, increasing temperatures result in increasing microbial activity, although some microorganisms have adapted to cold environments (Marquez-Rocha et al., 2005).
Because soil temperature varies with ambient temperature, there will be certain periods during the year when bacterial growth and degradation will diminish as a result. When ambient temperatures return to the optimal growth range, bacterial activity will be gradually restored. Temperature also has a significant effect upon the rate of biodegradation. During summer time, temperatures of 25-35°C may be realized within the soil piles, whilst during winter considerably slower degradation rates may be achieved when temperatures drop (Von Fahnestock, et al., 1998).

4.1.7 Textural Factors

Soil properties and texture have significant impacts on remediation efficiency as they affect the permeability, moisture content, and bulk density of the soil. To ensure that oxygen addition, nutrient distribution, and moisture content of the soils can be maintained within effective ranges, one must consider the texture of the soils. For example, soils that tend to clump together (such as clays) are difficult to aerate and result in low oxygen concentrations. High clay content soils retard the passage of water and air and may turn anaerobic. Aerobic hydrocarbon degrading bacteria in highly impermeable clay soils contaminated with petroleum hydrocarbons could easily deplete the available oxygen. When soils become anaerobic the rate of hydrocarbon degradation is markedly decreased and some compounds are not degraded (Fox, 1992).

It is also difficult to uniformly distribute nutrients throughout these clay-based soils and they tend to retain water for extended periods following a precipitation event. Ji, Dahmani, Ahlfeld, Lin, & Hill (1993) injected air into saturated porous media and found that air usually moves in continuous channels, with hydrocarbons volatizing across the air-water interface of the air channels into air phase. Normally, more channels were expected to form in coarser materials than in fine ones. This would mean that the distances between the air channels were closer together for coarser materials, resulting in a larger volume of subsurface media that would be affected by the air channels, and thus diffusion of volatiles into the air phase would be faster in coarser materials than in fine ones (Ji, Dahmani, et al., 1993). Consequently, the hydrocarbon removal efficiency in coarser materials would be higher than that in fine materials. The regular deposition of course grained sands and gravels in the surficial soils of the RPA are, therefore, an important factor in the selection of biopile technology for this area.
4.2 Application of Biopile Methods - Theory to Practice

Selecting the most appropriate strategy to treat a site is guided by considering three basic principles: the amenability of the pollutant to biological alteration to less toxic products, the accessibility of the contaminant to microorganisms (bioavailability) and the economic possibility of optimizing the biological activity. While biopile remediation has many advantages, it is decidedly site specific and successful treatment of hydrocarbon contaminated soil presents a challenge. In addition to final hydrocarbon concentrations, it is contingent to consider the cleanup goals proposed for the biopile soils. Below a certain threshold contaminant concentration, the bacteria cannot obtain sufficient carbon from degradation of the contaminants to maintain adequate biological activity, and degradation will essentially cease. Although the threshold limit varies greatly depending on bacteria and contaminant specific features, generally, contaminant concentrations below 0.1 ppm are not achievable by biological treatment alone, and experience has shown that reductions in hydrocarbon concentrations greater than 95 percent can be very difficult to achieve because of the presence of recalcitrants (USEPA, 1994).

Adequate preparation of contaminated soil coupled with measurable and controllable process variables such as aeration, carbon dioxide generation rates and moisture levels can theoretically lead to very efficient bioremediation operations; however, additional study is normally required to verify the ability of a biopile system to achieve reductions under the site conditions. As site and technology information is collected and reviewed, additional gaps in the data necessary for evaluating alternatives are identified. Treatability studies may be required to fill these data gaps (Balba et al., 1998).

Unfortunately, not all bioremediation efforts have been successful. In an attempt to develop bioremediation technology from the bench scale to the full-scale design, some practitioners have failed to understand the phenomena that influence bioremediation. Issues such as additional mass transport mechanisms/limitations, the presence of multiple phases, spatial heterogeneities, and unfavorable factors for bacterial growth represent only a few of the phenomena that can limit or complicate biodegradation (USEPA, 1994).
5 Treatability Testing Program

For many bioremediation projects, treatability studies are a necessary requisite. A gradualistic approach from bench-scale to pilot-scale to full-scale projects is vital to ensure that reliable degradation of contaminants can be achieved at each stage (Saber, 1995). Biotreatability studies (bench studies) are usually performed under laboratory or controlled field conditions and are planned so that the proper parameters are developed to design and implement the full-scale biopile system if the small scale studies are deemed successful (USEPA, 1989). Biotreatability testing is conducted prior to full-scale application of a bioremediation method in order to assess the expected outcome of treatment. The objective of treatability (biotreatability) testing is to save costs by identifying potential problems, quantifying operational parameters, and allowing for the comparison of alternative treatments prior to committing to full scale application. Treatability testing prior to full-scale application is especially beneficial for biopile bioremediation as processes that could be applied in the final treatment design can be effectively trialed. If biotreatability studies do not demonstrate effectiveness, or if further proof is deemed necessary, field trials or pilot studies can be implemented or another remedial approach may be evaluated.

5.1 The Treatability Approach and Purpose

Treatability testing for contaminated former oil and gas sites must account for the fact that such contamination is likely to be variable from site to site. In spite of this variability, the preferred approach is to develop generalized treatability guidelines that apply to all sites in an area in order to avoid the expense of individual site characterization. Therefore, this research project was directed at developing such generalizations about treatability that could be applied to all suitable sites in the RPA. The main goal of the treatability testing investigation was to develop a program using a biopile process which would demonstrate a reduction in the concentration of the petroleum hydrocarbons in the soil to levels below the Alberta Tier 1 guidelines (AENV, 2009a).

There are three keys to the successful implementation of a bioremediation treatability program; the presence of viable native bacteria in the impacted soils, the ability of those particular organisms to degrade the hydrocarbon contaminants, and the determination of suitable nutrient and operating processes to ensure optimum bacterial activity. In addition to identifying those key factors, the treatability
program was also to identify specific site characteristics of the RPA that could enhance or adversely affect efforts to remediate soil on site.

The basic types of biotreatability studies used to demonstrate biopile effectiveness are flask, typically completed in Erlenmeyer glass flasks, or pan studies, where tests are conducted in shallow pans. Each method begins with the characterization of baseline physical and chemical properties of the soils to be treated in the biopile. The objective of this initial stage of treatability testing was to determine how a planned biopile system would perform on actual site material, and to provide data on contaminants, ability of indigenous microorganisms to degrade those contaminants, optimal microbial growth conditions and degradation rates, and sufficiency of natural nutrients and minerals to support the degradation process (USEPA, 1994). A soil pan study was selected as the physical arrangement that more closely resembles a biopile configuration.

Employing a pan study the following variables are tested herein: (a) degradation by indigenous microorganisms, (b) degradation by seed microorganisms (bioaugmentation), (c) process optimization through biostimulant additions and (d) controls. Bioaugmentation involves the addition of external (either indigenous or exogenous) microbial populations to the waste. Biostimulation involves the addition of appropriate microbial nutrients to a waste stream to stimulate the indigenous microbial flora of the soil to bring about degradation of the contaminants.

Based upon the results of the bench-scale treatability study, a pilot scale biopile was constructed in 2008. Because this pilot scale testing involved both larger equipment than used in the soil pan study, and the processing of several hundred tonnes of actual material, it was carried out at a former operating site within the RPA.

5.2 Site Description and 2007 Field Program

A former operating battery site within the Redwater field has been selected by the owner for this project. The site is located approximately 12 kilometers southeast of the town of Redwater, Alberta on a parcel of land that is used primarily for oil and gas-related industrial activities. The site, constructed prior to 1950, originally included a tank farm containing five aboveground storage tanks, at least two underground storage tanks, a flare pit and a metering station. The property is 3.5 hectares in area, and is surrounded on all sides by native trees and shrubs. The site was abandoned in the mid 1970's and all
aboveground equipment was removed thereafter. Although a number of contaminated locations are known to exist within the site, the former tank farm area is of primary interest due to the nature of the contamination. In addition, the results of a number of intrusive investigations, including extensive soil, groundwater and geophysical analysis, appear to indicate that the tank farm area is prototypical of the RPA in terms of both its soil and contamination type (RemedX, 2007).

According to Komex (2001), the general soil condition at the site consists of dark brown sand to loamy-sand extending from the surface to approximately 0.75 mbgl. This material is underlain with grey to dark grey, medium to coarse sand extending to a depth of 5.5 mbgl. A shallow groundwater zone is encountered at approximately 2.5 mbgl. In the former tank farm area an estimated 5500 cubic meters of non-saline, non-sodic material is present that has been contaminated with benzene, toluene, ethylbenzene and xylenes (BTEX), variable petroleum hydrocarbon types and select polycyclic aromatic hydrocarbons to levels above applicable criteria. As noted earlier in this report, nearly all operating or abandoned sites in the RPA contain a flare pit, and many others have former waste areas or spills that have not been remediated to date. The soils in and around such pits or surface spills are contaminated with high levels of weathered hydrocarbons, and occasionally metals and salts (RemedX, 2007). As weathering of oil affected soil matrices occurs, they develop into a more condensed, asphaltenic structure. Furthermore over time, the oil becomes physically entrained within the soil matrix and the hydrophobic contaminants become increasingly sequestered into soil organic matter and/or diffused into soil nanopores (Huesemann, 1995). As a result, contaminant molecules are released very slowly into the aqueous phase of the oil-soil matrix and into surrounding soil or groundwater (Hatzinger & Alexander, 1997; Alexander, 2000) with the rate of contaminant biotransformation being severely limited. Therefore, the directly oil contacted soils (e.g. flare pit base and sidewalls, immediate release areas, etc.) are often recalcitrant (RemedX, 2007); however, due to partial partitioning of the source material a considerable quantity of less contaminated soil exists between this heavily contaminated layer and the periphery of the plume. It is this appreciably less contaminated soil resulting from the movement and partitioning of more mobile lighter weight hydrocarbons, which typically accounts for the vast majority of contaminated site soil that holds the most promise for bioremediation in the RPA and was thus selected for treatability analysis.
In order to confirm earlier investigations, an intrusive soil sampling program was completed at the site in 2007 where 21 test pits were dug, and core samples were collected across the site. Borehole analysis indicated a layer of heavy hydrocarbon contaminated sandy loam across the surface of the area, particularly in and around the former tank and metering locations, extending to a depth of between 0.5 to 1.25 mbgl. This layer was considered recalcitrant due to its heavy hydrocarbon nature and is similar to those conditions previously described (RemedX, 2007).

5.3 Soil Contaminant Analysis

Oil is a chemically complex and variable substance consisting of a wide array of hydrocarbons, and while there are some differences in the individual components of the oil produced between individual wells within a production area, overall the hydrocarbon composition tends to remain similar within a production zone. Nevertheless, the hydrocarbon fluids generated at oil and gas well sites can contain not only a variety of produced hydrocarbons, but also process chemicals, crude bitumen and salt water depending on the processes in place at each well site (Amatya et al, 2000). A distinct advantage in the RPA is that many of the sites were constructed and operated in a very similar fashion, and upon review, many of the contaminant situations at individual sites appear comparable (RemedX, 2005). The tank farm site described in section 5.2 is one such site with comparable characteristics to others within the RPA.

Immediately below the recalcitrant layer of surface material in the former tank farm area, as described, lies the aforementioned layer of medium to coarse sand, which although still hydrocarbon affected, is less contaminated compared to surface materials and encompasses the largest volume of contaminated soil at the site. This study will focus on this less contaminated soil because it is considered to be an excellent candidate for bioremediation due to its coarse matrix, amenable hydrocarbon contaminants and site logistics. Excavation and offsite disposal of the recalcitrant surface soil in the area of the former tank farm was initiated in September, 2007. The main focus of the removal program was the excavation of the tank farm area, although surface spills in other localized areas of the site were also removed at the time. The less contaminated sand layer was excavated, prepared and subjected to a number of different analyses which will be described in the following sections.
5.3.1 Treatability Test Soil Preparation

Prior to the material analysis and the initiation of the treatability program, it was contingent to prepare a biotreatability test soil that was as representative as possible of the site conditions. This material was obtained from the former tank farm site following the removal of the surface layer of recalcitrant materials. A 0.75 meter section of soil along the freshly exposed surface of the former tank farm was stripped and stockpiled with heavy equipment at the center of the site (approximately 400 cubic metres of soil). This pile was mixed roughly with a backhoe, allowed to drain/equilibrate for 18 weeks and placed within the pilot study biopile structure for eventual treatment in February 2008.

In February 2008, soil was retrieved by hand auger from the stockpiled soil within the constructed biocell, composited and placed into a large 205 liter plastic storage drum that had been lined with plastic sheet material and rinsed with clean water. The drum was sealed to limit moisture and volatile loss, transported to the laboratory where the treatability study was conducted and stored in a cooler. At the laboratory the bulk sample was mixed thoroughly for 30 minutes using a commercial cement mixer that had been cleaned and washed with warm, soapy water before the addition of the soil. Once mixed the soil was placed back into the bulk drum and placed into the cooler for later testing.

5.3.2 Hydrocarbon Quantification

The selection of appropriate analytical protocols are fundamental in the evaluation of the bioremediation process, and laboratory based analysis is compulsory both to ensure baseline comparison to treatment results and to ensure compliance with regulatory criteria such as the Alberta Tier 1 and Tier II Soil and Groundwater Remediation Guidelines. Capillary gas chromatography (GC) combined with flame ionization detection (FID) employing USEPA Method SW-846 8015 (USEPA, 1997) was selected as the primary analytical method for hydrocarbon enumeration and treatment tracking as it is well established in the environmental and petroleum engineering sciences. The GC method involves the separation and detection of the various components of the hydrocarbon in the sample as they pass through a capillary column in a gas state. The FID detects the separated analytes by measuring an electrical current generated by electrons from burning carbon particles in the sample. Although not as component specific as gas chromatograph-mass spectrometry (GCMS) methods, and not applicable to low molecular weight hydrocarbons (<carbon 10), the GCFID provides relatively inexpensive and accurate hydrocarbon results.
Biopile Soil Treatment in the Redwater Oil Production Area

(Dineen, Slater, Hicks & Holland, J., 1989), particularly within the mid to heavy carbon range typical of the hydrocarbon contaminants observed in the RPA soil as demonstrated below.

CCME soil petroleum hydrocarbon concentrations (PHC) were determined to identify the present PHC fractions equivalent to a carbon (C) scan standard. For data analysis and reporting purposes, four fractions were defined as follows: fraction 1: <C11, fraction 2: C11–C15, fraction 3: C16–C34 and fraction 4: C35-C60 (CCME, 2007). The fraction data provides more information than hydrocarbon totals alone, and aids in the assessment of mixtures. The composited and prepared pretreatment soil displayed a cumulative hydrocarbon value of 2300 milligrams per kilogram dry weight soil (mg kg\(^{-1}\) dw) of which 160 mg kg\(^{-1}\) dw was attributed to fraction 2, 1250 mg kg\(^{-1}\) dw as fraction 3 and 890 mg kg\(^{-1}\) dw as Fraction 4, with no fraction 1 components noted (see Appendix A1 for the pre treatment hydrocarbon GCFID result). This analysis confirmed the mid to heavy carbon range of the contaminants in the RPA soil.

The monoaromatic hydrocarbons benzene, toluene, ethylbenzene and xylenes (BTEX) and PHC hydrocarbon fractions were confirmed by GCMS using Soxhlet extraction. BTEX results were noted to be less than method detection limits, and PHC fraction 1 results were less than 12 mg kg\(^{-1}\) dw. Although these results would indicate that concentrations of BTEX and fraction 1 hydrocarbons are too low to be considered in the treatment planning for this study since they will dissipate through volatilization; concentrations of these two components will vary between sites in the RPA. The speciation of hydrocarbons indicates relatively consistent numbers across Fractions 2, 3 and 4, with no contaminants in the Fraction 1 range (i.e. less than 12 mg kg\(^{-1}\) dw) (see Appendix A2 for the pre treatment fraction 1 hydrocarbon results).

A real time field method of hydrocarbon quantification was also tested during this study. The PetroFLAG™ System is based on emulsion turbidimetry, which involves measurement of the light scattered by an emulsion. With the PetroFLAG™ system, a proprietary, nonpolar, organic solvent mixture composed of alcohols, is used to extract petroleum hydrocarbons from soil samples. A polar developer solution that acts as an emulsifier is added to a sample extract in order to emulsify the aromatic and aliphatic hydrocarbons and form uniformly sized micelles (USEPA, 1997). Light at a wavelength of 585 nanometers is passed through the emulsion, and the amount of light scattered by the emulsion at a 90-degree angle is measured using a turbidimeter. The total petroleum hydrocarbon concentration in the
emulsion is determined by comparing the turbidity of the emulsion to that for a reference standard or to a standard calibration curve. In this instance, a reference for diesel oil was selected for comparison (USEPA, 1997). For the prepared soil sample, the system returned a response of 2600 mg kg\(^{-1}\) dw, compared to a result of 2300 mg kg\(^{-1}\) dw obtained from the third party laboratory analysis. PetroFLAG™ was thus considered a reasonable and inexpensive method to use for screening soil samples for the relative reduction of total hydrocarbons during both the treatability and pilot phase studies.

5.3.3 Soil Physical Property Analysis

Soil physical characteristics are crucial in the understanding of biopile processes. Of primary importance is an understanding of the textural qualities of the soil as they will dictate operational parameters both in terms of the treatability study and full-scale operations. The soil at 1.60 to 1.80 mbgl, approximately consistent with the depth of study and the source of the treatability test soil material, is comprised of 7.4 percent clay, 91.1 percent sand, and the remaining 1.5 percent as silt (Komex, 2001).

Moisture is variable depending upon depth of sample; however, the prepared sample displayed a moisture content of 2.26 percent, which is not a measurement of field water capacity, but rather a total of all water in the sample, including moisture that may not be available to microorganisms. According to Paul & Clark, (1996), microbial activity is highest in soils near field water-holding capacity, where activity decreases at water contents higher or lower than this point, and where optimal contact between water and oxygen occurs. Field water capacity is measured with a capillary water test which determines the water holding capacity within the soil micropores under nonsaturated conditions (Baker et al., 1994). Field capacity of the prepared soil was determined by placing a 100 gram sample of the soil in a paper filter, saturating it with water and allowing it to drain under the influence of gravity. That soil was weighed and then dried until a constant weight was achieved. The difference between the saturated and dry weights was the amount of water present at field capacity.

Salinity and sodicity parameters of the subject soil include electrical conductivity levels between 0.392 and 0.94 deci Siemens/meter, sodium adsorption ratios between 0.53 and 0.74, and near neutral pH levels between 6.9 and 7.1. As expected in a sand matrix, the nitrogen level of the material is low both in terms of total nitrogen at 0.04 percent and a carbon to nitrogen ratio of 10 (Komex, 2001).
5.3.4 Microbial Analysis

Hydrocarbon degrading bacteria and fungi are widely distributed throughout marine, freshwater and soil habitats. In spite of this fact, confirmation of the presence and a sufficient population of naturally occurring bacteria that will contribute to degradation of petroleum constituents require laboratory analyses. Literature reports of the number of hydrocarbon utilizers identified during laboratory counts vary between studies because of methods used to enumerate microorganisms and speciation differences (Okoh, 2006). According to Margesin, Labbé, Schinner, Greer and Whyte (2003) while the purpose of enumerating microbial populations is to assess the potential for the biodegradation of hydrocarbons, this enumeration is associated with inconsistencies in both the methods and the interpretation of the results due to errors in both counting and organism recognition. This implies that estimating biodegradation strictly according to microbial population counts may be suspect and open to interpretation of the methods; nevertheless, an indication of non toxic conditions and the presence of bacteria were necessary to ensure degradation potential of the soil.

Field based studies are valuable in optimizing process parameters and determining the likely effectiveness of a remedial treatment action, given the nature of the contamination and circumstances of the site. In the interest of an accelerated field-based management approach, both laboratory analyses: degrader determination by cell counting, as well as a simplified field test for bacteria, further explained below, were initiated simultaneously.

A 500 mL sample of the homogenized soil was submitted to an independent laboratory for the completion of quantitative assays for bacteria and fungi, which were selected to provide a cross section of soil biological activity information for use in the treatability program. Results are summarized in Table 1 (see Appendix A3 for full laboratory analysis).
Table 1
Summary of Treatability Test Soil Bacteria and Fungi Enumerations

<table>
<thead>
<tr>
<th>Organism</th>
<th>μg/g</th>
<th>Expected Low*</th>
<th>Expected High*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Active Bacterial</td>
<td>36.2</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Total Bacterial</td>
<td>260</td>
<td>175</td>
<td>300</td>
</tr>
<tr>
<td>Active Fungal</td>
<td>4.56</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>Total Fungal</td>
<td>34.9</td>
<td>175</td>
<td>300</td>
</tr>
</tbody>
</table>

Note*: Expected low and high range values have been provided by the laboratory based on typical soil conditions.

Microscopic microbial counting measures the mass of aerobic bacteria and fungi that are actively feeding and reproducing. Active bacteria and fungi rapidly enhance soil structure, nutrient retention, disease suppression and residue/pollutant decomposition. Bioremediation is achieved successfully by employing an active mixed community of microorganisms of different species of bacteria and fungi.

According to Zucchi et al. (2003):

Bacterial communities in contaminated soils tend to be dominated by the strains that can survive toxicity and are able to utilize the contaminant itself for growth. As a response to bioremediation treatment, these populations may begin to actively degrade the pollutants and detoxify the soil, allowing other quiescent/starving populations to increase their numbers, leading to an increase of the bacterial community within the soil (p. 248).

A consortium of microorganisms is necessary to fully degrade most hydrocarbons. One group of microbes may be capable of degrading larger hydrocarbons into smaller hydrocarbons that can be used by another group of microorganisms. Ideally, the community will be sufficiently diverse that all the petroleum hydrocarbons will be mineralized. Given sufficient acclimation time, soil contaminated with petroleum often has enough indigenous hydrocarbon degrading microorganisms to support bioremediation (Bitton & Gerba, 1984; Cookson, 1995). The results of the bioassay (see table 1) would suggest that at a minimum two species exist in the host soil, albeit degrader organisms have not been specifically identified and no comparison to healthy soil is inferred, rather this testing confirms the treatability test soil is biologically active and may be amenable to treatment by biological methods.
Real time evidence of biological capability to degrade contaminants was vital for planning initiatives. A simple patented testing technique was assessed to evaluate its applicability for identifying biological activity. The Biological Activity Reaction Test (BART™) method is based on heterotrophic aerobic bacteria consuming dissolved oxygen. Bacterial activity is detected by looking for specific growth activities and reactions associated with BART in relation to the oxidation-reduction potential in the sample. The rates at which these activities and reactions occur can sometimes be used to quantify bacteria populations (Droycon Bioconcepts Inc., 2003), although this was not done in this study. This redox shift is determined by the methylene blue in the tester that turns blue under oxidative conditions and clear under reductive. The manner in which the methylene blue shifts from a blue to a clear color indicates which of the two major groups of heterotrophic bacteria (aerobic or anaerobic) is dominant. Once oxygen is consumed, methylene blue dye in the test vial becomes colorless, indicating aerobic bacterial activity. In this instance the test proved positive for aerobic activity, albeit it is recognized as only an indirect and qualitative test. Regardless, the test holds promise for simple, inexpensive and rapid site assessment for aerobic conditions in the biopile, and thus indirectly of biopile effectiveness although the preliminary nature of this type of field evaluation is emphasized.

5.4 Treatability Experiment

Pan studies use soils placed in holding pans and operated as microcosms that closely resemble biopiles. Degradation is measured by tracking contaminant concentration reduction, changes in bacterial population and other parameters over time. Typically, screening treatability studies are conducted at the bench scale under severe conditions, based on the available data and knowledge of the reaction chemistry, and the concentrations of the target contaminants in the soil are measured before and after treatment in order to determine the efficiency of the remedial process (Atlas et al., 1998). It was decided to operate the pan study not as a highly replicated experiment, but rather to test a variety of potential operating parameters that would more closely resemble those conditions present in an actual biopile scenario. U.S.EPA (1994) states that because soil pans are typically small, operating parameters (e.g. nutrient availability, pH, moisture, oxygen) are relatively easy to control and study costs are relatively low.

As outlined by the U.S. EPA (1994), a typical treatment evaluation using pan studies should include: (a) no treatment control samples, to measure the rate at which the existing bacteria in the soil
can degrade the contaminants under oxygenated conditions without the addition of supplemental nutrients, (b) nutrient adjusted samples, to determine the optimum adjusted nutrient ratio required to achieve maximum degradation rates, (c) inoculated samples, to determine if degradation can be increased by inoculation with bacteria known to degrade the contaminants at the site, (d) process optimization augmentation samples, to determine benefits, if any, of augments, and (e) sterile control samples, to determine the degradation rate due to abiotic processes as a baseline comparison with the other studies. Ten soil pan evaluations that encompassed these parameters were operated simultaneously under variable conditions in this study.

5.4.1 Methodology

This section describes the treatability study test objectives, and how these objectives will be used in evaluating biopile techniques for use in the RPA. Test objectives consist of meeting quantitative criteria-based performance goals, such as Alberta Tier I and making a qualitative engineering assessment of the process in terms of potential for large scale repeatability and logistics. The experimental design employed a series of soil pans, each of which was filled with the prepared, homogenized site soil described earlier. Process parameters to be controlled and monitored during the pan study included aeration, temperature, moisture levels and microbial respiration. The principle biodegradation tracking mechanism was CO$_2$ evolution. At the completion of the study, as indicated by reduced CO$_2$ production, the soil within was homogenized and submitted for hydrocarbon analysis to determine change in hydrocarbon levels of each pan.

Respiratory activity is a common biological assay used to measure CO$_2$ production rates as a reflection of the aerobic microbial activity in hydrocarbon contaminated soils (Zucchi et al., 2003). This assay has been used extensively to quantify biodegradation rates in soil samples containing ubiquitous hydrocarbon degrading microorganisms (Huessmann and Moore, 1994). Aerobic biodegradation of hydrocarbons results in the production of CO$_2$ while anaerobic biodegradation will result in the production of methane or hydrogen sulfide. The following equation (2) represents a hydrocarbon (CH$_2$)$_n$ being oxidized by bacteria for energy where O$_2$ is used as an electron acceptor (Van Hamme et al., 2003):

$$\text{CH}_2 + 1.5\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

(2)
Part of the energy obtained from the oxidation reaction in Equation 2 may be used for decomposition of the contaminants. The remaining energy is used for production of new cells, for cell maintenance and may be released exothermically. Cell synthesis, and indeed hydrocarbon decomposition itself, would increase O\textsubscript{2} consumption and CO\textsubscript{2} production, and the rate of CO\textsubscript{2} released from soils by microbial degradation of organic carbon can be used as an indicator of microbial activity. Generally, the aerobic degradation of 1 mg of a medium chain hydrocarbon requires 3 to 4 mg of oxygen (Dragun, 1998).

From CO\textsubscript{2} production and O\textsubscript{2} consumption data, quantities of organic carbon biodegraded can be estimated through stoichiometric calculations of microbial degradation processes. Fiuza & Vila (2005) demonstrated that the evolution of the carbon dioxide concentration in time clearly shows a trend and cycles that permits forecasting based on time series analysis; however, according to Soriano and Pereira (1998) the amount of activity per cell or per gram of biomass can vary widely based upon any number of material or site specific parameters from temperature to effective aeration, etc. This would imply that monitoring biodegradation strictly on the basis of respirometry may not be completely indicative of microbial performance, albeit a valuable indicator of activity, to be certain. As CO\textsubscript{2} production is indirectly related to microbial activity, measuring CO\textsubscript{2} release can corroborate that biodegradation is occurring, and allow evaluation of the control of parameters that are important to biodegradation by examining the kinetics of the rate of CO\textsubscript{2} release. It can also help monitor the phases of biodegradation within the pile such as the adaptation and active biodegradation stages (Baker et al., 1994).

5.4.2 Testing Apparatus and Methods

A series of 10 pan studies were conducted. Disposable clear acetate plastic pans, with sealable soft rubber lids, were used to hold 4 kilograms of homogenized site soil each, with 5 centimetres of freeboard void space between the soil and lid. Each square soil pan was 21.5 centimetres (cm) wide and 10.2 cm deep and had three, ¼ inch connection ports installed, two at the bottom (inlet and leachate) and one at the top of the pan (exhaust), each sealed with aquarium grade silicon (Figure 2).

The aeration system consisted of a series of two 0.050 m\textsuperscript{3}/minute capacity air pumps equipped with an inlet air filter; a by-pass pipe equipped with a series of main and individual pan control valves; polyethylene tubing and connectors; an inlet air nozzle; and a removable noxious gas activated carbon
filter at the gas exhaust port, which, when removed served also as the off gas measure port. Inside each pan, a 30 cm long commercial grade, perforated rubber hose that was shaped to form a continuous loop was attached to each inlet valve on the base of the soil pan. A 2 cm layer of aspen shavings was placed over the aeration pipe to protect it and provide a better overall distribution of air and water throughout the pan. Air was supplied at a rate of 0.005 m$^3$/minute to each pan based on studies that indicated the necessity of at least four air void volume exchanges every 24 hours (Pope & Matthews 1993).

Prior to soil addition each pan was filled with water to ensure that aeration, gauged by an in line rotameter, was adequate and equal. Moisture in the form of tap water was added to the surface of individual piles. The leachate port was normally closed, although each pan was drained monthly in order to inspect leach liquids for hydrocarbon sheen. Soils were mixed by hand on a weekly basis.

The process monitoring system was designed to control the soil pan working parameters, and to evaluate the rate of bioremediation. To provide information for controlling the mass balance during the bioreactor operation, the following parameters in the pan study were measured: inlet and exhaust gas flow rates, soil temperature, pH, moisture content and the aforementioned off gasses. All sampling was designed to be done in real time. Monitoring was completed by removing the carbon filter, and inserting a probe either above the soil for gas monitoring, or into the soil for temperature, moisture or pH monitoring.

Figure 2. Soil pan treatability apparatus displaying air management distribution system.
Carbon dioxide measurement was accomplished through the use of a Bacharach Model 2820 analyzer that employs infrared absorption principles to detect the presence of CO$_2$. Air samples are drawn through a sampling tube, desiccant filter and particulate filter into the analyzer which reads the CO$_2$ levels using infrared spectrophotometry. Accuracy is reported to be 50 parts per million (ppm) and the analyzer is able to measure to CO$_2$ levels up to 50,000 ppm (Bacharach, 2005).

Other off gasses were measured through the use of a factory calibrated BW Gas Alert Micro™ four gas analyzer, that is capable of simultaneously assessing oxygen, carbon monoxide, hydrogen sulfide and combustible gas levels. The oxygen gas sensor generates a current which is proportional to the rate of oxygen consumption if the passage of O$_2$ into the sensor is purely diffusion limited, as per Faraday’s Law, which states that the induced electromotive force in any closed circuit is equal to the time rate of change of the magnetic flux through the circuit. The oxygen gas sensor is capable of 0.1 percent resolution (BW Technologies, 2007)

Soil temperature was monitored using K Type thermocouple placed within the soil. Standard Type K thermocouples employ a chromium-nickel junction with a temperature range of 1370 degree Celsius. When the junction of the thermocouple is subjected to a given temperature, a current is produced which is indicative of the temperature at the junction which can be determined by a receiver module.

As described in section 4.1.4, an important environmental factor for efficient biopile performance is optimizing soil moisture. Generally, soil moisture should be maintained between 30 and 80 percent of field capacity during treatment (Dibble & Bartha, 1979). Field capacities typically range from 5 to 40 percent of the total weight of the soil depending on the soil texture. Therefore, a moisture level of 50 percent of field capacity might range from 2.5 to 20 percent total moisture by weight (Baker et al., 1994). In this case, a 40 percent field capacity was selected as a median and was maintained during the experiment by weighing the entire soil pan, subtracting the combined weight of the dry soil and the test apparatus, with the difference being the field capacity. Water was added as necessary to maintain the 40 percent field capacity. The pan weight was monitored weekly for moisture maintenance.
5.4.3 Soil Pan Operation

To study the biodegradation process of the contaminated soil, ten soil pan experimental trials were performed with different treatments, as presented in Table 2. Except for the treatments being evaluated, all samples as well as the experimental controls were prepared, mixed and handled in an identical manner. Additional explanation of treatment parameters is detailed in the following sections.

Table 2 Individual Soil Pan Treatability Test Operational Details

<table>
<thead>
<tr>
<th>Pan Test Details</th>
<th>Trial Label</th>
<th>Description</th>
<th>Treatment Time (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air/ H₂O</td>
<td>Run 1</td>
<td>Indigenous Control</td>
<td>120</td>
</tr>
<tr>
<td>Air/ H₂O/ Peat</td>
<td>Run 2</td>
<td>Process Optimization</td>
<td>120</td>
</tr>
<tr>
<td>Air/ H₂O/ Fertilizer (1 aliquot) added at with an addition every 30 days</td>
<td>Run 3</td>
<td>Nutrient Adjusted</td>
<td>120 and 300</td>
</tr>
<tr>
<td>Air/ H₂O/ Fertilizer added at (2 X aliquot) and Fertilizer (100-15-1-1) added at day 90</td>
<td>Run 4</td>
<td>Nutrient Adjusted</td>
<td>120</td>
</tr>
<tr>
<td>Air/ H₂O / Innoculant</td>
<td>Run 5</td>
<td>Innoculant Adjusted</td>
<td>120</td>
</tr>
<tr>
<td>Air/ H₂O / Humic Solid</td>
<td>Run 6</td>
<td>Biostimulant Adjusted</td>
<td>120</td>
</tr>
<tr>
<td>Air/ H₂O / Humic Liquid</td>
<td>Run 7</td>
<td>Biostimulant Adjusted</td>
<td>120</td>
</tr>
<tr>
<td>Air/ H₂O/ Fertilizer (1 aliquot) and Fertilizer (1 aliquot) @ day 90</td>
<td>Run 8</td>
<td>Nutrient Adjusted</td>
<td>120</td>
</tr>
<tr>
<td>Air/ H₂O/ Fertilizer (1 aliquot) / Innoculant / Humic Solid / Biostimulant</td>
<td>Run 9</td>
<td>Nutrient, Biostimulant and Innoculant Adjusted</td>
<td>120</td>
</tr>
<tr>
<td>Air/ H₂O / Biostimulant</td>
<td>Run 10</td>
<td>Biostimulant Adjusted</td>
<td>120</td>
</tr>
<tr>
<td>Abiotic Control</td>
<td>AC</td>
<td>Sodium Azide Neutralized</td>
<td>300</td>
</tr>
</tbody>
</table>

Note. All runs were aerated and watered regularly.

Runs 1 and 2 were conducted as baseline comparisons where only aeration and water were provided on a continuous basis to determine any differences with the various treatments. For Run 2 the soil was combined with 500 grams of sphagnum peat moss to determine if water holding capacity was a limiting factor to degradation of the hydrocarbon in the soil. All remaining soil pans, Run 3 through Run 10 were fertilized and/or variously augmented by commercial or natural substances or inoculated with microbial cultures to determine their effect on overall biodegradability of the site soil. These various treatment conditions will be outlined in more detail in sections 5.4.3.1 to 5.4.3.6 below.
The pan study was operated for 120 days during which time degradation trends were established. The soil pan experiment that was deemed to have the most favourable outcome, based upon hydrocarbon GC-FID results at the end of 120 days, was extended to determine if the degree of hydrocarbon degradation could be further enhanced over a longer timeframe.

### 5.4.3.1 Sphagnum Peat Moss

The addition of bulking agents including sewage sludge, compost, or alternative carbon sources can facilitate degradation of organic contaminants in soil because these additions play a role in supplementing nutrients, providing carbon sources, aerating contaminated soil and retaining moisture. The use of peat to stimulate microbial activity and bioavailability in soil can result in increased biodegradation of target organic chemicals (Saez-Navarrete, Gelmi, Reyes-Bozo and Godoy-Faundez, 2008). This method was investigated by Aprill & Sims (1990), who found that in soils with low levels of hydrocarbon contamination, humic matter may stimulate the biodegradation of toxic chemicals by providing exudates that serve as carbon and energy substrates for soil microorganisms and an enhanced environment by allowing heat, air and water to reach the microbes, resulting in bacterial growth and reproduction. Hesnawi & McCartney (2006) determined that the addition of compost to contaminated soil was effective in expediting the elimination of hydrocarbon compounds during composting bioremediation. In recognition of the distinctly low natural organic material content in the test soil, it was considered that the addition of peat moss may aid both as a physical conditioner, by allowing heat, air and water to reach the microbes, ensuring rapid bacterial growth and reproduction to support the retention of moisture, and as a possible source of carbon. Run 2 soil was mixed with 500 grams of sphagnum peat moss.

### 5.4.3.2 Nutrient Addition

Nutrients may be available in sufficient quantities in site soils but, more frequently, nutrients need to be added to the biopile soils to maintain bacterial populations and their optimal activity. Stimulation of microbial degrading activity is accomplished by the addition of inorganic or organic nutrients, normally in the form of nitrogen and phosphorus. Under aerobic conditions, nitrogen is consumed at a higher rate than in anaerobic conditions, which is indicative of the typically higher rate of cellular growth and of hydrocarbon biodegradation (Brook et al., 2001). Deciding on a suitable nitrogen source is an important challenge in enhancing hydrocarbon biodegradation since nitrogen can be readily lost through ammonia
volatilization, denitrification, and leaching processes. Generally, fertilizers that are ammonia-based are
the most effective for soil microorganisms, because ammonia is more energetically favorable for microbial
transformations than is nitrate (Ferguson et al., 2003). However, regardless of the source of nitrogen, its
availability is considered an essential variable in the bioremediation of hydrocarbon contaminated soils.

In the prepared soil sample, the naturally occurring available nitrogen content of the soil,
determined by Kjeldahl extraction, was very low. In addition, since humus acts as a reservoir for organic
phosphorous, and humus is limited in the sandy matrix soils of the RPA, the availability of phosphorus is
also low. A conservative approximation of the amount of nitrogen and phosphorus required for the optimal
degradation of petroleum products was calculated by assuming that the total mass of the hydrocarbon in
the soil represents the mass of carbon available for biodegradation and the nutrient levels are nil. As
noted above, since the sandy soil contains little humus, there is very little in terms of a carbon reservoir.
The typical carbon, nitrogen, phosphorus ratio necessary for biodegradation falls in the range of 100:20:1
to 100:1:0.5, depending on the specific constituents being degraded and the microorganisms involved in
the biodegradation process (USEPA, 1994).

A simplified, step-wise nutrient calculation model was presented by Von Fahnestock et al (1998),
in which a ratio of 100:15:1 (Carbon: Nitrogen: Phosphorous) is the suggested nutrient ratio to promote
biodegradation. This ratio was used in this study as it is established on field study experience rather than
laboratory study, and an appropriate percentage by weight of each nutrient was determined to reach this
ratio, based upon the contaminant level, the bulk density of the soil and the purity of the available
fertilizer. An aliquot of fertilizer for the volume of trial soil was calculated at 61.95 grams of Nitrogen, 6.83
grams of Phosphate and 1.34 grams of Potassium. Dry, commercial grade, slow release, granulated
fertilizers were used for nutrient addition, as it was considered that liquid or powder forms may be leached
through the sandy soil too rapidly to provide maximum benefit to the microbes. Fertilizers were combined
together and added to the surface of the soil in the test pan and mixed by hand to evenly distribute the
fertilizer granules into the soil.

Nitrogen is consumed at a higher rate under aerobic conditions than under anaerobic conditions,
which is indicative of the higher rate of aerobic biological activity, and by extension hydrocarbon
degradation (Atlas & Bartha, 1992). In order to investigate these possible effects and whether nitrogen is
a possible limiting factor to degradation, Run 3 and Run 4 were prepared accordingly. Run 3 was prepared with a single aliquot of fertilizer, but was designed to have a supplementary one half aliquot fertilizer added every 30 days during the experiment if deemed necessary according to off gas results. Run 4 was initiated using approximately twice the calculated fertilizer requirements and was supplemented at day 90 with an additional aliquot.

5.4.3.3 Commercial inoculant and biostimulant

While previous assays of the prepared soil indicated a healthy presence of microorganisms to ideally promote aerobic degradation, it was prudent to ascertain if the addition of commercial agents would accelerate remediation of the hydrocarbon-contaminated test soil. These agents fall into two categories: inoculants and biostimulants.

Bioaugmentation is the controlled addition of specifically formulated cultures (inoculants) to assist the naturally-occurring microbes in degrading the contaminants. The opinion regarding the use of commercial inoculants is divided, but the conclusions reached by this author after evaluating a number of peer-reviewed articles suggest that bioaugmentation appears to have limited benefit for the treatment of oil in an open environment, and further, that microbial addition has rarely been shown to work better than nutrient addition alone in many field trials. Although extensive field research has been conducted on oil bioremediation products, the effectiveness of these products has only rarely been convincingly demonstrated (Zhu, Venosa & Suidan, 2004). Most existing studies have concentrated on evaluating the factors affecting oil bioremediation, or testing favored products and methods in laboratory studies (Mearns, 1997).

Case studies, provided mainly by vendors of the commercial cultures, suggest that application of bioaugmentation products can accelerate the treatment of specific oil components, isolated spills in confined areas, or certain environments where oil-degrading microorganisms are deficient (USEPA, 2004b). Seemingly for every positive result using commercial agents (Aldrett, Bonner, McDonalds, Mills & Autenrieth, 1997; Bragg, Prince, Harner & Atlas, 1994), a negative case has been presented (Swannell, Croft, Grant & Lee, 1995; Venosa et al., 1993). Two commercial additives were employed in the study. The selected inoculant, BioBugs HC™, is described by the supplier as "a specially formulated range of adapted high performance microorganisms, which in addition to the bacteria element also contains a
complete micronutrient blend for microbial growth” (BioSystems International, 2009). Due to the presence of aerobic and facultative anaerobic microorganisms, it is reported to establish and maintain a biomass which is able to perform more effectively than the naturally occurring biomass. Biostimulants are used to describe any additives that stimulate biological growth. These may include live biological organisms, plant extracts, spores of microorganisms, plant growth regulators and even nutritional supplements (USEPA, 2004b). A number of small and large companies have introduced a myriad of products, which claim to not only stimulate the plants but also prevent some diseases by promoting plant health.

Compared to microbial products, few biostimulant additives have been developed and marketed specifically as commercial bioremediation agents, likely since common fertilizers are inexpensive, readily available, and have been shown to be effective if used properly. However, due to specific limitations of common fertilizers (e.g., being rapidly washed out due to their high water solubility), selected organic nutrient supplements, such as oleophilic nutrient products, have recently been evaluated and marketed as bioremediation agents (Margesin, Hämmerle & Tscherko, 2007). Oleophilic compounds have both hydrophobic and hydrophilic ends. As a result oleophilic fertilizers are able to adhere to oil and water, causing them to provide nutrients at the oil-water interface, and enhanced biodegradation should result without the need to increase nutrient concentrations. This approach can also be used to overcome the problem of water-soluble nutrients being rapidly washed out of the contaminated soil (Zhu et al., 2004), a perceived difficulty with the test soil. The augment, EC 4000 is marketed by the manufacturer as a “non-toxic, micronutrient-biostimulant substance” (EcoChem, 2008).

Run 5 soil was augmented with the manufacturer’s recommended dosage of inoculant BioBugs HC™ while Run 10 soil was treated with the suggested amount of liquid biostimulant EC 4000 for the volume of soil. As with most commercial additives in the field of bioremediation, precise formulations of each product are not available.

5.4.3.4 Humates

A remediation additive that has had reported success is the application of humates to petroleum-contaminated soils (Novak, Jayachandran, Moorman & Weber, 1995). In a geological sense, humates are highly carbonaceous rocks (e.g. mudstone or coal) that are rich in humic and fulvic acids, and originate from terrestrial, marine, or lacustrine organic matter. If a hydrocarbon molecule becomes sorbed to the
soil, the overall bioavailability of that hydrocarbon for a microorganism depends on how readily the molecule will desorb back into aqueous solution. If the contaminant becomes covalently bound to the soil through the polymerization processes responsible for the formation of humus, it becomes unavailable for breakdown by microbes. In contrast, contaminants sorbed to humic substances may be more readily desorbed, and are therefore more available to microorganisms than those contaminants that may become bound to soil particles through polymerization processes (Novak et al., 1995).

Microbes may also utilize humic substances as nutrient sources, and consequently release tightly sorbed contaminants in the process (Hsu & Bartha, 1976). While the exact mechanism by which humates facilitate biodegradation is unknown, possible explanations include: humates provide nutrients to support microbial growth; humates nonspecifically adsorb toxic or inhibitory compounds; humates provide favorable surfaces for microbial growth, or function as a kind of surfactant and/or chelating agent (Mosley, 1998). Regardless of the explanation for the mechanism, the general consensus is that they may, in soils that contain low levels of organic matter, enhance the solubilization process of hydrocarbons and thus increase their bioavailability (Lesage, Xu, Novakowski, Brown & Durham, 1995). The soil for Run 6 was combined with a highly soluble humified organic matter powder, Black Earth Dry Soluble 80, which was designed to dissolve readily in water to create a liquid humic solution, while the soil for Run 7 was combined with a commercial water soluble organic liquid hume, Black Earth Organo Liquid Hume.

5.4.3.5 Control

It is important to include appropriate controls, such as sterile treatments, in bench scale experiments to differentiate the effects of abiotic weathering from actual biodegradation of the oil (Balba, et al., 1998). Two types of controls were employed: the first was a non-augmented biological control, while the second control was an abiotic control. Run 1 was to evaluate non-augmented biological conditions, that is, to determine if the sample material would degrade with only the addition of oxygen and moisture. This run contained the same contaminated media, was mixed, containerized, stored, incubated, aerated, watered and sampled in an identical manner to the other test runs. Run 2 was an abiotic control. One liter of the prepared, non amended soil was mixed with 100 ml of 1-percent liquid sodium azide solution, containerized and placed into cold storage for analysis at the completion of bench studies. Sodium azide will prevent microbial activity, as it essentially sterilizes the soil, and thereby
restricts the microbial degradation process. At the completion of the bench scale experiment the abiotic control was analyzed to determine if hydrocarbon loss had occurred. If abiotic controls are not used, the disappearance of chemicals may be attributed to biological activity, though it may not play the major role in the degradation of the chemical. Thus, measurement of physical loss, as well as the partitioning of organic substances into the air and soil phases should be used in degradation studies to demonstrate that the disappearance of the contaminant is related to the activity of the biological components in the soil system (USEPA, 1993).

5.4.3.6 Experiment monitoring and maintenance

Regular temperature, moisture, carbon dioxide and oxygen off gas parameters were monitored in each test soil pan device using portable, real time, field instruments. In addition, carbon monoxide, pH, hydrogen sulphide and combustible gas levels were also measured weekly. All soil pans were watered to maintain a field capacity at or near 40 percent. This addition of water occurred approximately biweekly, depending on the weights for individual pans. The volume of water added per pan at each interval varied appreciably from zero to greater than 700 ml.

Air was provided equally to each soil pan, with the air pumps cycling intermittently on a 75 percent on: 25 percent off operating ratio. As plugging of the aeration system, compaction of the soil and preferential airflow through individual pans was possible; soil mixing of each pan was completed on a biweekly basis. Care was taken to ensure that the aeration system was not disturbed during soil mixing episodes and each line was adjusted to full pump output pressure on a bi monthly basis to ensure aeration lines remained clear. All testing was completed at room temperature, and bi monthly pH testing was performed on the soil to ensure near neutral conditions were maintained throughout the experiment.

At the completion of the bench scale experiment (120 days) the soil pans were allowed to normalize for 30 days. Composited 250 millilitre soil samples from each pan were submitted to a third party laboratory for GC-FID analysis to mirror pre-treatment analytical hydrocarbon testing. The material in the bottom 2 cm of each soil pan contained wood chips, soaked soil and fine silt, and thus was not included in the samples; however, sample R4-2 was retrieved from the bottom of the R4 soil pan to represent this bottom soil pan material, as it was considered of importance in determining possible flushing transport mechanisms that may have been occurring in the soil pans.
5.5 Treatability Testing Results and Discussion

A summary of the post treatment results of the soil pan experiments are presented in Table 3 and the complete laboratory hydrocarbon analysis is provided in Appendix A4. The post treatment hydrocarbon results of the soil pan experiments are noted to be different from the pre-treatment hydrocarbon results, as determined by statistical comparison, with the exception being the abiotic control which was found to be statistically similar to the pre treatment result indicating little or no degradation had occurred in that particular sample (see table 3).

Whether an individual treatment had a significant effect on the mean hydrocarbon levels (before and after treatment) was analyzed by a paired sample t test for dependent samples. In a before/after study, the difference between the after sample level minus the before sample level is taken for each pair, and the average of these differences is calculated. If this average of differences is determined to be different from zero, the conclusion is that there is a significant change. The null hypothesis (H₀) for each comparison is that there was no significant difference between the pre-treatment hydrocarbon contaminant level and those of the post-treated sample(s). The alternative hypothesis (H₁) being that there was evidence of a significant difference between mean pre-treatment and post-treated samples. Significance was accepted at p=0.05 (95% confidence level) for all statistical analysis. A small p-value such as this is indicates rejection of the null hypothesis and leads to the conclusion that the average difference between the hydrocarbon levels before and after treatment(s) is not zero, i.e., there is evidence of a significant (at the 0.05 level) change in hydrocarbon contaminants of these ten samples on average compared to the pre treatment sample (see Appendix A5 for summary of statistical results).

To ensure paired experimental design was appropriate, each post treated set of results were first compared using Pearson’s Correlation, which measures the strength of the linear relationship between the select group of results (i.e. post-treated sample to treated sample). In each case (see Appendix 5) the p value was determined to be less than 0.05 and rho positive which is indicative of a statistically significant relationship between the variables and their suitability for paired testing (TexasSoft, 2007).
Table 3

*Summary Of Soil Pan Treatability Test Results Displaying Fractionated Hydrocarbon Results.*

<table>
<thead>
<tr>
<th>Trial Label</th>
<th>Fraction 2 (ppm)</th>
<th>Fraction 3 (ppm)</th>
<th>Fraction 4 (ppm)</th>
<th>Total (ppm)</th>
<th>Reduction (ppm)</th>
<th>Reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>10</td>
<td>850</td>
<td>920</td>
<td>1780</td>
<td>520</td>
<td>22.61</td>
</tr>
<tr>
<td>Run 2</td>
<td>&lt;10</td>
<td>560</td>
<td>570</td>
<td>1130</td>
<td>1170</td>
<td>49.13</td>
</tr>
<tr>
<td>Run 3</td>
<td>&lt;10</td>
<td>230</td>
<td>180</td>
<td>410</td>
<td>1890</td>
<td>82.19</td>
</tr>
<tr>
<td>Run 3-30 day</td>
<td>80</td>
<td>1570</td>
<td>890</td>
<td>2540</td>
<td>+240</td>
<td>+1.10</td>
</tr>
<tr>
<td>Run 3-300 day</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Run 4</td>
<td>&lt;10</td>
<td>390</td>
<td>330</td>
<td>720</td>
<td>1580</td>
<td>68.70</td>
</tr>
<tr>
<td>Run 4-2</td>
<td>40</td>
<td>1000</td>
<td>840</td>
<td>1880</td>
<td>420</td>
<td>18.26</td>
</tr>
<tr>
<td>Run 5</td>
<td>30</td>
<td>740</td>
<td>650</td>
<td>1390</td>
<td>910</td>
<td>39.57</td>
</tr>
<tr>
<td>Run 6</td>
<td>30</td>
<td>740</td>
<td>680</td>
<td>1420</td>
<td>880</td>
<td>38.26</td>
</tr>
<tr>
<td>Run 7</td>
<td>&lt;10</td>
<td>530</td>
<td>450</td>
<td>980</td>
<td>1320</td>
<td>57.39</td>
</tr>
<tr>
<td>Run 8</td>
<td>&lt;10</td>
<td>510</td>
<td>430</td>
<td>940</td>
<td>1360</td>
<td>59.13</td>
</tr>
<tr>
<td>Run 9</td>
<td>&lt;10</td>
<td>510</td>
<td>440</td>
<td>950</td>
<td>1350</td>
<td>58.70</td>
</tr>
<tr>
<td>Run 10</td>
<td>10</td>
<td>740</td>
<td>600</td>
<td>1340</td>
<td>960</td>
<td>41.74</td>
</tr>
<tr>
<td>Pre Treat</td>
<td>160</td>
<td>1250</td>
<td>890</td>
<td>2300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abiotic Control</td>
<td>190</td>
<td>1460</td>
<td>570</td>
<td>2220</td>
<td>80</td>
<td>3.48</td>
</tr>
</tbody>
</table>

*Note A:* less than (<), implies that each carbon number in fraction is less than 10 ppm.

*Note B:* Reduction refers to the total hydrocarbon fraction after treatment subtracted from the pre treat fraction.

### 5.5.1 Carbon Dioxide Off Gas Results

Soil respiration is a measure of the total biological activity in soil and results from the degradation of organic matter, where the formation of CO$_2$ is the last in the series of steps of hydrocarbon mineralization (Yerushalmi, et al. 2003). Thus respirometric measurements of CO$_2$ production provide information on the biodegradability potential of hydrocarbons in soils, and are often used as a monitoring parameter during bioremediation treatments. The increase of CO$_2$ as measured by CO$_2$ production after test initiation indicates successful hydrocarbon mineralization (Margesin et al., 1999). The daily measurements of the quantity of CO$_2$ generated enabled the calculation of a value for the cumulative CO$_2$ production over the treatment period, daily respiration rates as well as periodically averaged respiration...
rates for each pan. Figures 3, 4, 5 and 6 show the daily averaged respiration rates for Runs 1 to 10, which have been displayed to represent treatment rate similarities and differences between trial runs.

The carbon dioxide respiration rates over time display the overall treatment trend of each soil pan and exhibit random irregularities, typical of soil respiration rates (Margesin et al., 1999) that tend to vary over short sample collection periods. The biological activities measured (respiration in terms of CO$_2$ evolution) display a significant correlation with hydrocarbon degradation in test samples and a negative correlation with the unaltered control runs. The addition of nutrients resulted in an increase in the respiration rates, highlighting the benefits of nutrient addition (see Figure 3).

![Graph showing carbon dioxide respiration rates over time for Runs 1 to 10.]

*Figure 3.* Fertilizer adjusted Runs 3, 4, 8 and control (Run 1) displaying carbon dioxide respiration rates versus time and general degradation trend periods.

Significant positive correlations were also found between the final hydrocarbon levels and soil respiration in a number of the test runs, which point to the adaptation of the indigenous microorganisms (in non augmented pans) to the contamination, and to the microbial utilization of hydrocarbon as an additional carbon source for growth (Cookson, 1995).
Whether an active biological treatment includes indigenous bacteria, added bacteria or added stimulants, the overall microbial activity will most certainly follow a typical four step process: acclimation, adaptation, maximum degradation and declining degradation (Alexander, 1999). All adjusted soil pan tests appear to show these typical trends, although at differing levels, whereas the control samples Run 1 and the process augmented control Run 2 (Figure 6) display little CO$_2$ respiration response overall (air only and air-peat, respectively). Figure 3 has been labeled to represent the generalized treatment trends of the degradation processes.

Acclimation describes the transition time during which the microbial population adjusts to new environmental conditions (Alexander, 1999) at the experiment initiation. CO$_2$ evolution at the beginning of the experiment ranged from 1100 ppm in the control sample (see Figure 3 or 6) to a high of 3000 ppm obtained from Run 4 (see Figure 3). It is notable in that even the unadjusted control (Run 1) apparently displayed a degree of respiration, although the early responses noted soon reduced to near background levels within 7 days. The largest response was Run 4, which was stimulated with the highest initial quantity of fertilizer (see Figure 3).

During the next phase, adaption; a general leveling off of CO$_2$ levels is noted at approximately 20 days for the nutrient adjusted runs (Figure 3). This may indicate that the more easily treated constituents of the hydrocarbon mass are degraded during the initial phase or that nutrients (other than the carbon source) were depleted rapidly in this early phase of the experiments. Logically bacteria would start degrading simple components first, followed by other bioavailable complex components (USEPA, 1992). Those components that are strongly adsorbed onto soil particles will probably persist until they are the sole carbon source, and are made available to bacteria by suitable transport or desorption mechanisms that may be attributed to cometabolism interactions (Baker et al., 1994). A striking feature is that the adaption period is almost identical at 5-35 days from the start of the treatment process for a number of the test runs (see Figures 3 to 6), and while magnitudes are variable, most achieved a CO$_2$ level of between 5,000 to 10,000 ppm. In particular, the magnitudes of the respiration are substantially higher in the case of nutrient adjusted runs, indicating that hydrocarbons are being used as a carbon source more quickly under these conditions, and which, therefore, demonstrate the benefit of nutrient addition in terms of respiration rates.
Figure 4. Innoculant adjusted Runs 5 and 9, biostimulant adjusted Run 10 and control (Run 1) displaying carbon dioxide respiration rates versus time.

Figure 5. Humate adjusted Runs 6, 7 and control (Run 1) displaying carbon dioxide respiration rates versus time.
It is noted that respiration rates in Run 3 (Figure 3) tended to increase after each successive addition of nutrient. In contrast Run 4 (double fertilizer aliquot), maintained a relatively consistent respiration level until day 40-50 at which time rates decreased substantially to less than 1000 ppm (see Figure 3).

![Graph showing carbon dioxide respiration rates versus time](image)

*Figure 6. Control Runs 1 (air only) and 2 (air and peat) displaying carbon dioxide respiration rates versus time.*

The highest average daily CO$_2$ respiration rates were observed in Run 3 (5389.66 ppm), Run 4 (4681.04 ppm) and Run 8 (4029.31 ppm), all of which were nutrient adjusted (see Figure 3). The lowest average daily respiration rate was observed in control Run 1 and Run 2, with rates of 329.31 ppm and 551.72 ppm, respectively (Figure 6). In order to further solidify the case that nutrients were a limiting factor in the degradation process, at day 90, after 30 days of successive low respiration rates, Run 4 and Run 8 were fertilized and a rapid increase in CO$_2$ rates followed (see Figure 3).

In general, the bioaugmented runs (Figures 4 and 5) did not display accelerated CO$_2$ respiration rates in comparison to the nutrient adjusted (Figure 3, runs 3, 4, 8). There was, however a gradual increase in respiration levels of both humate augmented Runs 6 and 7 (Figure 5), which may be indicative that over a longer period of time, humates may eventually allow petroleum hydrocarbons to
become bioavailable (Novak et al. 1995). There is a distinct correlation between average respiration daily rates and hydrocarbon degradation results across the series of soil pan tests as the largest total volumes of CO₂ respiration corresponded to the highest reductions in hydrocarbons (see Figure 3 and Table 3).

5.5.2 Hydrocarbon Removal

The concentrations of hydrocarbons at the beginning and at the conclusion of the experiment are presented in Table 3. The most direct way to measure bioremediation efficacy is to monitor the rate of hydrocarbon disappearance from the soil, which can occur via three main pathways: evaporation, leaching and biodegradation (Xu and Obbard, 2002). In this study, evaporation was considered to be negligible relative to biodegradation as the mixture of the hydrocarbon and soil in the test sample is already weathered and the quantity of volatile hydrocarbons present had stabilized over time. Leaching was also thought to be only a minor component of hydrocarbon disappearance as the soil-hydrocarbon material used for testing had been in place for decades, and that any further leaching of the hydrocarbon component was likely insignificant. Therefore, it is considered that the difference between the pre and post test hydrocarbon levels determined by the GC-FID analysis would be attributed to biodegradation of the hydrocarbon.

Figure 7. Run 3 hydrocarbon concentrations before and after treatment at 120 days.
Microbial degradation of hydrocarbons varies according to their molecular weight and structure; biodegradation rates are generally higher for saturates followed by monoaromatic (BTEX, phenols) and the lighter polyaromatic hydrocarbons (2, 3 and 4 ringed PAH's) (Environment Agency [EA], 2005). In general, there was a decrease in CCME fraction 2 hydrocarbons across all test runs when comparing laboratory results, with less dramatic decreases of fraction 3 and fraction 4 hydrocarbons (Figure 7). These results are in agreement with the experimental literature showing the same pattern of degradation with different types of hydrocarbon affected soil (Song, Wang & Bartha, 1990; Zhou & Crawford, 1995); with post treatment residuals remaining more prevalent for heavier distillates in the fraction 3 and 4 range. This is important to remedial planning in the RPA, as the weathered, older hydrocarbon contamination characteristic of the area (i.e. fractions 3, 4) may have poor bioavailability qualities or may be inherently recalcitrant, which could preclude the effective employment of bioremedial methods (Jorgensen, Puustinen & Suortti, 2000).

The results of the treatability study showed there was a distinct but variable decline in hydrocarbon concentrations in each of the test runs performed over the course of the 120 days of the experiment (see Table 3). Run 1, conducted under natural, non-augmented or stimulated conditions, displayed the least degradation over the course of the bench study at 1780 mg kg\(^{-1}\) dw, which is a reduction of 520 mg kg\(^{-1}\) dw total hydrocarbon (22.6 percent) as compared to the original pre treatment sample. The results of Run 3 show the greatest hydrocarbon reduction to 410 mg kg\(^{-1}\) dw (82.2 percent). Other hydrocarbon results were between these extremes after 120 days of treatment (see Table 3).

The hydrocarbon content over the experiment was reduced in the fertilizer only soil runs, specifically Run 3 and Run 4, while Run 8, which included a reduced quantity of fertilizer, displayed hydrocarbon results that were less significant. The reduced microbial activity observed in Run 8 may be a result of the limitation of the available nutrients in the Run 8 test, as both Run 3 and Run 4 received approximately twice the amount of fertilizer, either at experiment initiation (Run 4), or over the course of the experiment (Run 3). Those test runs that were augmented by inoculants (Run 5), humics (Run 6 and 7), biostimulant (Run 10) or combinations thereof (Run 9), displayed variable hydrocarbon reduction totals from a low of 88 mg kg\(^{-1}\) dw (38.26 percent) for Run 6 to a maximum reduction of 1350 mg kg\(^{-1}\) dw (58.7 percent) for Run 9 (see Table 3).
The results of the blank tests (Run 1 and 2) indicate that native microorganisms can degrade the hydrocarbon contaminants, but the efficiency of degradation was low (see Table 3), and may not meet the requirement to treat a site in a short period of time without nutrient amendments. As the experiment progressed, CO₂ monitoring indicated that little or slow degradation appeared to be occurring in the control (Run 1), Run 5 and Run 6. It was assumed that no further meaningful reductions in hydrocarbon levels would transpire for those Runs after the 120 day test period. The addition of peat did appear to have some beneficial effect on hydrocarbon removal (Run 2) as the hydrocarbon reduction was noted to be over two times that of Run 1 (see Table 3).

5.5.2.1 Thirty Day Hydrocarbon Analysis

At day 30 of the experiment a combined sample removed from Run 3 was analyzed to determine hydrocarbon levels (see Appendix A6). This time point was chosen because it was expected to be after the end of the initial treatment phase (see Figure 3). The cumulative GC-FID hydrocarbon scan displayed a level of 2540 mg kg⁻¹ dw, which was in excess of the pre-treatment hydrocarbon analysis of 2300 mg kg⁻¹ dw (see Table 3). Results of this type can seem surprising; however, such results are not an unusual circumstance, as often the bacteria that are active in the biodegradation of the contaminants excrete extracellular surfactant-like polymers during their metabolic cycle (Vance, 1991). These polymers may have helped to mobilize the hydrocarbon contaminants resulting in the observed increase hydrocarbon levels after the initial treatment period of 30 days (Margesin et al., 1999).

Hydrocarbon mobilization was also exhibited in the closure analysis of Run 4-2, using a sample retrieved from the base of soil pan Run 4. The post-treatment material remaining in the base of the soil pan was a combination of very fine silt, partially degraded wood chips and water. Analysis of this material indicated a cumulative hydrocarbon level of 1880 mg kg⁻¹ dw, which is considerably more contaminated than indicated by the sample from the treatment zone of Run 4 (720 mg kg⁻¹ dw). These results suggest that aside from the biodegradation component of soil treatment, that a physical process of desorption and flushing due to fugacity properties of the treating material has occurred, and may be an important factor to consider in the establishment of a pilot and full-scale biopile system.
5.5.2.2 Three Hundred Day Analysis

The test run deemed to have the maximum total reduction of hydrocarbon result (Run 3) was selected to be extended using the same basic operating conditions, to establish if hydrocarbon content could be further reduced (Figure 8). The extended trial was concluded when CO$_2$ readings indicated respiration had ended in the soil pan. Regular watering to maintain optimal moisture conditions (as described) and fertilizer amendments (10 grams, 15:1:1) were added at approximate 30 day intervals.

It is noted that CO$_2$ respiration rates were prolonged over the extended treatment period (see figure 8), suggesting that supplementary treatment of the soil over the extended time period is occurring. A composited sample was retrieved from the remaining soil within the soil pan and submitted for hydrocarbon GC-FID hydrocarbon analysis at 300 days. The results indicate a substantial reduction of the hydrocarbon levels to below method detection levels for each constituent (see Table 3). This would suggest that an extended treatment time, with the addition of quantified nutrients and suitable aeration and moisture control, will result in very efficient degradation of the contaminated soil (Refer to Appendix A7 for laboratory GC-FID results).

Figure 8. Run 3 carbon dioxide and temperature versus time, treatment period of 300 days.
In order to estimate the effects of treatment and toxicity on the microbial populations, soil samples were enumerated for microbes before treatment and after 300 days of treatment (Run 3). The active bacterial count at 300 days was noted to be reduced by 63.8 percent from the original analysis, with total bacteria counts actually increasing by 24 percent. Active fungal and total fungal numbers dropped by 28 and 71 percent respectively (Refer to Appendix A8). It could be postulated that both fungi and bacteria were the hydrocarbon degrading sources for this study, which has been noted by others (Atlas, 1981), although this is a broad assumption since the biodegradation process are complex and difficult to accurately predict.

5.5.2.3 Abiotic Control Analysis

As previously described, a prepared abiotic control was placed into cold storage to be analyzed at the completion of bench scale treatability studies. Whether the abiotic control treatment had a significant effect on the measured hydrocarbon parameters, as compared to the pre-treatment sample was analyzed using the paired t test for independent samples. The mean differences between the pre-treatment and control samples are estimated to be near zero, which would indicate with good confidence levels (>95 %) that the samples are similar, indicative of low hydrocarbon loss due to volatilization and that degradation had been effectively terminated by the bactericide/fungicide additive (See Appendix A5).

5.5.3 Effect of Nutrient Addition

Typically, the supply of inorganic nutrients such as phosphate and nitrate in a soil environment exceeds the needs of the resident microbial communities because carbon is the limiting nutrient element for heterotrophs in soils (Alexander, 1999). However, this situation is altered markedly in the case of a hydrocarbon being introduced to the soil environment. Under these circumstances, the supply of inorganic nutrients, which was not a limiting factor under normal soil conditions, may be at concentrations too low to meet the higher demand requirements that occur when carbon is no longer limiting. The rate and extent of hydrocarbon degradation are thus limited by the low availability of nitrogen and phosphorus (Atlas & Bartha, 1972). Consequently, growth of hydrocarbon-degrading bacteria and fungi in soil and hydrocarbon degradation can be strongly enhanced by the addition of fertilizer containing inorganic N and P. In order to obtain a more systematic understanding of the effects of nutrient addition on the contaminated soil, native microcosms in the soil pan experiment were treated with different levels of
inorganic nutrients to determine the effects of different levels of N and P supply on oil degradation and the bacteria and fungi community. Nutrient amendment over a wide range of concentrations significantly improved oil degradation, confirming that N and P limited degradation over the concentration range tested. The extent and rate of oil degradation were variable for each soil pan experiment, indicating that in this experiment, it was the overall amount of the addition of nutrients and possibly the systematic application of the nutrient that was most important operationally.

In all soil pan experiments treated with inorganic nutrients (runs 3, 4 and 8, the rate of carbon dioxide production strongly increased directly after fertilization relative to that of the control, and after 120 days (i.e. at the end of the runs), the amount of carbon dioxide produced was significantly higher than the untreated control (see Figure 3). Daily carbon dioxide production slowly declined over time, with nutrient amendments temporarily stimulating carbon dioxide production in those soil pans where addendum treatments were completed (Run 3, Run 4 and Run 8; see Figure 3). In general, the initial rate of carbon dioxide production appeared to increase with the amount of fertilizer added. Trends in carbon dioxide evolution and oil chemistry results clearly indicated that the addition of N and P significantly improved oil degradation, showing degradation was limited by the supply of N and P. Post treatment levels of nutrients were elevated compared to pre treatment analysis (Appendix B3).

Previous studies have indicated a negative effect of nutrition on the number of microbial hydrocarbon degraders and soil microbial activity, as measured by CO₂ evolution (Margesin et al., 1999; Hinchee, 1998). In contrast, Bragg et al. (1994) noted a positive relationship between the rate of oil biodegradation and nitrogen concentration in soil, demonstrating that the nutrient content was the most significant factor controlling the rate of oil degradation. The results of this study concur with Bragg’s 1994 results. Nutrient addition did significantly increase the oil biodegradation rate.

5.5.4 Effect of Bioaugments, Humates and Biostimulant

Bioaugmentation of native hydrocarbon contaminated soil to increase its biodegradative capabilities has been employed in a number of studies (Walter, 1997; Atlas & Unterman, 1999). The actual success of this approach in soils is marginal, since in the native habitat, the inoculum must overcome a number of possible limitations, including competition for nutrients, survival in an alien matrix and stresses associated with introduction into the new soil environment itself, and still maintain
degradative capabilities (Alexander, 1999). Therefore, the survival of introduced bacteria is normally low and as a result, the cost effectiveness of this approach may be questionable. Run 5, which employed a commercial inoculant, displayed a low respirometric response (see Figure 4) and appeared to have little positive effect upon hydrocarbon degradation (see Table 3). The degradation that did occur in Run 5 may have been attributable to the nutrient addition which accompanied the inoculum, while the inoculum itself may have been detrimental to hydrocarbon degradation because when compared to Run 8, with identical amounts of fertilizer, but no inoculum, resulted in better ultimate degradation (see Table 3).

Two test runs employed commercial humates: a liquid and solid formulation. The bioavailability of petroleum hydrocarbons in soils increases as the organic carbon content of the soil increases (Weissenfels, Beyer & Klein, 1992). In the presence of high amounts of organic carbon such as soil organic matter, the sorption of hydrocarbons becomes more pronounced, mainly because of hydrophobic partitioning of the compounds onto humic substances and diffusion of compounds into soil-humus matrices which enhances the aqueous solubility of the hydrocarbon contaminant making them more available for degradation (Hwang, Ramirez, Cutright & Ju, 2002). In neither experiment was a beneficial effect of the addition of humates noted equaling the solely fertilized test runs, although the liquid humate Run 7 was near the reduction level of fertilized Run 8 (see Table 3). The lower mineralization seen in the presence of humate additives suggests that they may interact with intermediates and prevent rapid degradation in this matrix although it is considered that humates may hold promise over a longer treatment term, since CO₂ levels (and presumably degradation) remain elevated at the end of the soil pan test period (120 days).

The commercial biostimulant was applied twice over the course of the experiment (Run 10) and while there appeared to be positive CO₂ evolution rates variously over the course of the study (Figure 4), this did not translate to enhanced hydrocarbon reduction equal to that of the nutrient adjusted tests (see Table 3). Similarly Run 9, which was augmented by all additives, displayed only average hydrocarbon degradation. It is considered that reduced degradation is linked to nutrient deficiency in these instances.

There are numerous soil biodegradation additives on the market; it would be inaccurate to assume that none of these would ameliorate favourably, but given the costs of these additives and additional treatability studies may put their value into question in this instance.
5.5.5 **Oxygen, Temperature and Moisture Monitoring**

The availability of oxygen is commonly a limiting factor in biodegradation of hydrocarbons, thus all soil pans were fully aerated throughout the experiment. As anticipated, oxygen consumption varied appreciably over the course of the experiment, generally in opposition to CO$_2$ evolution. Off gas oxygen levels were highest during episodes of low degradation in all soil pans (decreasing CO$_2$ production) and lowest during high CO$_2$ production (highest hydrocarbon degradation). Other authors have found a similar decrease in oxygen consumption during the course of bioremediation (Scow & Hutson, 1992; Jørgensen et al., 2000). The reason for this decreasing oxygen demand is the decreasing bioavailability of the hydrocarbon substrate because the concentration of easily biodegradable substrates is decreasing, and leaving a higher percentage of substrates that are difficult to degrade, which slows the metabolism of hydrocarbon degrading organisms and decreases their overall need for oxygen.

The highest amounts of total CO$_2$ produced correlated to when the temperatures were highest. Increasing temperature increases the availability of hydrocarbons by lowering their viscosity, which may account for higher CO$_2$ production. At low temperatures, the viscosity of the oil increases, the volatilization of toxic short-chain alkanes is reduced, and their water solubility is decreased, all of which contribute to delaying the onset of biodegradation (Leahy et al., 1990). In addition, microbial growth rates are a function of temperature (Gibb, Chu, Wong & Goddman, 2001), and rates of degradation decrease with decreasing temperature. This is a result primarily of decreased rates of enzymatic activity at low temperature (Leahy et al., 1990). Higher temperature increases the rate of hydrocarbon metabolism to a maximum, typically in the range of 30 to 40 °C, depending on the thermal stability of the hydrocarbon degrading enzymes involved.

Biotreatment is limited by soil water content (Baker et al, 1994). The findings of these experiments indicate that microbial activity tended to slow when soil volumetric water content was estimated to be less than 20 percent and presumably the reactions slowed. Conversely, when water content approached 70 percent capacity CO$_2$ evolution slowed considerably due to high saturation and decreased oxygen availability and increased as the soil dried.
6 Pilot Study Program

The second element of the treatability study was to use the information obtained in the bench study to scale up into the construction and operation of a field demonstration pilot study. The pilot study pragmatically demonstrated the efficiency of biopile soil remediation and its potential for a permanent treatment facility for use in the RPA. While the results of the bench study were encouraging, a pilot study was considered as the next step in ensuring that remediation was possible, economical and realistic in large scale.

To use an ex situ remediation approach such as biopiling, one must remove the contaminated soil from its original location and treat it above ground. Pilot scale testing provides a larger scale method for evaluating the effectiveness of a technology as applied to given soil conditions, and provides a close approximation to full scale operations. The increase in scale and complexity associated with a pilot scale study increases the overall cost of the treatability study, but decreases the uncertainty involved in the selection and design of the biopile treatment (Van Fahnestock et al., 1998). The pilot scale study explores a narrowed range of operating conditions that have been defined by the bench study. Field plots are designed to use techniques and equipment that are similar to those that are envisioned for full scale remediation, and as such they can model many of the issues expected for full scale implementation, such as material handling, system optimization and adjustments, and the employment of real time, ongoing analysis (USEPA, 1993). The performance of the treatment process can be monitored and unsuccessful processes, or the pilot in totality, may be altered with low environmental risk since the treatment pile remains above ground, protected from leaching, and is easily accessible to alternate remediation techniques. The biopile pilot treatment process utilizes commercially available blowers, leachate pumps, moisture probes, thermocouple temperature probes, and real time soil gas monitoring equipment to provide a mature and effective technology base for the operation and monitoring of the biopile (EA, 2002).

6.1 Transitioning from Bench-level to Full-scale Design

Systems at the bench level are relatively simple by design, whereas systems occurring in the field can be increasingly complex. At the bench scale individual parameters were controlled so that their relative impacts on the overall bioremediation process could be measured. A prepared, homogenized soil and single type of contaminant were used for the soil pan experiments, which were run in order to gather
information on the hydrocarbon degradation processes that could be applied to a full-scale site remediation design. However, field sites consist of heterogeneous soil and a mixture of contaminants, either of which may alter the observed degradation rates. Bioremediation laboratory studies are dominated by systematic approach and optimized process conditions; in the field, a more empirical approach is taken to soil preparation and supplying optimum concentrations of nutrients, moisture (both precipitation and supplied), and air (USEPA, 1993). Dibble and Bartha (1979), conducted laboratory biotreatment studies in order to optimize the degradation of oil sludge, and while they arrived at a number of optimal factors to promote effective hydrocarbon degradation, they also concluded that while laboratory results can be helpful in designing field processes, lab results may not adequately represent field conditions due to limitations in parameters that could not be tested in the lab. The function and performance of a biopile are affected by interacting physical and biological processes: transport of oxygen, moisture and heat due to airflow and diffusion, consumption of oxygen and water by microorganisms and heat generated by bioreactions (Li et al., 2003; Hejazi & Husain, 2004). Monitoring of all the parameters on an ongoing basis is critical because changes in one, such as increasing the oxygen supply by enhanced airflow through the biopile can also increase the loss of water and heat.

6.2 Methodology

The experimental bench study allowed the deduction of information and limitations from the soil pan experiments, delivered an indication of hydrocarbon degradability and allowed the estimation of residual concentrations after remediation using different augments and stimulants. In general, the simple adjustment of nutrient levels had the most favorable results in terms of hydrocarbon degradation. The goal for the pilot study was to match the bench scale conditions that were considered preferential for expedited hydrocarbon treatment, although it was recognized that the evaluation of hydrocarbon biodegradation under field conditions may be inherently more difficult than in laboratory studies due to factors such as variable temperatures and precipitation events (Atlas, 1991).

The success of the pilot study was evaluated based on three main objectives: to demonstrate a) the application of biopile as a viable cost-effective process to remediate contaminated sites, b) the ability of the remediation process to degrade typical hydrocarbon contamination, and c) evidence of biological destruction of petroleum from the contaminated material. Since a major benefit of bioremediation is
hydrocarbon destruction, it is important and significant to demonstrate that biodegradation is occurring. The evidence is expected to come primarily from comparison of the biopile material and soils analysis taken before, during and after the material is subjected to the treatment process, and the demonstration of a relatively simple and trouble-free operation (Quinn & Reinhart 1997). A critical factor is that the system will function with little or no down time and provide operating conditions that minimize fugitive air emissions and maximize biodegradation rates.

### 6.2.1 Pilot Test Construct

During the initial recalcitrant soil removal program, an approximate 2500 square meter area of the subject site, in close proximity to the excavation area, was leveled. On this leveled area berms were constructed to define the edges of the biopile cell that would be used for the pilot study.

![Schematic of the biopile pilot system.](image)

*Figure 9.* Schematic of the biopile pilot system.

Clean, sandy soil obtained from the site itself was employed for berm construction. The berms were built up to a level one meter above ground surface and sloped to form solid berms and drainage to a corner of
the cell that would act as an internal sump area (designated as the liquid holding sump in Figure 9). The berms were covered with a perforated geotextile to prevent deformation during biopile operations. On top of the base structure an impermeable, 20 millimeter thick, reinforced polyethylene liner was placed into the cell and over the berms and anchored using site material. The outside measurements of the cell were 15 meters wide by 20 meters in length, forming an operational area of approximately 175 square meters in the biopile cell, which was estimated to contain 382 cubic meters of soil once loaded. A schematic of the biopile cell is provided in Figure 9.

On the base of the constructed biocell, a 30 meter length of continuous 300 millimeter diameter perforated aeration pipe was installed directly over the base of the cell in a concentric pattern. Although normally multiple layers of aeration pipe are necessary to adequately aerate less porous soil media; the course sand nature of the soil in the RPA permitted a single layer on the cell base to suffice, as the air flows upwards and through the pile (Figure 10). The aeration pipes are perforated every 10 cm, and the entire pipe was covered with geotextile fabric to prevent soil from plugging the pipe. The aeration pipe was coupled to a non-perforated header pipe.

![Figure 10. Pilot study biopile construction, loading prepared soil over aeration pipe.](image)

A non-perforated connector pipe was laid over the berm of the biocell, and was directly connected to a 2 horsepower explosion-proof blower with a manufacturer stated air flow rate of 100 cubic feet per minute,
and set by timer to operate 16 hours daily to approximately imitate the soil pan study. This blower was situated outside the back berm of the biopile cell in a prefabricated building, which also contained the water recirculation pump (see figure 9). The pump was operated on a timer to recirculate the liquid collecting in the sump area back onto and through the biopile. The pump was connected to the sump by an above ground hose set into the sump area, and installed with a one way check valve at the suction point to maintain liquid head when the sump liquid was not recirculating through the biopile. A continuous drip irrigation rubber hose attached to the feed line (post pump) was placed on the upper surface of the biopile which fed liquid from the pump onto the pile twice daily for one hour daily. Based upon a pre operation flow test roughly 250 litres of water was introduced to the biopile during each watering.

6.2.2 Biopile Soil Preparation

During the recalcitrant excavation program 400 cubic meters of soil was retrieved with a backhoe from the freshly exposed surface of the excavation zone and stockpiled, as previously described in section 5.3, herein. The stockpiled soil was thoroughly mixed with the backhoe for one hour and placed within the cell with the backhoe directly over the aeration pipe (Figure 10).

The pile was shaped to approximate a windrow shape that was flat on the top surface and sloped rather sharply toward the bottom of the cell (see Figure 11). The soil in the biopile was left to normalize over the winter, and based upon preliminary results of the soil pan study was prepared in the spring for pilot operations. A small pile (3 m³) of soil was piled beside the biopile structure on a plastic liner, which was intended to be used as an untreated, unaugmented control.

The pilot biopile was roughly blended within the cell with 4400 kilograms of a dry commercial grade, pelletized fertilizer obtained from a local supplier with a carbon: nitrogen: phosphorous ratio of 100:15:1, which corresponded to optimal nutrient ratios determined in the bench scale soil pan studies (Section 5.4.3.2). No additional fertilizer was added during the pilot study as it was considered that any solubilized fertilizer that may have been washed through the pile would be reintroduced to the pile through the sump and its associated pump recirculating any collected leachate to the top of the biopile. Similarly, the high concentration of hydrocarbon-degrading bacteria and fungi in the leachate would serve as a continuous source of inoculum for the biopile as the leachate liquid was recirculated.
Three soil gas monitoring points were installed within the pile. Each monitoring point was constructed from 25 millimeter diameter solid polyvinyl chloride pipe fused to a 0.50 meter perforated section and placed on the bottom of the pipe. The perforated sections were covered by geotextile and the constructed device was driven to a depth of 1.5 meters off the base of the pile. Monitoring points were installed at three locations in order to detect any differences that may have occurred across the pile structure; these locations were at the near center of the pile, at the edge of the top of the pile, and at the pile side. At day 90 of the pilot study, the soil in the biopile was turned with a backhoe. This procedure is common practice in biopiles, and is thought both to improve the aeration, and to decrease the heterogeneity of the pile (Hejazi & Husain, 2004).

### 6.3 Biopile Monitoring

An ongoing monitoring program is an essential component of a pilot study program. Monitoring is used to assess degradation rates, and to determine if either system design or operational changes are necessary. The same real time analytical equipment used during the bench study was also used during the biopile pilot study, although both the temperature probe (extension thermocouple) and the CO₂ meter (moisture trap) were slightly modified for use under field conditions.
As suggested by Leeson & Hinchee (1997), in situ respiration tests can be an appropriate pre-testing and monitoring tool. Soil gas sampling establishes the effectiveness of the aeration system, and can be used to establish the microbial activity via a respiration test as the O\textsubscript{2} and CO\textsubscript{2} concentration profiles of the soil gas at different monitoring points can be a good indicator of aeration and degradation effectiveness (von Fahnestock et al., 1998). Soil gas samples were taken over the six month term of the pilot study by collecting gas samples from the monitoring points installed during the biopile construction, as described. Soil gas readings for oxygen, carbon dioxide, volatile hydrocarbons and air flow were taken, sampled directly through the soil gas detectors.

In order to expedite the soil gas collection process, a portable vacuum pump was attached to the monitoring point and allowed to pull air through the pump and the exhaust from the pump was used for analysis. The portable vacuum pump was attached to the quick connect and the soil gas was evacuated at approximately 5 liters per minute (L/min) until the oxygen readings stabilized, indicating that the readings are monitoring soil gasses within the biopile rather than well gases that have collected in the monitoring tubes. Next the monitoring meters were attached to a side stream of the vacuum pump, and measurements of O\textsubscript{2} and CO\textsubscript{2} (and occasional hydrocarbon vapour) were taken. Moisture monitoring was accomplished through the use of an Aquaterr\textsuperscript{tm} portable moisture probe, which allowed the measurement of soil moisture in situ by capacitance. In this fashion, it was possible to probe different parts of the biopile and ascertain moisture levels across all areas of the pile during treatment, which aided in optimizing irrigation hose coverage over the course of the experiment.

Composite samples were used to follow the hydrocarbon levels in the pile. To prepare the composite sample, the pile was first divided into four equal quadrants. In each quadrant, ten randomized locations and depths were sampled (1 liter each) and mixed to create a composite soil sample. The four composite quadrant samples were then combined into a single composite sample prior to on site analysis by emulsion turbidimetry methods (PetroFlag) or off site analysis by Agat Laboratories. Composite sampling was chosen because compositing reduces the variability in contaminant concentration, and provides accurate data before and after treatment (USEPA, 1993).

A direct measure of airflow through the biopile was accomplished by attaching a low flow rotameter directly to the installed monitoring points with a flex fitting and the flow adjusted appropriately at
the header to supply air at a rate of approximately 0.005 m³/minute; similar to the bench scale study. Air flow rates through the biopile measured with the rotameter remained relatively consistent over the course of the study although variance was noted immediately following irrigation. Generally, airflow decreased during increased moisture conditions and tended to slowly increase as the pile dried.

6.3.1 Carbon Dioxide Respiration

CO₂ evolution has often been used as indicator of bacterial respiration rate because carbon dioxide is a product of the bioremediation process (Kodres, 1997). Similar to the results observed in the nutrient-adjusted soil pan tests, the pilot biopile study displayed a pattern of adaption and acclimation periods, a period of maximum degradation and a period of decaying rates of degradation (Figure 12). CO₂ production rates measured by respirometry during the pilot study showed significant, albeit occasionally sporadic, CO₂ production.

CO₂ levels prior to nutrient stimulation were noted to occur at an average 280 ppm; this low level may be indicative of negligible hydrocarbon degradation occurring prior to system start up. These results also correlate with soil pan bench results that indicated hydrocarbon degradation in the control experiment without nutrient addition was negligible (see figure 6). However it should be noted that the microbial activity in the pre-operational biopile was impeded since it was not actively irrigated or supplied with air flow through the pile over the winter. It is probable that the low levels of degradation observed prior to start up were a result of the addition of oxygen from the mixing and placement of the soil, and moisture provided by natural precipitation events allowing the observed low level of hydrocarbon degradation (Yeung, Johnson & Xu, 1997).

Once initiated (day 0), CO₂ levels remained at less than 2000 ppm up to day 6 (see Figure 12). This was part of the adaption phase of growth for the microbes within the biopile. The length of the adaption phase will depend on the previous growth conditions of indigenous microbial population (Baker and Herson, 1994). Following the adaption phase, a period of increased cellular activity occurs as shown by the respectively elevated CO₂ concentrations observed on days 30-35 (see Figure 12). This activity is considered part of the acclimation phase where for a period of approximately 30 days, there are occasional releases of CO₂ followed by a period of relatively slow of CO₂ production until day 35. During
this phase, the microorganisms are placed in direct contact with the hydrocarbons, in a favorable environment; acclimation to these compounds may be occurring (Aelion, Dobbins & Pfaender 1989).

![Diagram of Pilot Biopile Carbon Dioxide Off Gas and Oxygen Concentrations versus Time]

*Figure 12.* Pilot biopile carbon dioxide off gas and oxygen concentrations versus time.

Different phenomena have been proposed to explain the acclimation phase. Wiggings, Jones & Alexander (1987) suggested that the acclimation phase involves a selection and a multiplication of specialized microorganisms and a physiological transformation in the metabolic systems of the microorganisms. In aerobic microbial communities, the acclimation periods typically range from several hours to several days (Wiggings et al., 1987). According to King, Long & Sheldon (1992), the longer a hydrocarbon has been in contact with a microbial population, the better acclimated that population will be to that hydrocarbon. A noticeable characteristic of the acclimation period of the pilot biopile is that its timing and length is similar to the nutrient-stimulated bench pan experiments indicative of internal consistency and further, that the use of indigenous organisms in the degradation process is independent of volume (refer to Figure 3).
After day 35, a period of significant CO₂ evolution is noted. This period extended over the next 30 days and was attributed to the microbes being in their exponential phase of growth. It is during the exponential phase that the microbial population is increasing at its maximal rate, so the population size will double as a function of the generation time, and the increasing CO₂ levels are a result of the increased microbial activity (Baker & Herson, 1994). As microbial numbers increase, eventually the rate of growth of the microbial population will slow due to the exhaustion of the available nutrients (including the carbon source), or the accumulation of inhibitory byproducts. This is a quasi-stationary state where the microbial population growth is approximately matched by the death rate of the organisms. It is considered that this phase occurred from day 45 to day 60 (Figure 12).

At day 90, the biopile was mixed. It is noted that for 5 days following the mixing, CO₂ levels continued to decrease. This secondary lag phase is followed by an increased rate of CO₂ production over the next 40 days (Figure 12). This renewed microbial activity and hydrocarbon degradation is likely a result of the redistribution of non-degraded hydrocarbons, remaining microbes and fertilizer and a reduction in pile density. Therefore, mixing is a vital operational consideration with respect to full scale operations, in that the physical turning of the pile appeared to result in additional treatment occurring.

6.3.2 Oxygen

O₂ levels were monitored in conjunction with the CO₂ levels employing sampling methods described in Section 6.2. The excavation and mixing of the source soil during the construction and loading of the biocell caused the soil to become highly aerated. An oxygen reading taken from the mid pile area directly after pile construction indicated oxygen levels near 20.5 percent (Figure 12). However, once hydrocarbon degradation was initiated, the high oxygen demand in the contaminated soil quite rapidly decreased the oxygen concentration in the biopile. An oxygen reading taken two weeks after construction of the biopile (before nutrient addition, aeration and watering operations commenced) showed O₂ levels were below 20 percent.

Without aeration, the oxygen concentration in a biopile may not be sufficient to support aerobic degradation of petroleum hydrocarbons (Van De Steene, Van Vooren & Verplancke, 2006). For approximately the first 6 days after turning on the aeration system, the oxygen levels decreased slightly, coinciding with the small increase in CO₂ concentrations during the acclimation phase. During
biodegradation, as expected the O$_2$ concentrations in the biopile decreased when increased CO$_2$ production (increased cellular respiration and oxygen demand) occurred with some inherent mechanistic delay. Although there seems to be a general correlation between O$_2$ and CO$_2$ levels and their relationship to degradation rates, a direct relationship is not considered applicable as it has been shown that aerobic mineralization is only inhibited at very low oxygen concentrations (Hurst et al. 1996). Previous authors have found a definitive decrease in oxygen consumption over the course of bioremediation (Scow & Hutson 1992; Patterson, Trefry, Simonsson, Davis & Briegel, 1999). The reason for the decreasing biological activity and oxygen demand noted by these authors is the declining bioavailability of the substrate, due to a net reduction in concentration of the easily biodegradable substrates, and a relative increase in the substrates that are more difficult to degrade.

### 6.3.3 Temperature

Bacterial growth rate is also a function of temperature. Soil microbial activity has been shown to significantly decrease at temperatures below 10 degrees Celsius, while maximum bioreaction rates are achieved when the temperature is between 20 and 30 degrees Celsius (Atlas, 1981). Biopiles are constructed and operated to remain within this temperature range. Solar radiation and changes in air temperature will create temperature gradients within the pile that will induce natural convection currents of the air through the pile (Seely, Falfa & Hunt, 1994). In addition, because many bioreactions are exothermic, the microbial activity also contributes heat to the biopile. Temperature affects flow properties such as viscosity, capillary pressure and relative permeabilities (Davis, 1994).

Because soil temperature varies with ambient temperature, there will be certain periods during the year when bacterial growth and, therefore, hydrocarbon degradation will diminish due to low temperatures. When ambient temperatures return to the optimal growth range, bacterial activity will be gradually restored (USEPA, 2008). This is an important consideration for the use of outdoor biopile techniques in the RPA as the seasons move towards winter. The biopile temperatures at 1.5 meter depth average are given as a function of time in Figure 12. The temperature differences in the biopile increased generally with time during what would be considered the active treatment (see Figure 13, day 35 to 45), with a general decrease noted towards the last months of operation (day 140-180). At the start of bioremediation, the biopile internal temperature was 19.5 °C, equal to the ambient air temperature during
pilling and normalization of the soil. Temperatures within the biopile varied over time and with depth ranging between 15.1 and 26.6 Celsius with an average of 21.6 Celsius. In general, more consistent temperature conditions occurred from a depth of 50 cm downwards into the pile as compared to near surface soil, which will be affected by ambient temperatures.

![Graph](image)

**Figure 13.** Pilot biopile carbon dioxide off gas and temperature versus time.

### 6.3.4 Moisture

Since the effect of soil water on biodegradation is very important (Linn & Doran, 1984; Orchard & Cook, 1983), managing optimal soil water conditions during biopile treatment could improve overall treatment efficiency. Orchard and Cook (1983) reported a direct relationship between soil microbial activity and moisture content in bench scale testing; a decrease in moisture content results in a decrease of microbial activity, and re-wetting causes a large and rapid increase in activity. Previous research has also suggested a linear relationship between microbial CO$_2$ generation and moisture content, independent of soil type, although extreme moisture conditions are unfavorable for microbial growth and metabolism (Leirós, Trasar-Cepeda, Seoane & Gil-Sotres, 1999).
A substantial variation in soil moisture levels between the bench scale and pilot studies is assumed because moisture cannot be as consistently controlled on a large scale. The addition of moisture through recirculation in the biopile is unlikely to be completely uniform, especially when field conditions and precipitation are not uniform over the course of the study. Generally, soil moisture should be maintained between 30 and 80 percent of field capacity during treatment (Dibble & Bartha, 1979). Although soil moisture was variable over the course of the study, a moisture level of 43.63 percent field capacity was nominally maintained throughout the pilot study (Figure 14). It is noted that carbon dioxide fluctuations do not coincide with moisture levels indicating that moisture was not a limiting factor in the biopile experiment.

**Figure 14.** Pilot biopile carbon dioxide off gas and field capacity moisture versus time.

### 6.4 Pilot Study Results and Discussion

Biological processes have been used successfully to remediate soil contaminated with petroleum hydrocarbons; such processes can effectively remove the petroleum hydrocarbons and shorten the remediation period as compared with natural attenuation. Degradation of organic pollutants can be
Biopile Soil Treatment in the Redwater Oil Production Area

enhanced by improving the limiting factors to promote the enzymatic degradation capacity of the indigenous microbial community in a biopile scenario. Sims, J., Sims, R. & Matthews (1989) summarized the critical factors affecting in situ biodegradation as: soil water, oxygen, pH, nutrients status, and temperature. The biopile pilot treatment investigation of RPA specific soil has shown that a properly engineered system can help ameliorate hydrocarbon contamination under controlled conditions.

Based on results obtained, biodegradation rates mainly depend on the activity of degrading microorganisms, the bioremediation time period, the concentration and the type of contaminants. Bartha (1986) noted that the composition and inherent biodegradability of petroleum hydrocarbons is the first and most important consideration when the suitability of a biodegradative cleanup approach is to be evaluated. Hydrocarbons can be rapidly and extensively biodegraded if favorable conditions prevail.

6.4.1 Hydrocarbon Degradation

The pilot study displayed a distinct decline in the hydrocarbon concentrations over the course of the experiment. Total petroleum hydrocarbon levels were monitored by employing emulsion turbidimetry (PetroFlag), which showed a generally consistent reduction of hydrocarbon concentrations over the course of the study period (Figure 15). The reader is reminded that the pre treatment soil displayed a cumulative hydrocarbon value of 2300 mg kg\(^{-1}\) dw (see Table 3). The final field hydrocarbon analysis, completed at the 200 day mark of experiment, indicated a TPH value of slightly over 200 mg kg\(^{-1}\) dw, although at contamination levels below 250 mg kg\(^{-1}\) dw the PetroFlag method becomes less accurate (USEPA, 1997).

In order to establish the strength of the association between time and hydrocarbon degradation, linear trend correlation and regression statistical analysis were performed on the results (see Figure 15). In this instance the relationship between two sets of data (x and y) is linear, and when the data is plotted the result is a straight line thus having a linear correlation and following the equation of a straight line. The calculated correlation coefficient, \(R^2\) which gives a measure of the reliability of the linear relationship between the x and y values is noted to be 0.9672 which is indicative of suitable linear reliability and the predictions based on the linear relationship is deemed reliable and that the variability in the system is accounted for by the relationship between time and hydrocarbon concentration.
As previously described, a small pile (3 m³) of soil was piled on a plastic tarp beside the biopile structure to be used as an untreated control. A composited sample of this soil displayed collected at 200 days displayed a reduction of 39.23 percent compared to the pretreatment sample with a hydrocarbon level at 1410 mg kg⁻¹ dw, (see Appendix B3) which indicates that native microorganisms can indeed degrade the hydrocarbon contaminant, but at comparatively low efficiency without nutrient amendments and controlled conditions of the active biopile TPH value of slightly over 200 mg kg⁻¹ dw. This is a positive indication that native microorganisms are viable at this location and that through the provision of effective process application and nutrient supplements that exemplary bioremedial results are possible. It is noted with interest that this result exceeded the reduction of Run 1 (control) in the pan study at 22.61 percent reduction and further exhibits the apparent advantages of the natural environment setting in biopile treatment.

\[ y = -12.631x + 2429.1 \]
\[ R^2 = 0.9672 \]

*Figure 15. Pilot biopile carbon dioxide and total petroleum hydrocarbon concentrations versus time.*
The third party laboratory analysis of the treated soil by GC-FID indicated hydrocarbon levels below method detection levels (see Appendix B1) of all petroleum hydrocarbon fractions 1 through 4, results which are below the applicable Alberta Tier I criteria for coarse soil (AENV, 2009). While this is an encouraging result that is indicative of successful remediation, and in approximate correlation with field analysis as described, it was considered probable that physical or partitioning processes may also have contributed to the dramatic decline in hydrocarbon levels in the biopile. In the bench studies it was supposed that hydrocarbon/soil bonds had been weakened as part of the biodegradation process, and thus the hydrocarbons were more easily mobilized within the soil matrix by either through gravity or partitioning occurring during moisture addition episodes, thus relocating a portion of the hydrocarbons to near the base of soil pan. Pollard et al. (2007) found that during biopile treatment that soil partitioning will often occur. Pollard’s group also reinforced the importance of accounting for this behaviour of both non-aqueous phase liquids and soil phases during biopile remediation (Pollard et al. 2007). In order to determine if the same phenomena had occurred in the pilot experiment, the soil pile was disassembled.

The upper 2.5 meters of soil in the biopile was removed by backhoe and placed outside of the cell to be used for eventual soil replacement in the former tank farm area. The soil throughout the upper zone appeared very clean and no hydrocarbon odour was noted. The soil below this level (i.e. 2.5 meters below surface) became increasingly moist, odorous and darker colored. The soil at this level was essentially below the cell maintenance water level. A composite sample was retrieved from this area of the biopile and was analyzed by field analysis and a third party laboratory which indicate hydrocarbon contamination of 1260 mg kg\(^{-1}\) dw (see Appendix B2). This suggests that the physical and partitioning process of leaching was occurring within the pile by gravity/leaching or that incomplete degradation may be occurring due to the restricted air flow paths in the lower, often below the liquid levels of the cell. A comparison with pre treatment hydrocarbon components indicates that fractions were reduced in concentrations by approximately 50 percent across the entire carbon spectrum (C\(_{10}\) to C\(_{60}\)) indicative of incomplete degradation (see Appendix A1 and B2, respectively). Under full-scale operational conditions, the pile is normally allowed to dry or at least drain in order that the entire cell is able to aerate sufficiently; however, in this pilot study the liquid level in the biopile was maintained to prevent pump cavitation, and the air passed through the liquid within the cell before it passed upwards and through the soil.
6.4.2 Estimation of Hydrocarbon Degradation Rates

It is useful to be able to translate observed CO$_2$ production levels to a level of hydrocarbon biodegradation. If increased levels of CO$_2$ production are considered to be approximately proportional to microbial respiration rates, then hydrocarbon degradation may be estimated by CO$_2$ production. The amount of hydrocarbon degraded from the soil pile was calculated from the amount of carbon dioxide evolved. For simplification, these calculations assume that all biodegraded hydrocarbons had the same molecular weight to carbon atom ratio (12:1) and that all CO$_2$ evolved was due to hydrocarbon degradation. Deviations from this assumption are considered relatively minor because the ratio of molecular weight to carbon atoms does not vary substantially for the compounds of interest. Using the generalized equation previously presented by Van Hamme et al. (2003), 44 grams of CO$_2$ would be produced for every 14 grams of hydrocarbon degraded in the biopile (see equation 2 in Section 5.4.1). These estimates are approximate and assume zero order degradation kinetics as the hydrocarbon is present in great excess and thus the rate of degradation is independent of the concentration of the reactant(s) and increasing the concentration of the reacting species will not speed up the rate of the reaction. Actual degradation rates are likely to be first order which will result in a decrease in hydrocarbon biodegradation over time as the TPH concentration decreases (Alexander, 1999), and as evidenced by the general decrease in CO$_2$ evolvement over time seen in the pilot study. Although differences between petroleum hydrocarbon degradation levels calculated from respirometric data and actual change in petroleum hydrocarbon concentration have been observed by others (Møller, Winther, Lund, Kirkebjerg & Westermann 1996; Jørgensen et al. 2000), the estimated reductions based on respirometric data are valuable in determining full scale biopile degradation capability for the RPA soils.

6.5 Treatability Program Summary

The bioremediation of hydrocarbon contaminated soil in the RPA by means of an engineered biopile system employing indigenous bacteria under optimized conditions, has clearly shown to be amenable. This study suggests that sufficient nutrients and controlled system processes enhanced biodegradation and minimized volatilization. Suitable contaminated soil preparation coupled with easily manipulated process variables such as aeration, nutrients and moisture can lead to efficient degradation. Other augments and stimulants selected for the bench scale study displayed less favourable results. The
results of the bench and pilot studies showed significant hydrocarbon reduction and thus confirm that biopile treatment of hydrocarbon contaminated soil is possible in technical terms.

Historically, the generation of remedial data has been an iterative process to the point where investigation work has often became the goal itself; unambiguous full characterization of a site as the ultimate goal. Performing a full treatability study for each site in the RPA should not be necessary, if results can be extrapolated from studies like this one on similar soils with similar contaminants and concentrations as is typical, albeit not universal, in the RPA. Little or no testing would be required when considering biopile treatment for the same type of sandy soils contaminated with low to moderate concentrations of light hydrocarbons (von Fahnestock et al., 1998). A simple microcosm flask or soil pan experiment should be considered to rapidly ascertain favourable biological conditions.

This study should give sufficient confidence to allow design of the biopile treatment option, with each project adding to the information base, and the process becoming more refined over time. A modicum of pretreatment analysis will be required to ensure non-toxic conditions for the indigenous microbes at each location considered for remediation, but field screening methods, combined with historical information from previous studies including herein, will be sufficient to confidently proceed with full-scale biopile treatment options in the RPA. Field screening techniques and operational respiration information will expedite the level of understanding of a contamination problem in a more economical fashion, not to replace quantitative analysis per say, but to spend monies expeditiously where needed.
7 Permanent Biopile Considerations and Design

The ultimate objective of remedial operations is to eliminate the risks to man and the environment, to prevent the dispersion of pollution, and to restore multifunctionality to the site in the shortest possible time. The current environmental standing of the RPA has effectively forced a decision to undertake remediation of the contaminated soil, due to political, corporate and economic influences; the question then becomes how best to remediate. It is safe to say that cost is one of the most important factors in site clean-up decision making. A basic rule of remediation is to maximize the contaminant mass removed for the money spent. Evaluation of the economics of a clean-up project is directly linked to the objectives of the site owner, and the constraints within which the remediation is to be performed, be they economic, technical or logistical. Once the site objectives and limitations have been clearly identified, a range of possible remedial approaches and technologies can be developed, and each option can be evaluated on a comparative basis. One of the most powerful tools for comparative options analysis is technical-economic analysis. This is an approach that combines the evaluation of technical feasibility and effect, with the consideration of capital, operational and maintenance costs over a selected time horizon. By constraining remedial alternatives within cost and time boundaries, possible solutions can be evaluated with respect to specific criteria (Hardisty, Bracken & Knight, 1998).

This chapter briefly outlines the planning and design processes that were undertaken in the construction of the Redwater Treatment Facility (RWTF). Based on the knowledge from the bench and pilot scale studies that contaminated soil treatment by bioremedial techniques was plausible and economical, it was determined to proceed with the construction of a full-scale treatment facility.

Soil remediation is a rapidly developing field which is currently seeing shifts in technology from radical, hard solutions such as excavation or pump-and-treat, to biological techniques, such as biopiling, which exploit natural attenuation phenomena (Walter, 1999). Extensive data on the site characteristics and the historical operations has been collected in the RPA, and a selection of treatment and management alternatives have been evaluated to identify a preferred remedial approach. Biopile remediation has been selected as the primary remedial technology from these alternatives for both technical and economic justifications. Simply put, the biopile method is cheaper, needs little expensive high-tech machinery, is non-labor intensive, and will work effectively in the RPA. The construction and
operation of a permanent biopile facility will significantly increase treatment capabilities over single site projects and result in a true recycling initiative for contaminated soil. However, cost issues are still a major constraint to remediation, and often projects have become economically unfeasible if careful planning, implementation and operations are not strictly adhered to. A critical path component of the analysis was a realization that the project would involve both construction costs that are expended at the beginning of a project (e.g. capital costs), and costs in subsequent years that are required to implement and maintain the facility after the initial construction period, such as operations and maintenance costs or ongoing treatment costs.

Once verified that biopile remediation had the potential to be effective, an evaluation of the design of the biopile system and an action plan was forwarded to the proponent that included a discussion of the rationale for the design, a conceptual engineering biopile design and a cost benefit analysis specific to hydrocarbon contaminants of the RPA.

7.1 The Business Case

Combining remediation strategies with business decisions can, when the circumstances are appropriate, provide additional opportunities for significant savings in total remedial cost, the effort required securing permits, or time required to complete the project. The greatest cost and time savings are realized when remediation, land use/reuse, and business factors can be aligned (USEPA, 1999). In the RPA, such a business strategy approach to remedial efforts is the objective of the proponent, and this approach is expected to result in significant savings in total time and costs.

Through effective management, work at RPA sites can proceed seamlessly from investigation to remediation and closeout. With careful advance planning and the use of rapid turnaround on-site analytical technologies, the investigation and cleanup objectives can be achieved in a fraction of the time (and thus at a lower cost) as compared to traditional approaches which rely on a narrow, linear development of phases and tasks. Opportunities for off-site remedial treatment at fixed treatment facilities are ideal because the process of obtaining permits is simplified if the waste materials are treated at one location. In addition, a fixed facility can draw from a larger area and operate more efficiently than a mobile facility, thereby offering its customers a unit cost reduction borne from the economics of scale. Considerable time savings can be realized by reducing the number of mobilizations to the field; by
performing multiple tasks simultaneously; and by taking advantage of economies of scale by emphasizing ways to address multiple sites simultaneously (Interstate Technology & Regulatory Council [ITRC], 2004).

Remediation business ventures are most promising in geographical areas where there has been considerable past industrial activity, so that large quantities of contaminated materials requiring remediation are likely to be present. Due to the proximity of field locations with respect to each other and the large quantities of hydrocarbon contaminated soil present in the RPA, a centralized treatment facility is a reasonable venture. As an example, in 2008 soil transport from the RPA, typically costing $40 to $50 per tonne and significant GHG production is dramatically reduced as soil relocation is reduced to a few minutes in the RPA as opposed to a minimum of 3 hour return trips to a landfill in Edmonton (RemedX, 2008).

Additional savings will be achieved by coordinating site investigation and remediation activities for multiple sites located relatively close together. Mobilization costs will be reduced by conducting sampling sequentially at sites and by purchasing remedial materials in bulk (ITRC, 2004). When the preferred remedial alternative is the same for multiple sites, and especially in situations where the sites are located near one another, treatment costs will be reduced by staging treatment processes for multiple sites. Savings result from reduced transportation costs and lower unit costs for treating larger volumes of material than would be generated by a single site.

Recognizing these factors, the proponent has proceeded with the construction of a permanent soil remediation facility, which was permitted, built and began operations in late 2008. The design of the Redwater Treatment Facility (RWTF) was based on a 20,000 tonne annual throughput model, with a twenty year active life. Although full cost analysis accounting cannot be completed until the facility is fully operational and soil is being actively treated (Spring, 2009) and recycled, it is reasonable to predict that the cost ¹ to treat and recycle hydrocarbon contaminated soil will be substantially less than soil excavation and replacement, particularly since it is anticipated that transport and disposal prices will continue to increase as landfill space becomes scarce in the RPA.

¹ Actual costs are not published at the request of the operating company due to internal and external price contracts and agreements.
The success of a project such as the RWTF will often hinge on the various regulatory agencies' willingness to consider such ventures. Since there was a local need for redevelopment of several contaminated sites, the area’s long-term cleanup needs were used as a logical argument to support the RWTF plan. Public and government perception of biological treatment processes is generally positive, and the inherent advantage over competing technologies is that the harmful constituents are no longer present in the soil at elevated concentrations after treatment. Public open houses were favourably attended and little resistance to the facility was encountered.

Table 4

<table>
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<tr>
<th>Redwater Treatment Facility Planning, Design and Construction Requirements</th>
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<tr>
<td>Planning Initiative</td>
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<td>Feasibility Planning and Site Selection</td>
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<td>Regulatory Permits/Public Meetings/Traffic Impact Study</td>
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<td>Facility Construction</td>
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<td>Process Commissioning and Commence Operations</td>
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As the RWTF is being employed solely for the purposes of the remediation of oil and gas contaminated materials, the site was licensed with the Alberta Energy Resources Conservation Board, although local and county regulatory bodies were kept apprised of the project, as development and road use permits were necessary. The entire planning and construction process required approximately two years to complete. A number of initiatives, as outlined in Table 4, were dovetailed to coincide over the course of planning, construction, and treatability testing (RemedX, 2008).
7.3 Design, Construction and Operations

The design and subsequent construction of the RWTF was expedited in that the proponent owns a substantial amount of suitable land in and around the RPA. Many of these properties are operating oil and gas sites for which power and access have already been established. The site selected for the RWTF is centrally located within the RPA, has an excellent network of access over high grade roadways, has no adjacent private landowners, is relatively level and is suitably disconnected from the upper groundwater bearing zone. The soil conditions at the site, however, were not found to be suitable for construction or groundwater protection purposes because they were composed of sandy-silt, so a source of clean clay fill was found in the town of Redwater where land was being cleared for a new subdivision. Approximately 12,000 m$^3$ of clay soil was transported to the site for use as base grade and side berm materials for biopile construction. The resulting treatment cell has an interior surface area of 10,000 m$^2$.

The treatment cell design at the facility is such that it will allow soil to be treated either in soil pile or landfarm type configurations. The cell design is a basic take off from landfill and pond applications, where a slightly sloped area of land is cleared, compacted and has sidewall berms built to form a “holding” area. Compacted soil berms and the base were constructed at the periphery of the treatment structure and are used for containment (von Fahnestock et al., 1998). As noted, the site subsoil conditions precluded the use of native soil for construction, and thus a manufactured liner system was employed for primary and secondary containment. Manufactured liner materials were placed within the constructed bermed area to provide secure containment. The primary and secondary lining material selected for use at the RWTF is a 40 mm thick, High Density Polyethylene (HDPE). This particular liner was selected for longevity, puncture resistance, chemical resistance to the soils to be treated, UV resistance, ease of installation and repair, elasticity, etc. Aside from the long term reliability of HDPE liner, the material can be cut and fused to fit specific shape requirements, and is relatively easy to repair. A prepared clay bed was placed on top of the liner system (see Figure 16), which protects the primary containment device, allows drainage of liquids to the liner for gravity transfer to the sump area, and provides a trafficable surface for equipment movement.

A continuous layer of engineered, plastic geonet provides lateral flow of interstitial fluids and protection between the two liners (see Figure 16) to an external concrete sump. The structure is sloped
with a bidirectional 2 percent grade to an internal sump. In this fashion, precipitation will be directed to
the sump and the collected liquids can be transferred over the biopile(s) to maintain moisture. The
structure of the treatment area is complemented by a 50 hp aeration blower and header system, a water
recirculation pump system, an over the berm access for transport trucks and equipment, a truck scale, an
office with on site laboratory capabilities, a groundwater monitoring network and security fencing.

Figure 16. Redwater Soil Treatment Facility lining system detail.

An advantage of an aboveground soil pile is that space requirements for soil treatment can be
minimized relative to some other ex-situ treatment methods. For example, in land farm applications where
aeration is achieved by tilling, the optimum treatment zone thickness is limited to approximately 0.3
meters. In contrast, a biopile that employs aeration pipes and blowers can increase the treatment zone
thickness to about 1.2 to 3 meters and the capacity of the cell is easily increased to over 20,000 m³.

In general, the cost to treat a unit volume of soil will decrease as the number of treatment cycles
per cell increases (von Fahnestock et al., 1998). Operational costs are essentially fixed for a consistent
level of contamination. Only routine inspection of the blower unit and the operation of an irrigation system
are required, and time requirements for each activity vary little in relation to treatment system size.
Because a more intensive level of monitoring is usually required during the field demonstration than during
full-scale operations, sampling stations may be spaced less densely; temperature, moisture, and respiration
testing may be performed less frequently; and sampling and analysis for contaminants of concern may be performed on a less frequent, and less regular basis for full-scale operations (USEPA, 2004).

An estimate of the anticipated yearly throughput of the facility is difficult to predict since the treatment of the soil will be dependent upon the type of soil, the contaminants present in the soils to be treated, and on the aggressiveness of the treatment programs initiated, but designs have been nominally based on a 15,000 tonne per year turnaround. The processing time per cycle is expected to be approximately six months, based upon the treatability testing completed herein, during which a monitoring program will be in place to ensure the performance of the remediation is maintained.

![Aerial view of the Redwater Soil Treatment Facility in October 2008.](image)

Monitoring data collected during remediation will be used to demonstrate the progress of the treatment; however, permit compliance will be based on the statistical validation of the analytical data collected (e.g. reduction of contaminant to acceptable levels, rates of CO₂ production, etc.). This data will continue to be collected until the soil meets the Alberta Tier I criteria (AENV, 2009) and has been verified over a specified period of time. Treatment may be continued beyond this point in order to ensure total compliance. Since operations have commenced, approximately 6000 tonnes of soil has been treated and stockpiled (fall 2009). Current plans (September, 2009) are to simultaneously haul contaminated soil to the facility for processing and transport the treated soil back to the excavation site as backfill.
8 Conclusions

In this final chapter, I briefly discuss the technical implications and value assumptions of the treatment of hydrocarbon contaminated soil in the RPA through biopile methods. The purpose of this study was to determine if the comparatively low technology option of biopile remediation was practicable in the RPA. I conclude that this remedial technique not only is feasible, but will allow for a better focus on uncertainty management, and an accelerated evaluation of the relative risks of each decision since each iteration of the excavation/treatment/recycle process will add to the base of knowledge. The primary advantage to these ex situ approaches is the degree of control that can be exerted over the processes being used to manipulate the system; these factors are now manageable when done so in a frame of long term, multi-year remediation and this will encourage strategic planning that will lower project costs, while ensuring that the desired levels of environmental cleanup can be achieved.

Worldwide, the theoretical best practice of the bioremediation approach has been promoted by many regulatory bodies (EA, 2005). Although any number of remedial techniques may be plausible for use in the RPA, the distinct advantages of a biopile arrangement are that it incorporates safe, reliable methods, results in the direct benefit of decontamination of land and water to levels of acceptable risk, and that the conditions can be augmented as necessary to enhance and accelerate degradation. The application of biopiling for hydrocarbon waste treatment has been assisted by a shift towards risk-based, remedial design and technology verification (Dupont, 1993).

While experience significantly aids in the design of a bioremediation project, experience can only be applied within limits. As stated previously, bioremediation is not a panacea; many variables are a function not only of the contaminated media and the contaminants, but also of the genetic variability of the indigenous microbial species. These effects are not subtle, and can determine the success or failure of a bioremediation project. The same contaminant can respond differently to what appears to be identical bioremediation techniques and microorganisms. However, the unique circumstances of the RPA reduce these uncertainties substantially because across much of the RPA a limited number of contaminants in a relatively homogeneous soil matrix ease uncertainty about the performance of biopile treatment. Through the auspicious use of real time measurement methods, uncertainty can be further reduced because an
even clearer picture of remedial potential of a soil can be acquired without the necessity of extensive site characterization at each site within the RPA.

The underlying objective of this study was to provide an uncomplicated, robust process that would include simplified monitoring and control protocols and tangible treatment results. Through the full consideration of existing information developed during past site studies (RemedX, 2008) as well as this specific treatability testing and pilot program, it has been confirmed that biological degradation is a reliable and expedient mechanism for contaminant reduction in the RPA. Systematic planning, backed by the collaborative use of real time monitoring will provide the context to identify and manage factors and issues that contribute to uncertainty.

The approaches outlined in this study adhere to the environmental principles and goals of the proponent, that is, to promote sustainability through soil conservation and remedial initiatives. The goals of biopile remediation in the Redwater Production Area will be to cleanup contaminated soil in a closed, safe fashion, quickly and efficiently. Remediation will result in the indirect benefit of enhancement of the amenity, the ecological status of the area, and in economic activity by removing contamination and encouraging regeneration. Excluding such esoteric principles, the RPA is expected to see tremendous industrial and population growth over the next decades and clean sites will become increasingly valuable to the proponent’s corporate bottom line (Sturgeon County, 2007).

The biopile technique has proven to be an affordable and effective alternative for future remedial activities in the RPA. The proponent has, hopefully with guidance from this study, been able arrive at a suitable technical and economical alternative. I believe this has been manifest in the construction of the Redwater Treatment Facility in 2008. The opportunities for sustainable practices with regards to treatment and recycling initiatives that are possible because the facility exists are truly remarkable.
9 References


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