#### **IN SITU BIOREMEDIATION OF A DIESEL FUEL**

## **SPILL IN NORTHERN MANITOBA**

BY

#### CLARK D. HRYHORUK

A Thesis Submitted to the Faculty of Graduate Studies in Partial Fulfilment of the Requirements for the Degree of

#### MASTER OF SCIENCE

Department of Civil & Geological Engineering University of Manitoba Winnipeg, Manitoba

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#### ABSTRACT

A pilot in situ bioremediation project was conducted at the Flin Flon Airport to evaluate the applicability of this technology in a cold northern climate. The site was contaminated with diesel fuel and confined within the unsaturated zone in silt and silty-sand. A two-phase remediation process was designed and implemented: a ground surface spray system and a pump-cycle system.

Ground surface spraying involved mixing nutrients (ammonium-nitrogen and orthophosphate) with water in a tank and then spraying the mixture on the ground surface above the diesel plume. The pump-cycle system involved pumping groundwater from below the diesel plume into one of two tanks in series. The groundwater underwent both nutrient addition (weekly) and aeration in the tanks; then it was pumped into eight feeder wells which circumscribed an extraction well.

Soil testing revealed that both remediation processes aided in increasing subsurface nutrient concentrations and the moisture content within the diesel plume. Also, high total coliform counts were observed in both the silt and silty-sand layers. Thus implying that conditions for suitable bioremediation can be developed in relatively fine grained soil. Intermittent soil sampling at three locations over a 14 month period revealed that the diesel plume decreased in size by about 30%; contaminant concentrations (diesel fuel) also decreased. Plume movement also occurred. The pump-cycle system remains operational.

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# LIST OF ABBREVIATIONS

BN	- Borehole Number
C:N:P	- Carbon:Nitrogen:Phosphorus
°C	- Degrees Celsius
CFU	- Colony Forming Units
DO	- Dissolved Oxygen
РАН	- Polynuclear Aromatic Hydrocarbons
PID	- Photoionization Detection
ppm	- parts per million
SVE	- Soil Vapour Extraction
TE	- Total Extractable (Petroleum Hydrocarbons
	in the $C_7$ to $C_{30}$ Carbon Range)
TOC	- Total Organic Carbon
TC	- Total Coliform
TPH	- Total Petroleum Hydrocarbons

#### **CHAPTER ONE**

#### INTRODUCTION

This thesis is one of four remediation research projects at the University of Manitoba. This project deals with in situ biological treatment technology. In particular, implementing processes for the purpose of biodegrading diesel fuel at a contaminated site at the Flin Flon Airport (Bakers Narrows). The other three projects deal/dealt with: (1) verifying that gasoline and diesel fuel can be degraded by indigenous microorganisms, (2) the effect surfactants have on hydraulic conductivity, and (3) the effect pore size has on the transport of microorganisms through soil.

Remediation of contaminated sites, in particular hydrocarbon contaminated sites, is a relatively new and rapidly expanding requirement in North America. This is due in part to increased knowledge of the hazards that hydrocarbon contaminated soil and groundwater represent. There are several different in situ and ex situ remediation technologies available. The four most commonly considered are physical, chemical, thermal and biological.

The emphasis of this project was to obtain a better understanding of biological remediation in a cold northern climate. The designs used in this research focused on improving subsurface conditions to make bioremediation possible year round.

Figure 1.0 outlines the flow pattern for the work associated with this research. The preliminary site investigation was conducted independently by Manitoba Hydro. Consent to use these results, and the results of a second, more detailed investigation, was readily granted by Manitoba Hydro's Geotechnical Department. The two remediation systems that were

implemented at the site were a ground surface spray system and a pump-cycle system. The pump-cycle system incorporated feeder wells circumscribing an extraction well, and the system was made to operate in subzero conditions. Reclamation started in July (1992) and continued until September (1993).



Figure 1.0 Research Flow Chart

# **CHAPTER TWO**

## **THESIS OBJECTIVES**

The bioremediation pilot project was undertaken at the Flin Flon Airport with the following objectives in mind: to determine (1) whether microorganisms indigenous to a cold northern site could be stimulated to biodegrade spilled diesel fuel in a reasonable amount of time (one year), (2) whether it was practical to attempt to sustain in situ bioremediation over the winter, and (3) whether diesel fuel could be degraded effectively without the aid of emulsifiers or surfactants.

#### **CHAPTER 3**

#### THEORY

The question most often asked is "what is bioremediation"? Bioremediation or biodegradation means "the process of degradation or remediation is biological". Bioremediation is a process where microorganisms, both bacteria and fungi, biologically oxidize organic compounds (substrate) into carbon dioxide, water and biomass (Autry and Ellis, 1992; Zitrides, 1990; Torpy et al., 1989) (in simpler terms, the decomposition of leaves is a process of bioremediation). Any form of organic substance may be susceptible to biodegradation, and this includes hydrocarbons.

# 3.1 Bioremediation Approaches

There are two different bioremediation approaches: (1) the microbiological approach, and (2) the microbial ecology approach (Golueke and Diaz, 1990; Piotrowski, 1991; Mayer and Hom, 1991).

## 3.1.1 Microbiological Approach

The microbiological approach involves inoculating contaminated soil with specific microorganisms (the so-called "superbugs"). The microorganisms used are either contaminant-specific or site-specific.

The first form, contaminant-specific degraders, are purchased commercially and arrive pre-packaged. The microorganisms are isolated from a contaminated site because of their

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inherent ability to degrade a particular contaminant. The microorganisms are further acclimated to degrade the contaminant at elevated concentrations. The strains having the ability to degrade the contaminant at elevated concentrations are then isolated, cultured in large numbers, and stored for use at other sites having the same contaminant.

The second form are site-specific degraders. Soil samples from the contaminated site are brought to a laboratory and the process of acclimating the microbial population to degrade the site specific contaminants at elevated concentrations begins. Again, strains having the ability to degrade the contaminants at elevated concentrations are isolated, cultured in large numbers, and then re-applied to the site from which they were obtained.

These two forms have the same objective, to use specific microbial strains to increase the rate of contaminant degradation.

# 3.1.2 Microbial Ecology Approach

The microbial ecology approach involves identifying and adjusting various physical and chemical parameters which may impede the rate of degradation by indigenous (site specific) microorganisms. This approach involves neutralizing the effects of Leibig's law of the minimum or Shelford's law of tolerance. According to these laws, the rate of a biological process, such as growth, is limited by the parameter that is furthest from the organisms requirements (e.g. nutrients) or tolerance (such as temperature, pH and so on) (Atlas and Bartha, 1993).

Once the rate limiting parameter is identified and adjusted, the indigenous microorganisms are left to degrade the contaminant. Little attention is given to isolating and

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identifying the degrading microorganisms. However, in most bioremediation systems, more than one parameter requires adjustment before the system is optimized.

#### 3.1.3 Advantages and Disadvantages

Each approach (microbiological and microbial ecology) has advantages and disadvantages over the other. The greatest advantage the microbiological approach has is that the microorganisms are contaminant specific. Therefore, an immediate increase in the rate of contaminant degradation occurs when the microbes are applied to the site. There is no acclimation period or the acclimation period is very short as compared to the microbial ecology approach.

Major disadvantages in using prepackaged microbes include: (1) acclimation is usually done at a higher temperature than the site temperature, this could result in the incorrect microbial temperature group being used in a cold climate (ie. microorganisms from the mesophile group are being used instead of microorganisms from the psychrophile group), (2) microbes may not fare-well under the conditions in which they are being used compared to the indigenous microorganisms, (3) not just one or two species are responsible for completely degrading the contaminants, (4) once nutrients are applied to the site, indigenous microorganisms can fare better because they are used to site conditions, and (5) purchasing or laboratory costs.

### 3.2 Bioremediation Parameters

There is a variety of different parameters that can hinder any bioremediation process.

Not all parameters will be discussed here. Only those parameters most often referred to in the literature dealing with in situ bioremediation will be discussed under the following three headings: physical, chemical and microbiological.

#### **3.2.1** Physical Factors

The physical parameters discussed most often in the literature include:

- \* temperature
- \* hydraulic conductivity and permeability
- \* contaminant type and concentration
- \* stratigraphy, lithology and hydrogeology

Each of these parameters will be discussed individually as to how they are associated with bioremediation.

### 3.2.1.1 Temperature

The average soil temperatures in the United States is about  $10^{\circ}$ C to  $15^{\circ}$ C (King et al., 1992). Depending on the soil depth, time of day, and period of the year, northern Manitoba soil temperatures can range from  $-4^{\circ}$ C to  $+20^{\circ}$ C. When the temperature is near  $15^{\circ}$ C, in situ bioremediation of diesel fuel usually requires six to twelve months.

Temperature has the most profound affect on the rate of microbial growth. Temperature may also effect chemical reactions, but mainly temperature concerns relate to the rate of growth. Usually, an increase in temperature results in an increase in the rate of microbial growth (Henson, 1991), providing the temperature increase is not above the organism's optimum temperature for growth. Figure 3.0 shows biodegradation rates of crude oil at different temperatures using a commercially available adapted bacterial formulation (Polybac Corporation, 1989).

Based on temperature, microorganisms can broadly be distinguished into three groups. The three groups are: psychrophiles, mesophiles and thermophiles. Each group has both a general and optimum temperature range for growth. The general growth range of one group does overlap the general growth range of the adjacent group. The mesophile group is the most predominant degrader of petroleum contaminants and has an optimum growth temperature of 27°C (Song et al., 1990). Lower temperatures will cause lower biodegradation rates, but biodegradation will still occur (Autry and Ellis, 1992). Waste Stream Technology estimates psychrophile microorganisms are about 60 - 70% as efficient as mesophiles (Mayer and Hom, 1991).

## 3.2.1.2 Hydraulic Conductivity and Permeability

In some older texts, hydraulic conductivity and coefficient of permeability are used synonymously. For clarity, the definitions of both hydraulic conductivity and permeability will be given here.

Darcy's law states that, the flow rate of a liquid through porous media is proportional to the head loss, h, and inversely proportional to the length, l, of flow path in one dimensional flow (equation 1) (Todd, 1980). The hydraulic conductivity, K, is the proportionality constant in Darcy's law.

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$$v = -K \frac{dh}{dl} = -K * i \tag{1}$$

where: v = Darcy velocity or specific discharge [L/T]

K = hydraulic conductivity [L/T]

h = length of head loss [L]

l = length of flow path [L]

 $\underline{dh} = i = hydraulic gradient [L/L] dl$ Note: The negative sign indicates the flow of fluid is in the direction of decreasing head.

The value of K is specific to the fluid. Physical factors such as particle size, distribution, shape, and porosity can affect the hydraulic conductivity of a soil or rock (LeGrand and Stringfield, 1971; Rasmussen, 1964).

The permeability of a soil or rock defines its ability to transmit any fluid. Hence, permeability is a property of the medium only and is independent of the fluid properties (Todd, 1980; Freeze and Cherry, 1979). Equation 2 shows the relationship between hydraulic conductivity and permeability.

$$K=k*\rho*\frac{g}{\mu}$$
 (2)

where

k = permeability [L<sup>2</sup>]

 $\rho =$ fluid density [FT<sup>2</sup>/L<sup>4</sup>]

g = acceleration of gravity [L/T<sup>2</sup>]

 $\mu$  = dynamic viscosity [FT/L<sup>2</sup>]

Substituting equation 2 into equation 1 yields:

$$v = -k * \rho * \frac{g}{\mu} \frac{dh}{dl}$$
(3)

The hydraulic conductivity and permeability vary for different rocks and unconsolidated deposits.

Hydraulic conductivity in the range of 10<sup>-4</sup> cm/sec or greater is suitable for in situ bioremediation (Thomas and Ward, 1989). A high hydraulic conductivity will aid in delivering oxygen, moisture (in the vadose zone) and nutrients to the contaminated zone. However, during remediation, chemical reactions, microbial growth, and various hydrocarbons can alter the hydraulic conductivity (Brown and Thomas, 1984; Brown et al., 1984; Dragun, 1988; Frankenberger et al., 1979).

Dragun (1988) explains two mechanisms by which the presence of hydrocarbons can increase the hydraulic conductivity. The first mechanism involves the dielectric constant. The dielectric constant represents the ability of a liquid to transmit a charge and most hydrocarbons have dielectric constants less than water. Hydrocarbons with dielectric constants less than water enter the inter-particle spaces in the soil matrix and force water and ions out. The hydrocarbons act as an insulator between adjacent particles and reduce electrostatic repulsion forces. A decrease in the repulsion forces decreases the distance between adjacent particles, which causes cracks and fissures to form. These cracks and fissures can permit preferential flow, which can increase the hydraulic conductivity.

The second mechanism involves the removal of dipolar water molecules from the inter-particle spacing, via mass action. This destroys the water structure that extends out from the particle surface. When a hydrocarbon has a very low dielectric constant, it will not exhibit any tendency to align itself with the surface oxygens of clay minerals. Therefore, no solvent structure extends out from the particle surface, and the inter-particle spacing becomes very small. This can also cause cracks and fissures, thus causing preferential flow.

Brown and Thomas (1984) reported diesel fuel caused a 40X, 1800X and 1400X increase in the hydraulic conductivity of a 26% mica-sand mixture, a 16% bentonite-sand mixture, respectively.

Fernandez and Quigley (1985) reported higher hydraulic conductivities for aromatic hydrocarbons than for water, alcohols and acetone in Sarnia soils. They also conducted several two and three stage sequential permeation tests. No increase in the hydraulic conductivity occurred during their two stage tests when samples were first permeated with water then with low soluble aromatic hydrocarbons (benzene, xylene and cyclohexane).

During their three stage tests, when samples were first permeated with water, then ethanol, then benzene, they noted four orders of magnitude increase in the hydraulic conductivity between benzene and water. However, when the permeation order was reversed, they noted three orders of magnitude decrease in the hydraulic conductivity between benzene and water.

As entrapped gas, microbial population or phosphatase activity increases, the

hydraulic conductivity decreases. (Frankenberger et al., 1979; Gupta and Swartzendruber, 1962; McCalla, 1950). Entrapped gases in the macro-voids can cause particle movement, swelling, or a reduction in the mean pore space, which can decrease the hydraulic conductivity. An increase in microbial quantity can cause pore clogging, which may restrict water flow and inevitably decrease the hydraulic conductivity.

## 3.2.1.3 Contaminant Type and Concentration

When considering petroleum products, the more complex the hydrocarbon and the more hydrophobic it is in nature, the more difficult it is for microorganisms to reduce it, and a longer time will be required for biodegradation (Kobayashi and Rittman, 1982). Microorganisms consume only soluble organic molecules and when they are placed in the presence of an insoluble molecule (such as a hydrocarbon), they synthesize and secrete a natural emulsifier to first pseudo-solubilize the hydrocarbon thus making it available for consumption (Goma et al., 1976).

Both high and low contaminant concentrations can inhibit microbial degradation (Bradford and Krishnamoorthy, 1991; Sulflita, 1989). Kobayashi and Rittman (1982) stated two reasons why low or residual concentrations may pose a problem: (1) substrate utilization kinetics may be too slow to provide efficient energy flux to sustain microbial activity; and (2) insufficient substrate concentration may not stimulate the microorganisms to produce the required enzymes. However, microorganisms were used to degrade residual oil in oil tankers and storage drums (Atlas, 1981), and the degradation rate will depend on the proper substrate being available (Griffiths et al., 1982). The contaminant concentration can also affect the rate of substrate (hydrocarbon) utilization. Arcangeli and Arvin (1992) reported the utilization rate of toluene (biodegradation) was first order when bulk concentrations were lower than 0.14 mg/l and zero order when the concentration was higher than 6-8 mg/l.

No.2 Diesel fuel is one of many petroleum products with compounds that can be biodegraded.. There are several different diesel fuel grades (such as arctic diesel, No.1 diesel, No.2 diesel, marine diesel, and SP type B diesel) that differ from one another as a result of processing. No.2 Diesel fuel is a mixture of petroleum hydrocarbons which boil between 300°F and 700°F (Block et al., 1991). Normal, branched and cyclic alkane hydrocarbons (paraffins) are the most abundant (~65% to 85%) in diesel fuel. Aromatic compounds may represent about 10% to 30% (Block et al., 1991; Stone Jr., 1991).

As previously stated, contaminant concentration can effect biodegradation rates. The in situ biodegradation rates of diesel fuel were estimated to range from 0.2 to 20 mg/kg/day for different pilot and full scale sites (Hinchee and Ong, 1992). Biodegradation rates can vary seasonally. Miller (1990) recorded biodegradation rates which varied from 2 to 20 mg/kg/day over a 9 month period. Waste Stream Technology degraded naphthalene starting at 8000 to 12000 ppm down to 100 ppm in five months using psychrophiles at temperatures below 20°F (Mayer and Hom, 1991).

## 3.2.1.4 Stratigraphy, Lithology and Hydrogeology

Stratigraphy, lithology and hydrogeology encompass such things as soil type and depth, grain size, moisture content, porosity or void ratio, and groundwater flow. These

factors affect biodegradation and influence system design.

Moisture levels between 20% and 80% of saturation are suitable for in situ bioremediation (Bossert and Bartha, 1984). However, at only 10% moisture, osmotic and matrix forces can reduce metabolic activity to marginal levels (Molnaa and Grubbs, 1989). At water activity values (the ratio of the vapour pressure of water in the air above the substance or solution and the vapour pressure of pure water at the same temperature) below 0.6, microorganisms can not grow (Biotol Team, 1992).

Hinchee (1989) found an increase in  $CO_2$  produced when the moisture content was increased from 25% to 75% field capacity. Field capacity is defined as the amount of moisture in the soil after the water from the macropores has drained out. When both moisture content and nutrients are increased, moisture content has a greater effect on hydrocarbon degradation than nutrients. Based on the mount of  $CO_2$  produced, DuPont et al. (1991) found nutrients affected biodegradation rates more than moisture. However, when Hinchee and Arthur (1991) analyzed the results from DuPont et al. and based them on total petroleum hydrocarbons (TPH) rather than on the amount of  $CO_2$  produced, they found moisture addition had a greater effect on the TPH than nutrients. An increase in the moisture content can increase the hydrocarbon concentrations.

The greater the surface area exposed to the microbes the faster will be the rate of bioremediation. Two major reasons are: (1) the rate of contaminant desorption increases, and (2) an increase in bioavailability occurs. Volkering et al. (1992) demonstrated the rate of dissolution or desorption may restrict bacteria growth. The dissolution rate is a function of total crystal surface. Under these conditions, microbial growth rates were proportional to

both dissolution properties and surface area.

In dense soils, grain size can reduce the rate of biodegradation when clogging reduces bioavailability. When land farming, bulking the soil will increase the surface area of the contaminant exposed to the microbes, which increases bioavailability. A laboratory land treatment study suggests, biodegradation is inversely proportional to aggregate size (Mott et al., 1990). Even though this research was based on land surface treatment and not on in situ treatment, the results will apply to in situ treatment because grain size controls contaminant bioavailability.

Soils high in organic carbon content can also hinder remediation by reducing bioavailability. Soils with high organic carbon content may increase the adsorption of hydrocarbons, in particular polynuclear aromatic hydrocarbons (PAHs). Adsorbed hydrocarbons are non-bioavailable and thus non-biodegradable (Weissenfels et al., 1992).

#### **3.2.2 Chemical Factors**

There are many chemical parameters that can effect biodegradation. However, the parameters most often requiring attention are:

\* nutrient levels

- \* oxygen availability
- \* soil pH and water pH

Other considerations dealing with oxidation and reduction are too numerous, complex and not well documented. Therefore, a discussion of them will not be included here.

## 3.2.2.1 Nutrient Level

Macronutrients (nitrogen and phosphorus), micronutrients (such as sulphur), and trace nutrients (K, Mg, Ca, Fe, Na, Co, Zn, Mo and Mn) are typically required by microorganisms (Prince and Sambasivam, 1993). However, in most bioremediation treatment systems, nitrogen and phosphorus are the key factors.

The optimum carbon:nitrogen:phosphorus (C:N:P) ratio will vary from one location to another. Usually, a C:N:P ratio from 100:10:1 to 100:10:5 will suffice, but may also depend on the type of treatment used and the phase (liquid or solid) in which the contaminant is found (Torpy et al., 1989). Westlake and Cook (1973) reported a C:N ratio of 10:1 is usually required by bacteria. Depending on whether degradation is aerobic or anaerobic, the nitrogen source can be applied as ammonium-nitrogen, ammonia-nitrogen or nitrate-nitrogen. The phosphorus required for biodegradation is usually applied using salt forms of orthophosphate (PO<sub>4</sub>). However, polyphosphates (e.g., pyrophosphate (P<sub>2</sub>O<sub>7</sub><sup>-4</sup>), tripolyphosphate (P<sub>3</sub>O<sub>10</sub><sup>-5</sup>), trimetaphosphate (P<sub>3</sub>O<sub>9</sub><sup>-3</sup>)) can also be used with orthophosphate (Aggarwal et al., 1991). In aqueous solution, polyphosphates will gradually hydrolyse and revert to the ortho form from which they were derived.

### 3.2.2.2 Oxygen Availability

There are many different ways to provide the oxygen that is required for aerobic in situ biodegradation. Reviewing the literature indicates aerated water, hydrogen peroxide and air extraction or injection wells are the three most common ways of delivering oxygen to the subsurface.

Depending on the type of hydrocarbons to degrade, 1.5 to 3.5 kg of oxygen may be required to aerobicly biodegrade 1 kg of hydrocarbons (Dineen et al., 1989; Lund et al., 1991). The maximum amount of oxygen in a saturated soil is about 8 mg/l. When hydrogen peroxide is used to carry oxygen to the saturated soil, dissolved oxygen levels could be increased to as much as 800 mg/l (Dineen et al., 1989). However, to avoid the formation of gas pockets and microbial toxicity, the concentration is usually kept around 100 ppm (Atlas and Bartha, 1993). Two moles of hydrogen peroxide produce two moles of water and one mole of oxygen. The two main mechanisms for hydrogen peroxide decomposition are enzymatic and non-enzymatic reactions (Huling et al., 1991). Enzymatic decomposition reactions are catalyzed by hydroperoxidases, catalase and peroxidase (Britton, 1985). The enzyme catalase, found in most aerobic bacteria, is primarily responsible for catalytically decomposing cell-synthesized hydrogen peroxide (Huling et al., 1991).

Air could also be used to deliver oxygen to the saturated or unsaturated zones. Air has a greater potential than water for delivering oxygen to the soil on a weight-to-weight and volume-to-volume basis (Sims and Sims, 1991).

## 3.2.2.3 Soil pH and Water pH

McLean (1982) states: "Soil pH is a measure of the activity of ionized hydrogen (H<sup>+</sup>) in the soil solution, and pH is based on the ion product of pure water." Most microorganisms can survive within 1 pH from their optimum. Soil or aqueous pHs between 6 and 8 are suitable for biodegradation (Henson, 1991; Golueke and Diaz, 1989; Staps, 1989; Barnhart and Myers, 1989). When the pH is not in this range, adjustment can be accomplished using basic or acidic compound(s) as required. O'Neill et al. (1993) stated, that aqueous acidic or basic solutions may affect the hydraulic conductivity and evidently affect the desorbing fluid by physical, forced-movement under a constant hydraulic gradient.

#### **3.2.3 Microbiological Factors**

Early as 1895, biodegradation was known to exist, but the subject received little attention until recently (Prince and Sambasivam, 1993). In the early part of the twentieth century researchers isolated many different species of microorganisms (e.g., *Thobacillus*, *Pseudomonas*, *Methanomonas*, *Micrococcus*, *Arthrobacter*, and *Bacillus*) having the ability to degrade complex hydrocarbons (e.g., crude asphalt, kerosene, naphthalene, rubber, and crude oil) (Beerstecher Jr., 1954). Downey and Elliott (1990) stated, "common soil microorganisms have the ability to degrade virtually all of the hydrocarbons found in common fuels". Isolating soil microbes revealed that the genus *Pseudomonas* and the genus *Arthrobacter* are the most common petroleum degrading microorganisms (Bossert and Bartha, 1984).

Biodegradation of petroleum hydrocarbons can take place under aerobic or anaerobic conditions (Atlas, 1991). Aerobic biodegradation of petroleum hydrocarbons under ideal laboratory conditions has been reported in the order of 2500 to 100000 g/m<sup>3</sup>/day. However, under in situ conditions, biodegradation rates are lower, in the range of 0.001 to 60 g/m<sup>3</sup>/day (Bartha and Atlas, 1987). Under anaerobic conditions, biodegradation rates are lower than aerobic rates. The low anaerobic rates may not be sufficient to biodegrade sites within acceptable time limits (Atlas, 1991).

Before biodegradation can take place, the microorganisms must first acclimate to the contaminant (Henson, 1991). This means the microbial population must have microorganisms present which have the inherent ability to degrade the contaminant. Dineen et al. (1989) reported that surface soils with adequate carbon, oxygen and nutrients typically contain about ten million to one billion ( $10^7$  to  $10^9$ ) microorganisms per gram, with about 0.1 to 1.0% being petroleum degraders. The number of petroleum degraders could increase by 100 to 1000 times once exposed to petroleum hydrocarbons.

#### 3.3 Remediation

A review of the literature indicates an array of remediation technologies (for example, bioremediation, soil washing, thermal processing, and soil vapour extraction) exist for hydrocarbon contaminated soils. Here only the technology of bioremediation will be discussed.

In situ bioremediation designs are basically site specific and therefore are unique. An array of parameters (e.g., soil pH, temperature, microbial population, contaminant, concentration, geology, and hydrogeology) is usually evaluated before the process of design begins.

In situ designs using either the microbiological or microbial ecology approach will incorporate both: (1) bioreactor(s); and (2) a nutrient, oxygen and microorganism delivery system. Tesla and Winegardner (1991) illustrated three different system designs (Figures 3.1a, b, and c) for treating contaminated soil in the saturated zone. In all three of these, a single extraction well is used to create a hydraulic gradient through the contaminated plume.

Even though the oxygenation and nutrient delivery systems differ, the objectives are the same, namely to continuously supply oxygen, nutrients, and (possibly) microorganisms to the contaminated plume.

Shown in Figure 3.2 is a continuous treatment process using a bioreactor and a single extraction well circumscribed by injection wells (Molnaa and Grubbs, 1989). The heater incorporated in this design increases the mixed-liquor temperature to enhance microbial growth rate based on the van't Hoff Arrhenius rule. The rule indicates, biological growth rates increase with increasing temperature. A general rule of thumb is the growth rate will double when the temperature is increased by 10°C when the initial temperature is under 20°C.

Ellis et al. (1990) treated groundwater and subsurface contaminated soil in situ over a fifteen week period by enhancing the groundwater with nutrients, oxygen, surfactants, and microorganisms. The in situ design (Figure 3.3) incorporated a bioreactor, infiltration trenches and eleven extraction wells (one central well and ten perimeter wells). By alternately extracting from the central well, then from the perimeter wells, the hydraulic gradient was reversed. Reversing the hydraulic gradient increased the probability of enhancing the entire contaminated plume with adequate amounts of oxygen, nutrients, surfactants, and microorganisms.

Occasionally, in situ bioremediation rates can be increased by incorporating biovents or combining bioremediation with soil vapour extraction (SVE). In bioventing, blower(s) are used to improve the oxygen concentration in and around the contaminated plume. Air is blown down into well(s) or extracted from well(s). The primary objective is to increase the dissolved oxygen concentration to enhance aerobic biodegradation. When SVE and biodegradation are combined, the objectives are two fold. First, SVE removes volatile hydrocarbons. Essentially, volatile hydrocarbons are those hydrocarbons that have a high vapour pressure and low aqueous solubility (high Henry's Law coefficient) (Reissenger et al., 1989). Second, SVE replaces the void space once filled by volatile hydrocarbons with fresh air. This increases subsurface oxygen levels in the contaminated plume, which enhances biodegradation. Essentially, the second objective is the same objective as in bioventing.

Other forms of bioremediation can be done on site using engineered pits or slurry reactors. Both of these technologies require the contaminated soil to be excavated. Therefore, two major advantages in using in situ treatment over these technologies is the amount of money saved in civil works and on on site management. But, the major advantages in using on site treatment in engineered pits or in slurry reactors include: (1) an increase in control over parameters such as temperature, pH, moisture content, dissolved oxygen, bioavailability, and nutrients, (2) the leachate is collected and also treated, (3) the time required for remediation is usually less for on site treatment than for in situ treatment.



Figure 3.0 Crude Oil Biodegradation Time at Various Temperatures (redrawn after Polybac Corporation Bioremediation Booklet)

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Figure 3.1a) Bioremediation Design using a Mixing Tank and a Surface Sprayer (redrawn after Tesla and Winegardner, 1991)







Figure 3.1c) Bioremediation Design using a Mixing Tank and an Air Sparger (redrawn alter Tesia and Winegardner, 1991)







Figure 3.3 Bioremediation Design which Reverses the Hydraulic Gradient (redrawn after Ellis et al., 1990)

#### **CHAPTER 4**

#### MATERIAL AND METHODS

## 4.1 Background

An in situ remediation pilot project was conducted at a decommissioned diesel electrical generating site at the Flin Flon Municipal Airport, about 20 kilometres south of the City of Flin Flon. The airport is adjacent to a community known as Bakers Narrows, and is just west of Provincial Trunk Highway 10 (Figure 4.0).

Figure 4.1 shows the location of three storage tanks used for a diesel generator. The tanks were located north of the powerhouse building. Two were buried, and one remained above ground. The three tanks were removed when the powerhouse was decommissioned several years ago, and only part of the clay liner used around the buried tanks remains. The tanks stored No. 2 diesel fuel. There are no records of any spills occurring at this site. The powerhouse is now used as a storage shed.

## 4.2 Site Investigations

Two separate investigations were conducted at the site. First, a preliminary site investigation was undertaken by Manitoba Hydro to determine whether or not any unrecorded spills had occurred near the storage tanks or near the powerhouse. Since diesel fuel contamination was detected during the preliminary site investigation, a detailed site investigation was undertaken to outline the size of the diesel plume, diesel concentrations, and subsurface conditions (ie. soil description, grain size, moisture content, and hydraulic conductivity).

# 4.2.1 Preliminary Sampling and Testing

Manitoba Hydro conducted the preliminary site investigation in 1991 using a Mobile B-40L drill rig equipped with both 150 mm solid stem, and 225 mm hollow stem augers. Standard penetration test equipment, with a split spoon sampler, was used. Fifteen boreholes were drilled in the preliminary site investigation.

A photoionization detector (PID), using the Photovac MicroTIP which measures airborne contaminants detectable by photoionization, and an electromagnetic ground conductivity meter (Geonics EM31-D) were used in the investigation.

Most of the methods pertaining to drilling, sample handling and PID detection in the preliminary site investigation are the same as those used in the detailed site investigation. Permission was granted by Manitoba Hydro's geotechnical department to quote transcripts from Manitoba Hydro's report on *Bakers Narrows Preliminary Soils Contamination Investigation* (Report No. 92-G07, File No. 62D1, prepared by D.I. Wilson, P.Eng.), as follows:

Initially, the investigation was conducted using stem auger, advanced at half metre intervals. Field observations determined the final depth of these boreholes taking into consideration the soil type and location of the water table. At each sampling interval, the auger was pulled back, and a grab sample was obtained from the auger flights. The soils, after being logged, were checked for volatile hydrocarbons using the Microtip PID unit and the following modified general headspace technique. 1. The soils were broken up and agitated inside a clean polyethylene sample bag.

2. The monitoring tip of the PID unit was then inserted into the bag, and a seal was made by inclosing the top of the bag around the monitoring tip by hand.

3. The maximum metered reading, time, and depth, were recorded in a daily journal.

The modified general headspace technique provided a relative measure of the soil's level of contamination and was used to identify which soil samples should be submitted for chemical analysis. The microtip was calibrated twice a day, using isobutylene at a concentration of 101 ppm in air. Recalibration was also preformed if a questionable reading was obtained.

Although sampling directly off the solid stem auger flights carried with it the risk of contamination from soils above the sample point, it was felt that any errors that occurred would be on the conservative side.

When a sample was recovered using the solid stem augers, it was divided into two parts. One portion of the sample was then taken off the auger flight using sterile, disposable gloves and put into a clean sample bottle. The sample bottle was sealed with aluminum foil, capped and labelled appropriately. All samples submitted for chemical analysis were stored in an electric cooler and then packed in ice in smaller coolers for transport to Enviro-Test Laboratories.

Selected samples were sent to Enviro-Test Laboratory in Edmonton, Alberta and analyzed for Total Extractables, in parts per million (ppm) content of contaminants. Total Extractables is a summation of the hydrocarbon concentration from the  $C_7$  to  $C_{30}$  carbon range, including toluene, ethylbenzene and xylenes, and is calculated against a calibrated diesel or gasoline standard (US EPA SW 846 Method-3550 or 3580/8000).

The second part of the sample was taken for a dynamic headspace test (apparatus shown in Figure 4.2). The "Dynamic Headspace -Polyethylene Bag" method and guildlines are documented in the EPA (United States Environmental Protection Agency) Manual 530/UST-90/003. A quart-sized, resealable, polyethylene freezer bag, with a small hole made about 50 mm down from the resealable end, was connected to a 3-way ball valve using 8 mm flexible tubing and connectors.

A standard volume of sample was placed into the freezer bag containing 100 ml of distilled water. After being sealed, the bag was inflated with air until taut. This was done through a 3-way ball valve, using the exhaust of the PID unit air pump. The 3-way ball valve was closed, and the sample and water mixture was agitated for about 4 minutes. The PID unit was then connected to the bag, through the ball valve, and the highest meter reading was recorded.

Hollow stem augers were also used to obtain a representative sample

of the contaminated soil. The hollow stem auger was used to auger down to the depth where the sample was to be taken. At this point the end plug was removed and a clean 25 mm diameter split spoon sampler was pushed ahead of the auger. The split spoon was Cleaned after each use with a biodegradable soap (Simple Green) and then rinsed in clean water. This method did not provide enough sample for analysis and was abandoned in favour of the solid stem auger sampling method. A larger diameter split spoon will be utilized in the future.

## 4.2.1.1 Geophysical Survey

An electromagnetic conductivity survey was also conducted during the preliminary site investigation. Readings were taken at various stations using the Geonics EM31-D. At each station, vertical and horizontal readings were obtained using the EM31-D at hip level and at the ground surface. The EM data was calculated by normalizing the apparent conductivity with a chosen background value, and then plotted in decibels. A slight variation in decibel readings over the site may reflect changes in the underlying overburden material.

# 4.2.2 Detailed Sampling and Testing

When soil samples from the preliminary site investigation confirmed high diesel fuel concentrations near BN #09 and BN #10, a detailed site investigation was undertaken in June (1992).

Figure 4.3 shows the location of all the boreholes drilled in the preliminary and

detailed site investigations. To establish the size of the diesel plume, boreholes were drilled using a two meter grid pattern around borehole #10. However, after drilling five boreholes, the grid size was increased to four metres. Drilling with a split spoon and sample handling were discussed in section 4.2.1. Various soil samples, from different boreholes and depths, were sent to Enviro-Test Laboratories for total extractable (TE) analysis.

A portion of the same soil samples that were sent to Enviro-Test Laboratories for TE analysis was also sent to Independent Test-Lab Limited. Independent Test-Lab Limited conducted soil description, moisture content, grain size, and hydraulic conductivity analyses on various soil samples.

# 4.2.2.1 Soil Description and Moisture Content

Soil description and moisture content were determined on various samples by Independent-Test Lab Limited using applicable ASTM Standards, D2488 and D4959, respectively.

# 4.2.2.2 Grain Size and Hydraulic Conductivity

Grain size analyses (sieve and hydrometer) and falling head hydraulic conductivity tests were performed on various soil samples from different boreholes and depths. Independent Test-Lab Limited used ASTM Standard D422 for the grain size analyses.

Falling head testing was utilized in the hydraulic conductivity analyses: ASTM Standard D5084. However, Manitoba Hydro requested three specimens be molded at natural moisture within a Standard 4 inch Permeameter Proctor mold in a `loose' state, at 15 blows,

and at 25 blows with a Standard Proctor hammer. However, an insufficient amount of material was provided. Therefore, Independent Test-Lab Limited used only one layer (approximately 1/3 of the proctor mold height) molded within the permeameter mold to determine hydraulic conductivities.

## 4.2.3 Soil Sampling Periodically

To analyze remediation progress, one borehole was drilled within 0.2 to 0.3 metres of boreholes #21, #27, and #30 in September (1992), June (1993) and September (1993). These boreholes were drilled manually using a 4 inch handauger. At various depths, grab samples were collected and sent to Enviro-Test Labs for total extractable (TE) and moisture content analysis. Most of the time, about ten times the sample volume required for TE analysis was collected from a depth range of 0.2 to 0.3 metres. Each grab sample was placed in a plastic pail, and mixed thoroughly. A representative sample of 200 ml was then placed in a glass bottle, and sent to Enviro-Test Labs. Between sampling, the auger and pail were rinsed with non-contaminated water.

#### 4.3 System Designs

Remediation at the Flin Flon site employed both ground surface spraying and a pumpcycle system. Both systems were based on treating the site in situ (i.e., no part of the contaminated zone was excavated then treated). The systems were designed to improve soil conditions for bioremediation by increasing the moisture content, nutrient level, and oxygen supply in and near the diesel plume.

## 4.3.1 Ground Surface Spraying

Ground surface spraying was conducted between July (1992) and August (1992), and June (1993) and August (1993). Local water, mixed with common fertilizers or technicalgrade compounds, underwent aeration in either a 3000 or a 1000 litre mixing tank and then was sprayed on the ground surface over the diesel plume. The surface area sprayed was about  $100 \text{ m}^2$  and the rate of application was about 500 l/hr. Figure 4.4 illustrates the system used for ground surface spraying.

Periodically, when standing water was present or after a heavy rain, the quantity sprayed was reduced and nutrients were added to the ground surface over and near the diesel plume (applied surface area was about  $100 \text{ m}^2$ ).

## 4.3.2 Pump-Cycle System

A pump-cycle system was implemented in August (1992). Figures 4.5a and 4.5b illustrate the system design. Conceptually, the system was designed to operate as follows: A pump in the extraction well would pump groundwater into one tank of two in series. This would create a hydraulic gradient below the diesel plume in an attempt to maintain a closed system and prevent contaminant migration. The water in this tank would overflow into the second tank before being injected into eight feeder wells circumscribing the extraction well. The second tank was primarily used for storage, to ensure a plentiful supply of nutrient-rich water would be injected into the feeder wells. The water in the tanks would undergo both aeration and nutrient addition (ammonia-nitrogen and orthophosphate), to enhance indigenous microbial activity.

The tanks would thus serve as reactors to biologically degrade the dissolved hydrocarbons pumped up in the groundwater. The target retention time was 12 hours.

Initially, the extraction pump and injection pumps (to the feeder wells) operated sequentially via a relay-switch. The extraction pump would operate until the second tank contained about 2500 litres. Groundwater extraction would then stop, and the 2500 litres in the second tank would be injected into the feeder wells. Once the second tank was empty, groundwater extraction would start again, and the cycle would continue.

However, the inability to control surges from the extraction pump caused a significant reduction in the retention time to about 3.5 hours. Since the tanks served as bioreactors, a short retention time could limit or prevent biodegradation in the tanks. Therefore, the extraction pump was changed to operate on a timer in February (1993) and only the injection pumps operated via the relay-switch. How the altered system operated is described below.

The extraction pump would operate four times daily for 1/2 hour at a rate of about 40 l/min, regardless of the quantity of water in the second tank. However, silt build-up around and in the extraction well and the lowering of the water table, decreased the pumping rate to an average of 11 l/min; which corresponds to a retention time of about 45 hours. The relay-switch inside the second tank would close when the tank contained about 2500 litres, and the switch would open when the tank was empty.

The flow to each of the eight feeder wells was controlled manually by means of valves. The initial setting was 2 litres per minute per feeder well. However, in June (1993) feeder well #08 was disconnected and a new feeder well, #09, was installed. Feeder well #08 was five metres from the edge of the diesel plume, whereas feeder well #09 was installed at the edge of the plume. By moving one feeder well, an evaluation regarding the distance of the feeder wells from the diesel plume could be made.

Two small infiltration trenches were also installed directly above the diesel plume in June (1993) (Figure 4.5a) using coarse sand. The infiltration trenches were installed in an attempt to improve both moisture content and nutrient levels in the diesel plume. Also in June (1993), the flows to feeder wells #04, #05, #06 and #07 were reduced to 1 litre per minute per feeder well. These feeder wells were four to six metres from the diesel plume, and contributed little to increasing both moisture content and nutrient levels in the plume.

During the operation of the pump-cycle system, feeder well flows may have varied from time to time because of line clogging or clogging of the manifold (where the feeder lines are all connected). Also, one of the pumps in the second tank malfunctioned and was not replaced since it was found that the one remaining pump would be sufficient to maintain the required flows to the feeder wells.

All feeder wells were drilled manually using a 4 inch handauger. The depths and design of the feeder wells are presented in Table 4.0 and Figure 4.6, respectively. Slotted 1.5 inch PVC pipe was placed inside each well and loosely backfilled with the original soil. All feeder wells were impervious for the first half metre below ground surface. Initially, the expected depth of all feeder wells was 5 metres. However, subsurface conditions prevented some of the feeder wells from being drilled to this depth.

## 4.3.2.1 Wintering Pump-Cycle System

The pump-cycle system (Figure 4.7) was wintered between September (1992) and

June (1993). Wintering consisted of: (1) adding additional insulation inside the trailer and heating it via two 1500 watt baseboard heaters; (2) placing 10 cm of white styrofoam insulation on the ground surface ( $\sim$ 175 m<sup>2</sup>) above the diesel plume, adding pink fibreglass insulation bats around the styrofoam perimeter to improve the seal between the styrofoam insulation and the ground surface, and then covering the styrofoam and fibreglass insulation with a 6 mil polyethylene sheet; (3) wrapping the plastic pipes, leading to the feeder wells, with thermal heating coils; and (4) placing insulated plywood covers over the extraction well and feeder wells.

#### 4.4 Nutrient Enrichment

Nutrients (nitrogen and phosphorus) were applied to the ground surface and mixed into the second tank. The nitrogen and phosphorus were obtained from fertilizers (N:P:K of 21:7:7 and 12:6:3) and technical grade compounds (diammonium-orthophosphate, ammonium-nitrate, and mono- & dipotasium-orthophosphate). The date, nutrient concentrations, and quantity applied to the ground surface and mixed in the second tank are shown in Tables 4.1 and 4.2, respectively.

The fertilizers (21:7:7 and 12:6:3) were initially used as the nutrient source after the N:P ratio was tested. The fertilizers, 21:7:7 and 12:6:3, were found to have N:P ratios of 5:1 and 4.5:1, respectively. This would have been acceptable, but a portion of the fertilizers did not dissolve immediately when mixed into the second tank. Therefore, the N:P ratio desired was not obtained. As a result, technical grade compounds were purchased and used. By using technical grade compounds, control over the N:P ratio improved and the form of

nutrients applied were better suited for microbial up-take.

## 4.5 Tested and Monitored Parameters

Shown below are the parameters tested and the method used on various soil and water samples, respectively.

## Soil Sample Parameters Tested

1. pH: Electrometric Method in Water and in 0.01  $\underline{M}$  CaCl<sub>2</sub>, Method of Soil Analysis, American Society of Agronomy, No.9, Part 2, 2nd ed., pp. 199-224, 1982. also, Manual on Soil Sampling and Methods of Analysis, Canadian Society of Soil Science, J.A. McKeague, 2nd ed., 1978, method-3.13.

2. Total Coliform: Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 17th ed., 1989, method-9221 (MPN).

3. Ammonium-Nitrogen (NH<sub>3</sub>-N): Automated Phenate Colorimetry, Manual on Soil Sampling and Methods of Analysis, Canadian Society of Soil Science, J.A. McKeague, 2nd ed., 1978, method-4.25.

4. Nitrate/Nitrite (NO<sub>3</sub>/NO<sub>2</sub>): Automated Cadmium Reduction Method, Manual on Soil Sampling and Methods of Analysis, Canadian Society of Soil Science, J.A. McKeague, 2nd ed., 1978, method-4.311.

5. Orthophosphate (PO<sub>4</sub>): Manual on Soil Sampling and Methods of Analysis, Canadian Society of Soil Science, J.A. McKeague, 2nd ed., 1978.

# **Extraction and Injection Water Sample Parameters Tested**

1. pH: Electrometric Method and Litmus Paper, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 17th ed., 1989, method-4500-H<sup>+</sup>.

2. Total Organic Carbon (TOC): Persulfate-Ultraviolet Oxidation Method, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 17th ed., 1989, method-5310.

3. Ammonia-Nitrogen (NH<sub>3</sub>-N): Semi-Micro Kjeldahl Method with titration to the end point using 0.01 N HCl titrant and Boric Acid indicator, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 17th ed., 1989, method-4500-NH<sub>3</sub>.

4. Nitrate/Nitrite ( $NO_3/NO_2$ ): Automated Cadmium Reduction Method, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 17th ed., 1989, method-4500-NO<sub>3</sub>.

5. Orthophosphate (PO<sub>4</sub>): Automated Stannous Chloride Method, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 17th ed., 1989, method-4500-P.

6. Total Phosphate: Automated Stannous Chloride Method, Standard Methods for the Examination of Water and Wastewater, American Public Health Association, 17th ed., 1989, method-4500-P.

7. Temperature: Automated Instrumentation.

8. Water Elevation: Automated Instrumentation.

Not all soil samples obtained were tested for the five soil parameters mentioned above. Soil testing was conducted in June, August and September (1993). In June (1993), the Department of Soil Science, University of Manitoba tested six soil samples for pH from feeder well #09. Except for the six samples tested for pH by the Department of Soil Science, Norwest Labs, Winnipeg, Manitoba did all the soil testing for the above mentioned parameters.

Water samples from the extraction well and to the feeder wells were tested for pH, nitrogen, orthophosphate, and total organic carbon about once a week. Testing for total organic carbon started in August (1992) and stopped in September (1993). Testing for pH, nitrogen, and orthophosphate started in January (1993) and stopped in September (1993).

Water samples obtained from June (1992) to July (1993) were tested by myself at the Department of Environmental Engineering, University of Manitoba, Winnipeg, Manitoba. All other samples after July (1993) were tested by Norwest Labs, Winnipeg, Manitoba.

Given that the aim of this research was not to study in situ bioremediation per se, rigorous soil sampling for nutrients and microorganisms was not conducted. The strain of microorganisms doing the degrading was considered to be of secondary interest, and no laboratory analysis was conducted to isolate them. Also, funding for such analysis was not provided. The available funding was used instead to determine the actual in situ diesel fuel concentrations and diesel plume size.

To conclusively monitor the progress of in situ bioremediation, a complex pump-cycle system, and more on site monitoring and management would have been required. However, funding for such monitoring and management was not available. Therefore, a simple pumpcycle system and surface spray system were used to improve subsurface nutrient and moisture conditions in an attempt to stimulate the indigenous microorganisms to biodegrade the diesel fuel and reduce the plume size in a reasonable amount of time. Since the groundwater was not contaminated, influent (extraction well) concentrations were monitored using the simple inexpensive TOC test. If seepage of diesel fuel into the groundwater had occurred, the TOC test should have detected it.

#### 4.6 Tracer Tests

Two chloride tracer tests using ammonium chloride were conducted in feeder well #03 and borehole #17 (piezometer). No changes were made to either the extraction pump rate or the timer controlling the extraction pump during the two tracer tests.

The Mohr (Argentometric) titration method (Standard Methods 407) was used to quantify the chloride concentration using 30 ml sample volumes. The chloride tracer tests were gravity fed (Figure 4.8), which resulted in a slight reduction to the injection rate with decreasing volume.

#### 4.6.1 Chloride Tracer Tests

The first chloride tracer test was conducted in feeder well #03. Two separate concentrations of ammonium chloride were injected in sequence. First, about 1100 litres of water, with a 8.3 mg/l Cl<sup>-</sup> concentration, were mixed with 10 kg of ammonium chloride (~9090 mg/l NH<sub>4</sub>Cl or ~6025 mg/l Cl<sup>-</sup>) and injected at a rate of 700 ml/min (~1000 l/day). Second, 25 kg of ammonium chloride (~22725 mg/l NH<sub>4</sub>Cl or ~15063 mg/l Cl<sup>-</sup>) were mixed

with about 1100 litres and again injected at a rate of 700 ml/min (~1000 l/day).

The second chloride tracer test was conducted in borehole #17, a piezometer. The chloride concentration and injection rate used were ~22725 mg/l  $NH_4Cl$  (or ~15063 mg/l Cl<sup>-</sup>) and 900 ml/sec (1296 l/day), respectively. The volumes for a first and a second injection were about 1100 and 950 litres, respectively.



Figure 4.0 Location of the City of Flin Flon (~ 855 km north of Winnipeg)



Figure 4.1 Location of Diesel Fuel Storage Tanks



Figure 4.2 Apparatus Setup for Polyethylene Bag Sampling System



Figure 4.3 Location of Boreholes from Preliminary and Detailed Site Investigations



Figure 4.4 Schematic of Ground Surface Spray System



Figure 4.5a) Plan View of Pump-Cycle System



Figure 4.5 b) Simplified Profile View of Treatment Processes

Feeder Well	Drill Depth	Slotted	
Number	(m)	Length (m)	
#01	5.0	4.5	
#02	5.0	4.5	
#03	5.0	4.5	
#04	5.0	4.5	
#05	4.5	4.0	
#06	5.0	4.5	
#07	3.5	3.0	
#08	5.0	4.5	
#09 5.0		4.5	

Table 4.0 Data on Feeder Wells







Figure 4.7 Section View of Winter Covering





Date	NH3-N	PO4-P	Quantity			
	(mg/l)	(mg/l)	Sprayed (I)			
1992			·			
July 17	3.27	6.6	3000			
July 19	3.75	7.8	3000			
July 22	3.44	6.8	1500			
July 23	2.43	4.9	2300			
July 24	3.31	6.2	3000			
July 25	3.05	7.6	3000			
July 26	5 (1)	1 (1)	3000			
July 27	5 (1)	1 (1)	2800			
July 30	5 (1)	1 (1)	2000			
Aug. 05	4.77	0.95	1100			
Aug. 11	1.5	0	1000			
Aug. 12	5 (1)	1 (1)	1000			
Aug. 29	5 (1)	1 (1)	3000			
1993						
June 07	11	52	1000			
June 11	11	52	1000			
June 17	11	52	1000			
July 19	9	1	1000			
July 27	(2) Applied to Ground Surface					
Aug. 03	(3) Applied to Ground Surface					
Aug. 26	100	280	1100			
(1) = based on lab testing of nutrients:						
20 ml per I of 21-7-7 yielded 500 mg/l						
NH3-N and 100 mg/I PO4-P.						
20 ml per l of 12-6-3 yielded 450 mg/l						
NH3-N and 100 mg/l of PO4-P.						
(2) = 50 kg of NH4NO3 and 5 kg of K2HPO4						
and 3.75 kg of KH2PO4.						
(3) = 25 kg of NH4NO3 and 2.2 kg of K2HPO4						
and 1.8 kg of KH2PO4.						

Table 4.1 Nutrients Sprayed on Ground Surface

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Nutrients Added into Tank 2						
Date	NH3-N	PO4-P	Quantity			
	(mg/l)	(mg/l)	0			
1992						
Sept. 3	5 (1)	1 (1)	2500			
Sept 10	5(1)	1 (1)	2500			
Sept. 17	5(1)	1 (1)	2500			
Sent 23	5 (1)		2500			
Oct 09	5(1)		2500			
Oct 08	3(1)	1 (1)	2500			
Oct. 15	5(1)	1 (1)	2500			
Oct. 22	5 (1)	1 (1)	2500			
Oct. 29	5 (1)	1 (1)	2500			
Nov. 05	5 (1)	1 (1)	2500			
Nov. 19	5 (1)	1 (1)	2500			
Nov. 26	5 (1)	1 (1)	2500			
Dec. 05	5 (1)	1 (1)	2500			
Dec. 22	5(1)	1(1)	2500			
Dec 31	5 (1)	1 1 (1)	2500			
1003	<u> </u>	1 (0	2000			
1333	E (1)	1				
Jan. 07	3(1)	1 (1)	2500			
Jan. 14	5 (1)	1 (1)	2500			
Jan. 28	5 (1)	1 (1)	2500			
Feb. 04	5 (1)	1 (1)	2500			
Feb. 11	5 (1)	1 (1)	2500			
Feb. 18	5 (1)	1 (1)	2500			
March 01	5 (1)	1 (1)	2500			
March 08	5 (1)	1 (1)	2500			
March 12	5(1)	1 (1)	2500			
March 18	5 (1)	1 (1)	2500			
March 25	5 (1)	1 (1)	2500			
April 01	5(1)	1 (1)	2500			
April 08	5(1)	1(1)	2500			
April 45	5(1)	1 (1)	2500			
April 15	5(1)	1 (1)	2500			
April 22	5 (1)	1 (1)	2500			
April 30	5 (1)	1 (1)	2500			
May 06	5 (1)	1 (1)	2500			
May 19	5 (1)	1 (1)	2500			
May 31	5 (1)	1 (1)	2500			
July 21	90 (2)	10 (2)	2500			
July 22	90 (2)	10 (2)	2500			
July 23	90 (2)	10 (2)	2500			
July 24	90 (2)	10 (2)	2500			
Aug 19	90 (2)	10 (2)	2500			
Aug. 20	00 (2)	10 (2)	2500			
Aug. 20	<u> </u>	10 (2)	2500			
Aug. 21	90 (2)	10 (2)	2500			
Aug. 22	90 (2)	10 (2)	2500			
Aug. 23	90 (2)	10 (2)	2500			
Aug. 24	90 (2)	10 (2)	2500			
Aug. 25	90 (2)	10 (2)	2500			
Aug. 26	90 (2)	10 (2)	2500			
Sept. 04	90 (2)	10 (2)	2500			
Sept. 05	90 (2)	10 (2)	2500			
Sept 06	90 (2)	10 (2)	2500			
Sent 07	90 (2)	10 (2)	2500			
Sept 02		10 (2)	2000			
	30 (2)	10 (2)	2500			
i) = based on Lab Testing of Nutrients:						
o mi per i or 21-7-7 yielded 500 mg/l						
1H3-N and 10	) mg/l PO4-F	P.				
U mi per l of 12-6-3 yielded 450 mg/l						
IH3-N and 100 mg/l of PO4-P.						
2) - Nutrianta Bread D-						

Table 4.2

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#### **CHAPTER 5**

#### RESULTS

#### 5.1 Background

The site was chosen over other sites to conduct an in situ bioremediation pilot project because: (1) it is located within the boundary of the Flin Flon Airport (Figure 5.0), (2) the airport is owned by the Manitoba Government and access would be provided to clean-up any contaminants found, (3) Manitoba Hydro is responsible for cleaning-up any diesel spills that may have occurred when the diesel generator was in operation, (4) Manitoba Hydro agreed to fund the project and provide on site management to maintain system operations throughout the winter months, (5) Manitoba Hydro has other sites with similar subsurfaces (silt and siltysand) to clean-up, and view Baker's Narrows as the best site at which to attempt an in situ bioremediation pilot project, (6) most of Manitoba Hydro's former diesel sites are contaminated with diesel fuel and other available technologies are either too expensive, such as thermal treatment, or not very effective, such as soil vapour extraction, and (7) access to the site is restricted, which reduced the probability of vandalism.

The site terrain is flat with a few small trees and some weed cover. The site is visible from Highway #10; it is approximately 25 metres from the highway, and about 75 metres from Sally's Beach on Lake Athapapuskow.

The daily low and high ambient temperatures, and the mean monthly low and high temperatures taken at the airport from June (1992) to September (1993) are shown in Figures 5.1 and 5.2, respectively. During remediation, the mean monthly low and high ambient temperatures ranged from  $-25^{\circ}$ C to  $+22^{\circ}$ C, respectively. Total monthly precipitation (rain

and snow) is shown in Figure 5.3. The maximum total precipitation was 141 mm and recorded in July (1993); the minimum was 5.4 mm and recorded in March (1993).

Monthly normal soil temperature at depths 5, 10, 20, 50, 100, 150, and 300 cm for a region 100 km south of the airport are shown in Figures 5.4 to 5.7, inclusive. These normal soil temperatures are from 1951 to 1980. Normal soil temperatures during remediation at the airport were not recorded. The normal soil temperatures taken 100 km south of the airport were assumed to represent the normal soil temperatures at the airport. The soil temperature varied depending on depth, time of day, and time of year, for instance at a depth of 5 cm, the temperature ranged from  $+20^{\circ}$ C to  $-3.5^{\circ}$ C.

Since the site contains a large amount of silt and is located in the north, two main concerns were, (1) bioremediation may not occur in the silt as a result of either microbial filtration or insufficient oxygen, moisture or nutrients, and (2) the cost associated with maintaining system operations in subzero temperatures (-40°C does occur in the Flin Flon region).

## 5.2 Site Investigations

#### 5.2.1 Preliminary

Of the fifteen boreholes drilled, only samples from boreholes #09 and #10 had photoionization readings above 100 ppm. Based on these readings, two additional holes (BN #09A and BN #10A) were drilled within two metres of the original boreholes. Samples from these boreholes were tested for TE, and found to contain diesel fuel concentrations as high as 15000 ppm. Since these additional boreholes were relatively close to the original boreholes, the soil logs from the original holes were used in what follows.

## 5.2.1.1 Geophysical Survey

A contour map, using the vertical readings of electromagnetic conductivity at hip level, is shown in Figure 5.8. The EM data was calculated by normalizing the apparent conductivity with a chosen background value, and plotted in decibels. From Figure 5.8, no correlation could be observed between the decibel contours and the diesel plume known to exist near boreholes #09 and #10.

# 5.2.1.2 Total Extractables and Photoionization

Table 5.0 and Figure 5.9 give the photoionization (general headspace, and dynamic headspace) and TE results from boreholes #09A and #10A, respectively. These results are assumed to represent the original boreholes (#09 and #10) as well.

#### 5.2.2 Detailed

In the detailed site investigation an additional 29 boreholes (Figure 5.10) were drilled to better define the diesel plume and subsurface conditions. Soil samples from different boreholes and depths were tested for grain size, moisture content, hydraulic conductivity, and TE.

## 5.2.2.1 Soil Description and Moisture Content

Figure 5.11 shows the location of the boreholes used to create three profiles

(Figures 5.12, 5.13 and 5.14) of the subsurface. At borehole #10, for instance, the subsurface to a depth of about 0.2 m was fine to coarse grained sand fill. Below the fill, for about 2 metres, the subsurface consisted of silt. Silty-sand underlies the silt. At this location, the water table is about 7.5 m below the ground surface.

The moisture content for the soil samples from the 12 boreholes used to generate the three soil profiles are shown in Figures 5.15, 5.16 and 5.17. The moisture content basically decreased with depth in the silt layer and then increased in the silty-sand region, below the silt layer. A moisture content of about 20% corresponds to saturation. The moisture content within the diesel plume ranged from 2.4 to 29.1%.

## 5.2.2.2 Grain Size and Hydraulic Conductivity

Grain size analyses on thirteen soil samples from different boreholes and depths are shown in Appendix A. Below the surface fill, the silt region consisted of 58.3 to 85.4% silt and 10.6 to 37.46% sand; small quantities of both gravel and clay were also present. In the silty-sand region, below the silt layer, 58 to 93.4% was sand and 5 to 38.8% was silt, with small traces of clay.

Shown in Table 5.1 are the results from the hydraulic conductivity analyses conducted on the thirteen samples. Tabulated is the average hydraulic conductivity from four falling head tests per sample. The hydraulic conductivity was obtained from samples in three states: `loose', 15, and 25 blows (blows from a Standard Proctor Hammer). The hydraulic conductivity in the silt and silty-sand regions ranged from 10<sup>-5</sup> to 10<sup>-7</sup> cm/sec and 10<sup>-3</sup> to 10<sup>-4</sup> cm/sec, respectively.

## 5.2.2.3 Total Extractables and Photoionization

TE and PID tests were conducted on seventy-six soil samples from different boreholes and depths in and around the diesel plume. The results are shown in Table 5.2. The contaminant, as expected, was found to be diesel fuel.

Based on the TE results from the detailed site investigation, six profile views were drawn to define the diesel plume. Figure 5.18 shows a plan view of the plume and the location of twenty boreholes used to create six profiles of the plume. The profiles are shown in Figures 5.19 to 5.24, inclusive. Estimated TE contours of 10000, 5000 and 1000 ppm are shown in these profiles based on the measured TE concentrations. About 260 m<sup>3</sup> of soil is contaminated above 1000 ppm. The calculations of the initial and final volume of soil contaminated above 1000 ppm is shown in Appendix B.

## 5.3 Tested and Monitored Parameters

Various soil samples were tested for TE and moisture content in September (1992), June (1993) and September (1993). The TE and moisture content of all soil samples are tabulated in Appendix C. The soil samples came from within the diesel plume at three concentrated points (within 0.2 to 0.3 m from boreholes #21, #27 and #30). Soil samples from different boreholes were also tested for TE, moisture content, pH, nutrients (NH<sub>3</sub>-N, NO<sub>3</sub>-N, and PO<sub>4</sub>), and total coliform in September (1993). The locations of all these boreholes are shown in Figure 5.25 (the extraction well and feeder wells are also shown).

The pump-cycle system (influent and effluent) was monitored approximately once a week for TOC (starting in August (1992) and ending September (1993)), pH and nutrients

(NH<sub>3</sub>-N, NO<sub>3</sub>-N & NO<sub>2</sub>-N and PO<sub>4</sub>-P) (starting in January (1992) and ending September (1993)). The results from monitoring the pump-cycle system are tabulated in Appendix D. DO was also monitored weekly starting in June (1992) and ending August (1993).

# 5.3.1 Total Extractables and Moisture Content

Profiles of the diesel plume showing the initial and periodical TE results are shown in Figures 5.26 to 5.29, inclusive. To assist in evaluating the significant contaminant reduction near borehole #27 from June (1993) to September (1993), two additional profiles (Figures 5.30 and 5.31) were drawn perpendicular to borehole #27. Also, shown in Figures 5.29 and 5.31 are total coliform counts from various soil samples. The initial moisture content and three subsequent moisture contents near boreholes 21, 27, and 30 are shown in Figures 5.32, 5.33 and 5.34, respectively.

## 5.2.2 Soil pH, Nutrients and Microbiology

Twenty-five soil samples were tested for pH. The results are shown in Table 5.3, with the borehole locations shown in Figure 5.25. From Table 5.3, the pH can be seen to range from 7.1 to 8.1 in a 1:1 (w/v) paste in water. The pH ranged from 6.7 to 7.0 for six soil samples from feeder well #09 tested in 0.01  $\underline{M}$  CaCl<sub>2</sub> (1:2 (w/v)). Nineteen of the twenty-five soil samples were also tested for nutrients, electric conductivity and total coliform.

## 5.3.3 Pump-Cycle System

Results from monitoring the pump-cycle system for pH, TOC, NH<sub>3</sub>-N, NO<sub>3</sub>-N & NO<sub>2</sub>-

N,  $PO_4$ -P, and DO are shown from Figures 5.35 to 5.40, respectively. In Figure 5.39, twelve samples were tested for total phosphorus. These samples were to have been tested for orthophosphate, and an error in communication must have occurred. Nevertheless, the results are presented and discussed.

Automated instrumentation measured the temperature and water elevation continuously on the pump-cycle system from mid-December (1992) to the end of August (1993). (The readings are contained in the report, *Automated Instrumentation from the In-Situ Remediation Pilot Project at the Flin Flon Airport*. This report can be obtained from Professor D. Shields, Civil Engineering Department, University of Manitoba).

Temperature and water elevations were recorded in both tanks, borehole #43 (extraction well), and the eight feeder wells (feeder well #08 readings are actually from feeder well #09 from June (1993)). Two readings of temperature and water elevation were made in boreholes #52, #53 and #54. The trailer temperature was also recorded. Note that the elevation of 50 corresponds to the ground surface.

The temperature in the tanks varied between 3°C and 7°C from December (1992) to March (1993). However, from March to September (1993), the temperature fluctuated between 12°C and 24°C. During the corresponding periods, the trailer temperature fluctuated in a similar pattern to the temperature in the tanks. Periodically, the trailer temperature did decrease below the tank temperatures, but primarily it remained 7°C to 10°C above the tank temperatures.

The temperature ranged between 5°C and 12°C for the eight feeder wells, and borehole #43 (extraction well). Both temperature readings in boreholes #52, #53, and #54

were also between 5°C and 12°C. Periodically, the temperature dipped and peaked to 4°C and 14°C. However, in April and May (1993) temperature increases of 20°C from the norm were recorded for feeder wells #02 and #04.

The injection rate can be obtained from the instrumentation data for tank #2. However, the instrumentation for this tank did not function from February (1993) to August (1993). During groundwater extraction, the water table decreased by 2 m in borehole #43 (extraction well) and 0.16 m in borehole #53 (note: borehole #53 is called prob #2 in the automated instrumentation report).

## 5.4 Chloride Tracer Tests

Chloride tracer tests (Figures 5.41 and 5.42) indicate a breakthrough time of about 55 hours for feeder well #03, and 75 to 115 hours for borehole #17. The sporadic chloride concentrations which were measured before the second injection into borehole #17 (Figure 5.42) are probably due to traces of chloride still leaching into the groundwater from the chloride tracer test conducted in feeder well #03. Also, for borehole #17 there are two peaks, one occurring at about 75 hours and the other at 115 hours. The first peak of 75 hours corresponds to either chloride from the injections into feeder well #03, or the true breakthrough time of borehole #17. Less than 1% of the chloride injected in either test was recycled.



Figure 5.0 Location of Remediation Site at the Flin Flon Airport














Figure 5.4 Normal Soil Temperatures taken about 100 km South of the Flin Flon Airport, (c) 1951-1980



Figure 5.5 Normal Soil Temperatures tanken about 100 km South of the Flin Flin Airport, (c) 1951 - 1980



Figure 5.6 Normal Soil Temperatures taken about 100 km South of the Flin Flon Airport, (c) 1951 - 1980



Figure 5.7 Normal Soil Temperatures taken from about 100 km South of the Flin Flon Airport, (c) 1951 - 1980



Figure 5.8 Geophysical Survey (from Manitoba Hydro's report on Bakers Narrows Preliminary Solls Contamination Investigation report No. 92-G07, File No. 62D1, prepared by D.I. Wilson, P.Eng.)

PID and TE Results from BN #09 and #10							
Borehole	Depth	PID PID		TE			
Number	(m)	General	General Dynamic				
		Headspace	space   Headspace				
		(ppm)	(ppm)				
BN # 09A	1.6	168	101	3900			
BN # 09A	2.2	182	29.4	0			
BN # 10A	3.7	204	338	15000			
BN # 10A	4.2	296	109	10000			
BN # 10A	# 10A 7.3		48.5	33			

Table 5.0 PID and TE Results from BN #09 and #10



Figure 5.9 Plot of PID and TE Concentrations



Figure 5.10 Some of the Boreholes Drilled in the Detailed Site Investigation of Locate the Diesel Plume



Figure 5.11 Boreholes Used to Create Soil and Moisture Content Profiles



Figure 5.12 Soil Description Profile, Section A-A







Figure 5.13 Soil Description Profile, Section B-B



Figure 5.16 Moisture Content Profile, Section B-B



Figure 5.14 Soil Description Profile, Section C-C





Sample	Denth	Number	1 Kan - 141				
Number		Number of Kavg (					
BN #22	(m)	Blows	(cm/sec)				
DIN #23	5.25 - 6.03	Loose	1.1E-03				
	1	15	9.5E-04				
		25	9.1E-04				
BN #25	4.98 - 6.01	Loose	1.7E-04				
		15	1.8E-04				
		25	1.7E-04				
BN #27	2.98 - 3.47	Loose	1.0E-03				
		15	4.9E-04				
L		25	3.2E-04				
BN #27	7.49 - 9.10	Loose	3.7E-04				
		15	2.5E-04				
		25	2.5E-04				
BN #28	3.64 - 4.64	Loose	1.1E-03				
		15	5.5E-04				
		25	2.9E-04				
BN #30	4.59 - 5.19	Loose	8.6E-04				
		15	4.9E-04				
		25	3.9E-04				
BN #32	1.48 - 2.08	Loose	9.9E-06				
		15	3.0E-05				
		25	1.1E-05				
BN #32	4.53 - 5.36	Loose	2.3E-04				
		15	2.5E-04				
		25	2.5E-04				
BN #34	0.15 - 1.41	Loose	1.7E-05				
		15	5.0E-06				
		25	2 0E-06				
BN #34	2.90 - 3.40	Loose	9.0E-04				
		15	4.95-04				
		25	4.35-04				
BN #35	1 55 - 2 20	10059	1.35.03				
		15	5 55 07				
	ŀ	25	3.3E-U/				
BN #35	3 33 4 36	20	4.40				
5.7 #00	0.00 - 4.00		1.7E-03				
Ì	ŀ	15	1.62-03				
BN #27	5 82 6 00	20	1.5E-03				
014 #01 0.02 + 0.20 LOOSe		LOOSE	1.8E-03				
		15	1.4E-03				
(1) 1		25	9.9E-04				
(1) Average value from four tests.							

Table 5.1	
Falling Head Hydraulic Conduct	ivity

			Torri Docu	ica one nivesti	Janon		
Borehole	Depth	TE	PID	Borehole	Depth	TE	PID
Number #	(m)	(ppm)	(ppm)	Number #	(m)	(mag)	(maa)
16	4.5	N.D.	4.2	27	9.1	N.D.	61.5
17	4.6	5.6	3.7	27	10.6	50	164
19	1.5	N.D.	622	27	13.6	7	17.1
19	4.5	68	27.6	28	1.6	N.D.	199
19	5.7	33	337	28	3.1	N.D.	5.4
19	8.9	N.D.	26.9	29	3	N.D.	8.3
20	4.6	N.D.	22.3	30	1.4	N.D.	7.6
20	6.1	20	54.6	30	3	8400	85.6
20	7.6	N.D	3.4	30	4.6	N.D.	6.3
21	1.1	N.D.	145	31	7.2	N.D.	5.8
21	3	1300	35.7	32	4	N.D.	5.7
21	4.1	8000	265	33	2.8	8.9	16.1
21	5.7	940	227	34	1.4	N.D.	19.1
21	7.3	N.D.	24.8	35	4.4	N.D.	7.5
22	2.9	N.D	4	36	2.8	N.D.	6.5
22	4.5	26	81.1	37	4.5	N.D.	4.5
22	5.8	N.D.	34.1	37	5.8	13	44.4
22	7.4	N.D.	4.2	37	7.2	N.D.	11.9
23	1.6	40	510	38	4.5	N.D.	7.5
23	3	N.D.	8.8	39	1.5	N.D.	18.6
23	4.5	N.D.	385	40	1.5	330	245
23	6	N.D.	101	40	2.9	N.D.	16.9
23	7.5	N.D.	9.4	41	4.4	N.D.	12.2
24	1.4	N.D.	118	42	3	N.D.	14.1
24	2.9	N.D.	9.5	44	2.8	N.D.	5.4
24	6	19	101	45	1.4	N.D.	68.1
24	7.5	N.D.	11.4	45	3	N.D.	10.1
25	3	N.D.	5.3	46	1.5	N.D.	34.3
25	4.5	N.D.	56	46	5.6	N.D.	7.9
25	6	N.D.	8.3	47	6	N.D.	7.5
26	1.5	6600	464	47	9.1	N.D.	10.5
26	4.5	N.D.	26.2	48	3	N.D.	9.4
26	7.5	N.D.	20.2	48	4.6	N.D.	26.3
26	9.1	N.D.	7.4	49	0.4	2200	-
27	1.5	17000	413	49	3	N.D.	26.9
27	3	4300	391	49A	1.5	2200	130
27	4.4	4200	234	50	4.6	N.D.	10.1
27	5.8	N.D.	11.2	51	1.5	N.D.	7,7
V.D. = Not Detected, Less than Detection Limit							
Detection Limit = 5.0 ppm							

Table 5.2 Total Extractables and Photoionization Detection Results from Detailed Site Investigation



Figure 5.18 Approximate Outline of the Diesel Plume, and the Boreholes used to Create Six Profiles of the Plume



Figure 5.19 Profile of the Diesel Plume, Section A-A



Figure 5.20 Profile of the Diesel Plume, Section B-B



Figure 5.21 Profile of the Diesel Plume, Section C-C



Figure 5.23 Profile of the Diesel Plume, Section E-E







Figure 5.26 Total Extractables and Diesel Plume Size in June (1992)



Figure 5.27 Total Extractables and Diesel Plume Size in September (1992)























Figure 5.33 Moisture Contents from Soil Sampling Periodically





#### Table 5.3 Soil pH and Nutrients

Sample	Depth	pH 1:1 (w/v)	pH 1:2 (w/v)	NH3-N	NO3-N	P04.9		Ele etcia	<b>T</b>
Number	(m)	in Water	0.01 M CaCI2	(ppm of	(opm or	(0000 00	/	Cleculo	Total
(1)		1		ug/g)		ud/a)	(ppm or	(de/m)	Coliform
FW3	1.5	7.1	N.T.	390	52	29/9/	20	(0s/m)	CF0/100 mi
FW3	3	7.8	N.T.	3	<10	< 10	32	4.99	N.1.
FW3	6	7,7	N.T.	13.2	1.0	<u> </u>	12	0.2	N.T.
EW2	1.5	7.7	NT	0.6			24	0.2	N. T.
EW2	3	8.1	NT	17	0	< 1.0		0.8	N.T.
EW2	6	8.1	N T	2.5		<u> (1.0</u>	24	0.2	N.T.
BN #58	1.5	74	NT	0.3		2	30	0.2	N.T.
BN #58	2.8	7.6	N.T.	0.3	9	. <u>1</u>	23	0.2	92000
BN #59	1.3	7.5	N.T.	0.3	< 1.0	1	17	0.2	17000
BN #59	24	4.5	N.7.	37.4	20	44	52	0.4	33
8N #59	43	7 1	N.T.	30.4	22	7	32	0.4	130
BN #60	2.0	7.1	IN. I.	0.6	15	3	23	0.4	79
SN #60	2.0	7.3	N.I.	0.4	1	1	20	0.8	140
BN #60	3.9	- 7.6	N.T.	1.1	2	2	18	0.2	160000
GN #00	0.2	7.5	N. Г.	1.2	1	4	30	0.2	17000
DN #080	1.5	7.1	<u>N.T.</u>	1.5	5	10	52	0.2	23
BN #080	2.7	7.3	<u>N.T.</u>	0.5	< 1.0	1	23	0.2	11
FW #09	0.5	7.2	6.8	N.T.	N.T.	N.T.	N.T.	N.T.	NT
FW #09	1	7.4	6.7	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
FW #09	2	7.5	7.0	N.T.	N.T.	N.T.	N.T.	N.T.	NT
FW #09	3	7.4	8.8	N.T.	N.T.	N.T.	N.T.	N.T.	NT
FW #09	4	7.6	6.8	N.T.	N.T.	N.T.	N.T.	N.T.	NT
FW #09	5	7.6	6.8	N.T.	N.T.	N.T.	NT	NT	NT
BN #62	3.2	7.8	N.T.	3.2	1.8	87	31	02	160000
BN #62	4.2	7.6	N.T.	2.3	1.4	145	34	02	17
BN #62	5.2	7.2	N.T.	20.5	5.6	17	45	0.2	
(1) = Month When Samples Were Collected and Tested in 1993; FW #09 in June:									
BN #08b in August; All Others in September.									
CFU = Colony Forming Units									
N.T. = Not Tested									



Figure 5.35 pH of the Water Samples from Extraction Well and to Feeder Wells























Figure 5.41 Chloride Tracer Test for Feeder Well #03





#### CHAPTER 6

#### DISCUSSION

#### 6.1 Site Investigations

#### 6.1.1 Preliminary

During the preliminary site investigation, a geophysical survey was conducted to determine whether electromagnetic conductivity in decibels would correlate with the diesel fuel concentrations in the ground. The conductivity contours, shown in Figure 5.8, do not correlate with the diesel fuel concentrations or the known location of the diesel plume.

When samples from boreholes #09A and #10A were tested with the photoionization detector, no correlation was apparent between the detector readings and diesel concentrations. The detection methods only detect volatile organic carbons (VOCs), which are low in diesel fuel (in comparison with, say, gasoline).

#### 6.1.2 Detailed

From the detailed site investigation, it was found that the subsurface consists of a thin surface layer (about 0.2 metres) of medium to coarse sand underlain by a 2 to 4 metre thick layer of silt, then silty-sand. The hydraulic conductivities of the silt layer (10<sup>-5</sup> to 10<sup>-7</sup> cm/s) are relatively low when considering oxygen transfer (between the air and soil) and microorganism infiltration. However, dissolved nutrients should be able to pass through the silt layer to the diesel plume. The primary concern about the silt layer dealt with microbial filtration. The silt layer was predominantly well-graded silt containing a small percentage of

fine sand.

The silty-sandy layer, underlying the silt layer, was poorly graded fine sand containing as much as 38 percent silt. The silty-sand layer hydraulic conductivity was in the order of  $10^{-3}$  to  $10^{-4}$  cm/s. Hydraulic conductivities in this order could still pose problems with microorganism filtration, but would pose less of a problem with respect to the transport of nutrients to and through the diesel plume.

The presence of the silt layer indicated that the site was not ideal for in situ bioremediation. However, conducting a pilot project at this location would nevertheless provide information pertaining to in situ bioremediation in silt and silty-sand in a cold northern climate.

The moisture content profiles (Figures 5.15, 5.16, and 5.17) showed a decrease in moisture content in the lower portion of the silt layer and in the silty-sand layer just below the silt layer. The moisture content then gradually increased to about 20%, near the water table. A moisture content of 20% and above probably signified the soil was saturated.

### 6.2 System Designs

The pump-cycle system was designed to circulate groundwater that underwent nutrient addition and aeration through the diesel plume. Also, the ground surface spray system was designed to ensure nutrients would be delivered over the plume on the ground surface and, ideally, infiltrate into and through the plume. The two systems were designed to stimulate microbial activity to enhance biodegradation.

# 6.2.1 Ground Surface Spray System

Ground surface spraying was conducted only in the summer months of 1992 and 1993. Mixing nutrients with water in a tank, then spraying the solution on the ground surface over the diesel plume increased the probability of increasing subsurface nutrient concentrations and moisture content. Higher nutrient concentrations and moisture content. Higher nutrient concentrations and moisture content can increase the rate of biodegradation. The 'even-spray' sprinkler was effective in distributing nutrients and water uniformly, and spraying did aid in increasing the moisture content (Figure 5.32 to 5.34) in and around the diesel plume. The infiltration rate may have varied across the site, based on subsurface characteristics, but moisture and nutrient enhancement did occur (discussed in later sections).

#### 6.2.2 Pump-Cycle System

The pump-cycle system was operational in late August (1992), but the trenches and feeder well #09 were not installed until June (1993). The location of the feeder wells was based on the PID results during the detailed site investigation. However, based on the TE analysis, feeder wells #05, #06, #07 and #08 would have been more effective if they were located about 2 to 3 metres closer to the diesel plume.

Nevertheless, the feeder wells did aid in the remediation process by increasing subsurface nutrient concentrations and moisture content. Feeder well #08 was eventually moved to the edge of the plume and became feeder well #09, infiltration trenches were installed, and an increase in the quantity of nutrients was applied. These changes were made in June (1993) and appeared to lead to the greatest reduction in TE (from June (1993) to

September (1993)). The reduction at this location can be seen by comparing Figure 5.28 to 5.29, and Figure 5.30 to 5.31.

# 6.2.2.1 Chloride Tracer Tests

The two chloride tracer tests in feeder well #03 and borehole #17 were conducted to evaluate: (1) the percentage of the chloride that was recycled, and (2) the cycle time. From the chloride tracer tests, only a small amount of chloride was recycled. Feeder well #03 and borehole #17 (Figures 5.41 and 5.42) showed only 0.12 and 0.06% of the chloride injected was recycled, respectively. Based on this finding, it is unlikely that nutrients injected into the feeder wells had any great probability of reaching the extraction well.

The cycle times for feeder well #03 and borehole #17 were 55 and 75 (or 115 hours), respectively. (The percent recycled for borehole #17 was based on the second peak at 115 hours, since the quantity recycled was greater.) The tracer tests indicated the system did recycle, and that the cycle time was a function of both injection location (distance) and subsurface conditions.

#### 6.3 Tested and Monitored Parameters

A variety of different soil and water parameters were tested and monitored and are discussed separately in sections 6.3.1 and 6.3.2, respectively.

# 6.3.1 Soil

Soil parameters tested included pH, nutrients, and total coliform. These three

parameters are discussed individually. Various soil samples were also tested for TE and moisture content, and the finding are discussed in section 6.4.

#### 6.3.1.1 pH

Soil pH values are shown in Table 5.3. Since, initial soil pH values were not obtained, it was not possible to determine whether nutrients either sprayed on the ground surface or injected into the feeder wells altered the soil pH. However, the final soil pH ranged from 7.1 to 8.1 (1:1 w/v in water) within and around the diesel plume. pH values in this range usually do not require adjustment, and should not impede microbial growth or biodegradation.

The form and concentration of the nutrients which were applied should not have altered the pH by any significant amount. Since, the soil pH from borehole #08b was within the pH range of those soil samples collected in the contaminated plume in September (1993), it could be assumed nutrient enhancement did not adversely effect the soil pH and impede bioremediation.

#### 6.3.1.2 Nutrient Levels

Soil nutrient concentrations are shown in Table 5.3. In August (1993) soil nutrients were obtained from borehole #08b, about 23 metres away from the diesel plume (Figure 5.25). Since, the location near borehole #08b was not treated, nutrient concentrations obtained there were assumed to represent initial (background) nutrient concentrations at the site. According to borehole #08b, the original nutrient concentrations (ammonium-nitrogen, nitrate-nitrogen, orthophosphate and potassium) and total coliform (colony forming units

(CFU) per 100 ml) decreased slightly with depth.

All other soil samples (shown in Table 5.3) tested for nutrients were obtained in September (1993). Soil samples from borehole FW3 showed significant concentrations of ammonium-nitrogen and nitrate-nitrogen about 1.5 metres below ground surface. The high nitrogen concentrations probably resulted from the ammonium chloride injected into feeder well #03 during the tracer tests. The ammonium-chloride would breakdown to form chloride ions and ammonium- & nitrate-nitrogen. Borehole FW3 was located only 0.5 metres away from feeder well #03. Overflow from feeder well #03, subsurface seepage during the tracer tests, ground surface application and/or spraying are probably the primary reasons for the measured high nitrogen concentrations. All nutrient concentrations decreased at a depth of 3 metres, and then increased slightly at a depth of 6 metres.

Low nutrient concentrations were observed for soil samples from borehole EW2, except for the nitrate-nitrogen concentration of 60 ppm at a depth of 1.5 metres. Again, overflow from feeder well #03, subsurface seepage during the chloride tracer tests, ground surface application and/or spraying are probably the primary reasons for the reading at 1.5 metres. Both boreholes #58 and #60 had low nutrient concentrations, relative to the background values, except at a depth of 1.5 metres, where borehole #58 had a nitratenitrogen concentration of 9 ppm, about twice the assumed background value.

At a depth of about 1.5 metres, borehole #59 had about 25 times the ammoniumnitrogen assumed background value and 4 times the nitrate-nitrogen assumed background value. The ammonium-nitrogen concentration decreased slightly for the next 2 metres while the nitrate-nitrogen basically remained the same; then both decreased with increasing depth. Orthophosphate concentrations were about 4 and 10 times the assumed background values at a depth of 1.5 and 2.5 metres, respectively.

Soil samples from borehole #62 (0.2 metres from feeder well #09) had relatively low ammonium- and nitrate-nitrogen concentrations at depths 3.2 and 4.2 metres. However, at the depth of 5.2 metres, the ammonium- and nitrate-nitrogen concentrations are about 9 and 4 times higher, respectively. Orthophosphate concentrations in these three samples should be adequate for microbial growth.

The seventeen soil samples tested for nutrients in the diesel plume indicate that the methods used to apply the nutrients were effective. Some of the soil samples did have higher nutrient concentrations than others, but microbial activity, dilution, and advection could account for the differences in nutrient concentrations with depth and location. Also, preferential flow within the silt and silty-sand layers could also account for the variations in nutrient concentrations, and microbial up-take to degrade the diesel fuel.

The most notable effect the feeder wells had is on soil samples from borehole #62. These samples were obtained from within 0.2 metres of feeder well #09. The nutrient concentrations reveal the feeder wells were effective in increasing the nutrient concentrations close to and below each well. Nutrient concentrations from borehole #59 imply the trenches could have aided in increasing nutrient concentrations in the plume. In borehole #59 high nutrient concentrations were measured in the silt layer, which implies nutrients penetrated into and probably through the layer. Since nutrient concentrations varied with depth and location, it is probable that nutrient concentrations within the plume increased above their initial concentrations at various times.

#### 6.3.1.3 Total Coliform Counts

Total coliform counts from borehole #08b was 23 and 11 CFU per 100 ml at depths 1.5 and 2.7 metres, respectively. Boreholes #58 and #59 had 92000 and 33 CFU per 100 ml at the depth of about 1.5 metres, respectively, and 17000 and 130 CFU per 100 ml at the depth of about 2.7 metres, respectively. Borehole #60, at a depth 2.8 metres, had 140 CFU per 100 ml. However, at depths of 3.9 and 6.2 metres, borehole #60 had 160000 and 17000 CFU per 100 ml, respectively. Borehole #62 had 160000, 17 and 33 CFU per 100 ml at depths 3.2, 4.2 and 5.2 metres.

Since no biological counts were conducted before treatment began, the total coliform counts from borehole #08b were assumed to represent the initial (background) values within the diesel plume. Assuming this, all samples within the plume had higher final CFU per 100 ml. Most notable are the samples from boreholes #58, #60 and #62.

In borehole #58, the samples with high CFU are just above and below the silt layer and in boreholes #60 and #62, the samples with high CFU are in the silty-sand layer. Even though analysis of soil nutrients indicated low levels of nutrients in some zones, nutrients were delivered to the silt and silty-sand according to the coliform counts. However, the low coliform counts in the silt probably imply that the microbes had difficulty penetrating this material and/or an insufficient amount of nutrients were available to stimulate microbial reproduction at certain locations.

Shown in Figures 5.29 and 5.31 are total coliform counts with respect to the diesel plume. Total coliform counts are high in locations that contain or had contained high TE readings. These high coliform counts within the plume imply bioremediation is taking place,

and probably had been taking place for some time.

A low temperature will contribute to low coliform counts. Since temperature probes were not inserted directly into the ground at various depths, the water temperature reading in the feeder wells and the two temperature readings in boreholes #52, #53, and #54 are assumed to be indicative of the soil temperature. Based on this assumption, the in situ temperature mainly ranged from 5°C to 12°C throughout the winter months. This indicates the subsurface did not freeze, and, in fact, the subsurface was maintained above normal soil temperatures (see Figures 5.4 to 5.7 for normal soil temperatures for the Flin Flon region). The monitored water temperatures are lower than the ideal temperature of 27°C for efficient biodegradation (Song et al., 1990), but biodegradation will still occur at a lower rate (Autry and Ellis, 1992). The affect temperature has on the rate of biodegradation of crude oil is shown in Figure 3.0.

#### 6.3.2 Pump-Cycle System

The pump-cycle system was monitored for pH, nutrients, total organic carbon and dissolved oxygen at different times during remediation. Each of these parameters is discussed below.

#### 6.3.2.1 pH

The extraction well (influent) and feeder well (effluent) pHs were basically the same at any time and varied concurrently (Figure 5.35). They fluctuated between 6.8 and 8.9. Initially, both pHs were above 8, but after three weeks the pHs decreased below 8. Only periodically, in April and May (1993), did they once again increase above 8. Small fluctuations in pH could be caused by abiotic or biotic reactions. A pH above 8.0 could inhibit microbial growth and hydrocarbon degradation. The ground surface spraying, feeder well injections, or the chloride tracer tests did not appear to adversely effect the influent or effluent pHs.

#### 6.3.2.2 Nutrient Levels

Extraction well (influent) and feeder well (effluent) ammonia-nitrogen and nitrate- & nitrite-nitrogen are shown in Figures 5.37 and 5.38, respectively. From Figure 5.37 it is seen that the effluent ammonia-nitrogen was always greater than the influent value, except in January (1993). The lower effluent concentrations in January (1993) were probably due to insufficient nutrient addition or microbial utilization within the tanks. Effluent concentrations should always have been greater than influent concentrations because nutrients were added to the water in the tanks on a regular basis.

Having a constant level of ammonia-nitrogen or nitrate-nitrogen in the effluent was not possible because the nutrients were added on a weekly basis. Initially, the nutrient forms which were added did not dissolve immediately, (i.e. they released nitrogen and phosphorus slowly). Therefore, the theoretical nutrient concentrations based on the amount added did not correspond to the concentrations analyzed. Small quantities of ammonia-nitrate were not added until late July (1993).

Based on the chloride tracer tests, only small concentrations of nutrients would be recycled. If not utilized by the microbes, the nutrients would simply become diluted and

escape the system. Based on the percent of chloride recycled in feeder well #03, high effluent nutrient concentrations should not have led to high influent nutrient concentrations. This seems to have been the case based on the findings discussed below.

From February to June (1993) effluent ammonia-nitrogen concentrations fluctuated between 4 and 17 mg/l. In July (1993), effluent concentrations significantly increased. The one extremely high effluent concentration (~1600 mg/l) was probably caused by sampling too soon after the nutrients were added to tank #2. If samples were collected soon after nutrient addition, and a uniform mixture throughout tank #2 was not obtained, an incorrect too high concentration reading could result.

The influent ammonia-nitrogen concentrations, except for three samples, remained below 4 mg/l throughout the treatment processes. The two high influent concentrations, in July (1993), were probably caused by seepage into the extraction well during ground surface spraying or immediately after direct ground surface nutrient application.

From Figures 5.37 and 5.38, it appears that about 1 to 3 mg/l of effluent ammonianitrogen was oxidized to nitrate- & nitrite-nitrogen. A small increase in effluent nitrate- & nitrite-nitrogen occurred after February (1993). All samples of influent nitrate- & nitritenitrogen concentrations collected before July (1993) were below 2.0 mg/l and basically remained constant. Thus, the high post-February effluent nitrate- & nitrite-nitrogen concentrations did not appear to have effected the influent concentrations. In July (1993) two influent nitrate- & nitrite-nitrogen samples were higher than the norm. However, seepage into the extraction well could have occurred, and was the probable cause.

Before July (1993), influent orthophosphate concentrations (Figure 5.39) were

basically non-existent, while effluent concentrations fluctuated between 0.5 and 5.5 mg/l. This findings reinforced the conclusion of the tracer tests and that there was little recycling or short-circuiting occurring in the system.

In July (1993), influent and effluent samples were tested for total phosphorus by mistake. Three of the effluent total phosphorus concentrations (after July, 1993) were relatively high. However, since no tests for total phosphorus were done initially, and total phosphorus is the sum of organic and inorganic phosphorus, not much use can be made of this information.

## 6.3.2.3 Total Organic Carbon

Total Organic Carbon (TOC) test results on samples from the extraction well (influent) and from the feeder wells (effluent) are shown in Figure 5.36. Influent and effluent TOCs fluctuated constantly, and in November and December (1992) some of the effluent TOCs were substantially above the norm. Initially, the effluent TOC was greater than the influent, but as treatment progressed, the effluent TOC became less than the influent.

When the pump-cycle system was first operational, a substantial amount of dissolved and undissolved diesel fuel was pumped into the tanks. A substantial amount of diesel fuel floated on the water surface in tank #1, and a strong odour of diesel fuel was present. Unfortunately no samples were collected and tested for TOC at this time. Sampling did not start until one week later.

The one week influent TOC was about 33 mg/l. The TOC decreased to 10 to 15 mg/l within a few weeks, which indicates a flush of diesel fuel from the ground had occurred.

After the system had been operational for a few weeks, biomass growth was present in both tanks.

High influent and effluent TOCs were recorded in November and December (1992). Percolating water from the pump-cycle system could have finally reached parts of the diesel plume. Microorganisms producing the required enzymes for degradation could have released diesel fuel from the surface of the sand grains, thereby increasing the influent TOC. After December (1992), effluent TOCs were mostly lower than influent TOCs. Two possible reasons are air-stripping and/or microbial degradation.

## 6.3.2.4 Dissolved Oxygen

Testing the influent and effluent for dissolved oxygen (DO) was not conducted on a regular basis before June (1993) (Figure 5.40). Initially, the influent and effluent DO was above 2.0 mg/l. However, in June (1993) additional testing revealed the effluent DO was near or below 2.0 mg/l, and less than the influent DO. This drop in DO could have been due to the oxygen demand of aerobic microorganisms in the tanks. DO below 2 mg/l can inhibit aerobic biodegradation. At this time, an additional aerator was installed and the effluent DO increased.

Influent DO fluctuated between 2.0 mg/l and 5.0 mg/l, basically. The influent DO did appear to increase with time after the additional aerator was installed. However, based on the tracer tests which showed only a small percentage of chloride was recycled, it is unlikely that the additional aerator caused the change in influent DO.

While adding the additional aerator did increase the effluent DO concentrations,
nevertheless three subsequent tests gave low effluent DO values. The low DO values may have resulted from the water samples having been taken before a fresh batch of nutrients dissolved or after incomplete mixing of the nutrients. Oxidation of the ammonia-nitrogen to nitrate-nitrogen could decrease the DO in the BOD bottles.

## 6.4 Soil Sampling Periodically

Soil samples from various depths were obtained periodically near boreholes #21, #27, and #30. They were tested for TE and moisture content in September (1992), June (1993) and September (1993). The results are discussed below.

## **6.4.1** Total Extractables

Figures 5.26, 5.27, 5.28 and 5.29 are the TE results from soil samples taken at various times. Estimated diesel plume outlines are given (borehole locations shown in Figure 5.25). Figure 5.26 illustrates the initial plume based on the earliest measured TE concentrations. The remaining three figures depict the plume in September (1992), June (1993) and September (1993).

The most significant TE reduction, from June (1992) to September (1992), was near borehole #30. At a depth of 3 metres, the TE concentration decreased from 8400 to 180 ppm in about 3 months. However, near borehole #27, the TE increased from 17000 to 32000 ppm during the same time period. The pump-cycle system may have caused contaminant movement through the ground fissures and a `puddling' of the contaminant in new areas.

Additional samples collected and tested for TE in June (1993) at the same location

and depth near borehole #27 are substantially below the 32000 ppm recorded in September (1992). Also, comparing other June (1992) with June (1993) TE concentrations, at the same depth, indicates a reduction from 17000 to 13000 ppm. From September (1992) to June (1993), TE concentrations near borehole #21 also reduced from 7500 to 2600 ppm. Basically, the overall TE concentrations decreased from September (1992) to June (1993).

Treatment from June (1993) to September (1993) showed a significant contaminant reduction near borehole #27 from 8400 to 21 ppm, 13000 to 12 ppm and 7200 to 35 ppm at depths 1.2, 1.5 and 2 metres, respectively. However, during this same time period, an increase from 430 to 2000 ppm was recorded near borehole #30 at a depth of 3 metres. Also, increases near borehole #21 from 2600 to 6500 ppm and 2200 to 7500 ppm were recorded at depths 3.5 and 5.5 metres, respectively. These increases confirm that the plume migrated somewhat through the ground during the remediation process. However, comparing Figure 5.26 to 5.29, the overall plume size decreased from June (1992) to September (1993).

To evaluate whether the reduction near borehole #27 was caused by remediation or contaminant movement, a cross-section was drawn through feeder well #09, and boreholes #56, #59, #61 and #62 (Figures 5.30 and 5.31). These figures clearly indicate a reduction in the diesel plume size took place from June (1993) to September (1993) near (the initial) borehole #27. The TE tests in June (1993), from feeder well #09 and borehole #56 (near borehole #27), revealed carbon molecules in the C<sub>9</sub> to C<sub>25</sub> and C<sub>7</sub> to C<sub>20</sub> range, a pattern indicative of diesel fuel. However, in September (1993) analysis showed major components in the C<sub>9</sub> to C<sub>20</sub> and C<sub>15</sub> to C<sub>20</sub> carbon range, with no discernable pattern. Also, high total coliform counts were recorded in boreholes #58 (near borehole #30), #60 (near borehole #21)

and #62 (near feeder well #09) in September (1993). The change in carbon components and the measured biological counts indicate remediation had occurred during this time period, and the remediation process was probably biological. Hence, the reductions in TE may not have been due to contaminant migration. The fact that the plume size decreased also supports the contention that remediation took place.

## 6.4.2 Moisture Content

Moisture contents from the same three groups of soil samples collected and analyzed for TE are shown in Figures 5.32, 5.33 and 5.34. From Figure 5.32, corresponding to boreholes #21, #54, #57 and #60, the moisture content did increase periodically within the diesel plume.

From Figure 5.33, corresponding to boreholes #27, #53, #56 and #59, the moisture content did increase in September (1992), June (1993) and September (1993), from June (1992) within the plume. From Figure 5.34, boreholes #30, #52, #55 and #58, the moisture content increased from June (1992) to September (1992), but, then decreased and remained near the original values.

Moisture content can effect the rate of biodegradation. A moisture content corresponding to a degree of saturation greater than 25% should be sufficient for biodegradation. However, as moisture content increases, so can the rate of biodegradation (Hinchee, 1989). The moisture content from the three borehole groups (Figures 5.32, 5.33 and 5.34) did increase periodically during treatment. Increases in the moisture content imply nutrients and possibly microorganisms were delivered throughout the diesel plume, which

$$n = \frac{e}{1 + e}$$
(7)

where:

 $\eta = porosity$ 

$$h_c \rho_w g = \frac{2T}{r} \tag{8}$$

where:

from BN #10:

assumptions are:

therefore:

 $h_c = capillary pressure [L]$ T = surface tension [F/L]r = radius of pores [L] mass of wet sample = 399.24 g mass of dry sample = 333.26 g  $h_{c} = 0.2 m$ S = 100%  $G_{s} = 2.65$  $\rho_w = 1000 \text{ kg/m}^3$ T = 0.072 N/m $\rho_w = 1000 \text{ kg/m}^3$  $g = 9.81 \text{ m/s}^2$ w = 19.8% e = 0.525 $\rho_{sat} = 2082 \text{ kg/m}^3$ n = 0.34 $r = 7.34 \ 10^{-5} \text{ m or } 73.4 \ \mu\text{m} \ (147 \ \mu\text{m in diameter})$ 

100

#### CHAPTER 7

## CONCLUSIONS

1) High coliform counts in both the silt and silt-sand layers indicate that the conditions for enhanced in situ bioremediation of the diesel fuel were developed. Within 14 months, the diesel plume had decreased from about 260 m<sup>3</sup> to about 183 m<sup>3</sup>, a 30% improvement.

2) The temperatures which were recorded in the wells throughout the winter confirm that the thermal protective covering was adequate to maintain system operations, and prevent subsurface freezing. Based on the reduction of the diesel concentrations from the boreholes drilled in September (1992) and in June (1993), the covering maintained adequately high temperatures to sustain in situ bioremediation.

3) Since no surfactants or emulsifiers were used, they are not necessarily required to degrade diesel fuel in a cold climate.

4) Both ground surface spraying and the pump-cycle system were effective in increasing subsurface nutrient and moisture conditions. Some of the feeder wells proved not to be in optimum locations and therefore, they did not contribute much to the remediation process.

5) When the pump-cycle system was made operational, a film layer indicative to biomass growth was noticed in the tanks within two weeks. This implies that a sufficient amount of

diesel fuel was being washed out with the groundwater to maintain microbial activity in the tanks, as no other carbon source was present.

6) Photoionization detection was not a helpful method for determining diesel fuel concentrations in soil, probably due to the low percentage of volatile hydrocarbons in diesel fuel.

## **CHAPTER 8**

## SIGNIFICANCE OF RESEARCH

This research was undertaken to evaluate whether in situ bioremediation could be sustained year-round in a cold northern climate using a simple pump-cycle system. Experience elsewhere has shown that bioremediation in silts or silty-sands requires longer time, as compared to coarse sand and gravel. The remediation time of 14 months associated with this research led to an estimated 30% reduction in the diesel plume size. This reduction represents a clean-up rate that is slow even for silt or silty-sand (in a warm climate). A subsurface temperature in the order of 5°C to 12°C no doubt contributed to the slow rate.

Ground surface spraying and the pump-cycle system were effective in delivering nutrients to the diesel plume. The pump-cycle system functioned well, and was economical to install. A completely automated pump-cycle system can be established in remote northern locations where contamination has occurred and in situ bioremediation is desirable.

From these observations, it is concluded that when the time required for remediation is not a factor (that is to say where there is no immediate human or ecological threat as a result of contamination), in situ bioremediation is a viable remediation option in remote locations in a cold northern climate.

#### **CHAPTER 9**

## RECOMMENDATIONS

1) Photoionization detection and electromagnetic detection are not reliable methods to use to evaluate in situ diesel fuel contamination. A better detection method is required.

2) At a site containing a surface silt layer trenching through the silt layer to the underlying contaminated soil should be considered to improve the infiltration rate of nutrient rich water.

3) Fully automated systems would improve system control, in particular nutrient delivery, and would reduce the amount of on site management that is required.

4) Consideration should be given to warming-up the ground at northern sites. Methods may include, steam injection, heated water, or heated air.

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# APPENDIX A



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis



Grain Size Analysis

# APPENDIX B

Calculations conducted to obtain the initial and final diesel plume volumes; based on the 1000 ppm contour. Shown on the following pages are the figures used to obtain the volumes. The initial volume,  $V_{i}$ , was calculated from equations (i), (ii), and (iii). The final volume was calculated from equations (iv), (v), (vi), and (vii). The percent remediated was calculated from equation (viii), and found to be ~ 30%.

$$V_{i} = A_{a-a} * L_{a} + A_{b-b} * L_{b} + A_{c-c} * L_{c}$$
(i)

where:  $A_{a-a}$ ,  $A_{b-b}$ , and  $A_{c-c}$  = inner area of the 1000 ppm contour in section A-A, section B-B, and section C-C, respectively.

 $L_{a}$ ,  $L_{b}$  and  $L_{c}$  = average length of the 1000 ppm contour effected by the area  $A_{a-a}$ ,  $A_{b-b}$ , and  $A_{c-c}$ , respective, as shown in a plan view.

$$L_{a} = \frac{A_{ai}}{W_{ai}}, \quad L_{b} = \frac{A_{bi}}{W_{ai}}, \quad L_{c} = \frac{A_{ci}}{W_{ci}}$$
(ii)

where:

 $A_{ab}$ ,  $A_{bi}$ , and  $A_{ci}$  = initial areas of section A-A, section B-B, and section C-C, respectively, as shown in a plan view.

 $W_{ab}$ ,  $W_{bi}$ ,  $W_{ci}$  = average widths effected by areas  $A_{ai}$ ,  $A_{bi}$ , and  $A_{ci}$ , respectively.

$$W_{ai} = \frac{\sum W_{aix}}{x}, \quad W_{bi} = \frac{\sum W_{bix}}{x}, \quad W_{ci} = \frac{\sum W_{aix}}{x}, \quad x \ge 2$$
(iii)

$$V_r = A_r * W_{rp} \tag{iv}$$

where:

 $V_r$  = volume of soil remediated

 $A_r$  = area of soil remediated as shown in cross-section.

 $W_{rp}$  = average width of the remediated soil as shown in a plan view.

$$A_r = A_{June/92} - A_{Sept/93} \tag{V}$$

where:

 $A_{June/92}$ , and  $A_{Sept./93}$  = the cross-sections of the plume in June (1992), and September (1993), respectively.

$$W_{rp} = \frac{A_{rp}}{L_{rp}}$$
(vi)

where:  $A_{rp}$  = area of soil remediated as shown in a plan view in September (1993).  $L_{rp}$  = average length of  $A_{rp}$  in a plan view in September (1993).

$$L_{rp} = \frac{\sum L_{rpx}}{x} \quad x \ge 2 \tag{vii}$$

$$R = \frac{V_r}{V_i} 100$$
 (viii)

where:

 $\mathbf{R}$  = percent of soil remediated above 1000 ppm.

therefore:  $A_{a-a}$ , from section A-A = 11.5 m<sup>2</sup>

 $A_{b-b}$ , from section B-B = 31.3 m<sup>2</sup>

 $A_{c-c}$ , from section C-C = 28.5 m<sup>2</sup>

 $A_{ai} = 17 \text{ m}^2$ 

$$A_{bi} = 30 \text{ m}^2$$

$$A_{ci} = 29 \text{ m}^2$$

 $W_{ai}$ , of area  $A_{ai} = 5.8 \text{ m}$ 

 $W_{bi}, of area A_{bi} = 8.0 m$  $W_{ci}, of area A_{ci} = 7.4 m$  $L_{a} = 2.9 m$  $L_{b} = 3.7 m$  $L_{c} = 3.9 m$  $V_{i} = 260 m^{3}$  $A_{June/92} = 44 m^{2}$  $A_{Sept./93} = 26.7 m^{2}$  $A_{r} = 17.3 m^{2}$  $A_{rp} = 23.2 m^{2}$  $L_{rp} = 5.2 m$  $W_{rp} = 4.5 m$  $V_{r} = 77 m_{3}$ R = 30%



Initial Approximate Contour of 1000 ppm of the Diesel Plume



Profile of the Diesel Plume, Section A-A



Profile of the Diesel Plume, Section B-B



Profile of the Diesel Plume, Section C-C







Total Extractables and Diesel Plume Size in June (1992)



Total Extractables and Diesel Plume Size in September (1993)

# APPENDIX C

Date	Borehole	Depth	TE	Moistur	Date	Borehole	Depth	TF	Moisture
	Number #	(m)	(ppm)	Content		Number #	(m)	(0000)	Content
June, 1992	16	4.5	N.D.	1.8	June, 1992	31	7.2		19.0
June, 1992	17	4.6	5.6 (1)	3.8	June, 1992	32	4	N D	29
June, 1992	19	1.5	N.D.	16.4	June, 1992	33	2.8	89(1)	14
June, 1992	19	4.5	68 (2)	10.2	June, 1992	34	1.4	N D	16.8
June, 1992	19	5.7	33 (3)	3.5	June, 1992	35	44	ND	33
June, 1992	19	8.9	N.D.	18.4	June, 1992	36	28	N D	11.6
June, 1992	20	4.6	N.D.	17.2	June, 1992	37	45	N.D.	14.2
June, 1992	20	6.1	20 (3)	5.6	June, 1992	37	5.8	13 (3)	26
June, 1992	20	7.6	N.D	19.2	June 1992	37	7.2		14.0
June, 1992	21	1.1	N.D.	15.1	June 1992	38	45	ND.	19.0
June, 1992	21	3	1300 (2)	12.2	June 1992	39	15	N.D.	15.7
June, 1992	21	4.1	8000 (2)	2.6	June, 1992	40	1.0	330 (2)	13.6
June, 1992	21	5.7	940 (2)	7.7	June 1992	40	29	550 (2) N D	15.0
June, 1992	21	7.3	N.D.	18.2	June 1992	40	Δ.Ο	N.D.	10.0
June, 1992	22	2.9	N.D	12.7	June 1992	42	 2	N.D.	57
June, 1992	22	4.5	26 (3)	3.3	June 1992	44	28	N.D.	5.7
June, 1992	22	5.8	N.D.	4.5	June, 1992	45	14	N.D.	14.5
June, 1992	22	7.4	N.D.	18.8	June 1992	45	3	N.D.	26
June, 1992	23	1.6	40 (3)	17.9	June, 1992	46	15	N.D.	73
June, 1992	23	3	N.D.	12.2	June, 1992	46	5.6	N.D.	0.1
June, 1992	23	4.5	N.D.	7.5	June, 1992	47	6	ND.	1/ 0
June, 1992	23	<sup>`</sup> 6	N.D.	5.4	June 1992	47	91	N.D.	19.0
June, 1992	23	7.5	N.D.	18.0	June 1992	48	3	N.D.	19.0
June, 1992	24	1.4	N.D.	21.2	June 1992	48	4.6	N.D.	20.0
June, 1992	24	2.9	N.D.	19.1	June 1992	49	4.0 0.4	2200 (5)	12.6
June, 1992	24	6	19 (3)	28	June 1992	40	3	2200 (0)	12.0
June, 1992	24	7.5	N.D.	18.7	June 1992	494	15	2200 (5)	9.0
June, 1992	25	3	N.D.	42	Juné 1992	50	1.0	2200 (3)	60
June, 1992	25	4.5	N.D.	43	June 1992	51	1.5	N.D.	7.2
June, 1992	25	6	N.D.	18.6	Sept 1992	52	0.66 to 1.16	N.D.	21.0
June, 1992	26	1.5	6600 (2)	17.8	Sept. 1992	52	1 16 to 1 5	N.D.	13.9
June, 1992	26	4.5	N.D.	3.6	Sept 1992	52	2 3 to 2 62	N.D.	14.4
June, 1992	26	7.5	N.D.	18.2	Sept. 1992	52	2 62 to 3 05	180 (6)	47
June, 1992	26	9.1	N.D.	16.8	Sept. 1992	52	3 05 to 3 67	20 (7)	10.3
June, 1992	27	1.5	17000 (2)	9.5	Sept. 1992	52	3 67 to 4 5		22.3
June, 1992	27	3	4300 (2)	8.0	Sept. 1992	52	45 to 54	ND.	22.3
June, 1992	27	4.4	4200 (2)	4.7	Sept. 1992	52	54 to 61	72 (8)	10.1
June, 1992	27	5.8	N.D.	7.8	Sept. 1992	52	66 to 72		21.1
June, 1992	27	9.1	N.D.	0.5	Sept. 1992	53	0.4 to 0.6	1600 (6)	15.6
June, 1992	27	10.6	50 (3)	19.1	Sept. 1992	53	0.6 to 1.0		14.0
June, 1992	27	13.6	7 (4)	15.9	Sept., 1992	53	1.0 to 1.2	3800 (6)	17.0
June, 1992	28	1.6	N.D.	18.9	Sept., 1992	53	1.2 to 1.6	32000 (6)	14 4
June, 1992	28	3.1	N.D.	7,0	Sept., 1992	53	1.6 to 1.9	12000 (0)	15.6
June, 1992	29	3	N.D.	14.3	Sept. 1992	53	1.9 to 2.2	9300 (6)	14.0
June, 1992	30	1.4	N.D.	11.9	Sept., 1992	53	2.2 to 3.0	7300 (6)	75
June, 1992	30	3	8400 (2)	2.6	Sept., 1992	53	3.0 to 4.5	4800 (6)	10.4
June, 1992	30	4.6	N.D.	8.0	Sept., 1992	53	4.5 to 6.0	N.D.	8.1

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Date	Borehole	Depth	TE	Moisture	Date	Borehole	Depth	TE	Moisture
	Number #	(m)	(ppm)	Content		Number #	(m)	(ppm)	Content
Sept., 1992	53	6.1 to 7.0	N.D.	23.0	Sept., 1993	58	2.7 to 3.0	2000 (6)	5.3
Sept., 1992	53	7.0 to 7.5	N.D.	21.5	Sept., 1993	58	3.0 to 3.3	30 (6)	6.3
Sept., 1992	54	0.2 to 0.9	310 (6)	13.8	Sept., 1993	59	1.0 to 1.2	21 (9)	9.6
Sept., 1992	54	0.9 to 1.5	N.D.	17.9	Sept., 1993	59	1.2 to 1.6	12 (9)	9.8
Sept., 1992	54	1.5 to 2.35	120 (8)	16.0	Sept., 1993	59	2.2 to 2.5	35 (9)	13.1
Sept., 1992	54	2.35 to 3.0	N.D.	14.8	Sept., 1993	59	4.2 to 4.5	36 (9)	15.2
Sept., 1992	54	3.05 to 3.9	4100 (6)	15.1	Sept., 1993	59	4.7 to 5.0	16 (9)	16.3
Sept., 1992	54	3.9 to 4.5	7500 (6)	4.7	Sept., 1993	60	2.7 to 3.05	N.D.	9.9
Sept., 1992	54	4.5 to 6.0	7000 (6)	3.4	Sept., 1993	60	3.8 to 4.1	6500 (10)	5.6
Sept., 1992	54	6.1 to 6.7	N.D.	17.9	Sept., 1993	60	5.4 to 5.7	7500 (6)	6.0
Sept., 1992	54	6.7 to 6.9	N.D.	25.0	Sept., 1993	60	6.0 to 6.3	220 (6)	15.2
Sept., 1992	54	6.9 to 7.6	N.D.	22.6	June, 1992	09	1.5 to 2.0	3900	
June, 1993	55	1.4 to 1.7	N.D.	25.9	Sept., 1993	61	1.5 to 2.0	2800 (10)	11.5
June, 1993	55	2.7 to 3.0	430 (9)	3.8	June, 1993	F.W. #09	3.1 ot 3.2	3000 (11)	2.8
June, 1993	55	3.0 to 3.3	100 (9)	5.2	June, 1993	F.W. #09	4.0 to 4.1	2400 (11)	5.3
June, 1993	56	1.0 to 1.2	8400 (9)	25.7	June, 1993	F.W. #09	5.0 to 5.1	16 (8)	9.9
June, 1993	56	1.2 to 1.6	13000 (9)	27.7	Sept., 1993	62	3.1 ot 3.2	650 (12)	5.3
June, 1993	56	2.2 to 2.5	7200 (9)	23.7	Sept., 1993	62	4.0 to 4.1	N.D.	7.7
June, 1993	56	4.2 to 4.5	180 (9)	12.8	Sept., 1993	62	5.0 to 5.1	N.D.	16.8
June, 1993	56	4.7 to 5.0	200 (9)	6.2	Sept., 1993	FW3	1.5	3000 (6)	20.7
June, 1993	57	2.7 to 3.05	N.D.	13.4	Sept., 1993	FW3	3	N.D.	4.6
June, 1993	57	3.8 to 4.1	2600 (9)	4.8	Sept., 1993	FW3	6	17 (12)	10.7
June, 1993	57	5.4 to 5.7	2200 (9)	21.5	Sept., 1993	EW2	1.5	1900 (6)	11.9
June, 1993	57	6.0 to 6.3	100 (9)	12.4	Sept., 1993	EW2	3	12000 (6)	21.8
Sept., 1993	58	1.4 to 1.7	N.D.	13.6	Sept., 1993	EW2	6	58 (6)	7.8

N.D. = Not Detected, Detection Limit = 5.0 ppm

1. GC/FID analysis of total extractables showed major components in the C13 - C18 carbon range with no discernable pattern.

2. GC/FID analysis of total extractables showed major components in the C7 - C20 carbon range with a pattern indicative of diesel.

3. GC/FID analysis of total extractables showed major components in the C10 - C18 carbon range indicative of weathered diesel.

4. GC/FID analysis of total extractables showed major components in the C16 - C20 carbon range with heavier components which had no discernable pattern.

5. GC/FID analysis of total extractables showed major components in the C7 - C20 carbon range with a pattern indicative of diesel, heavier components were also present.

6. GC/FID analysis of total extractables showed major components in the C9 - C20 carbon range with a pattern indicative of diesel.

7. GC/FID analysis of total extractables showed major components in the C18 - C30 carbon range with no discernable pattern.

8. GC/FID analysis of total extractables showed major components in the C11 - C20 carbon range with no discernable pattern.

9. GC/FID analysis of total extractables showed major components in the C15 - C20 carbon range with no discernable pattern.

10. GC/FID analysis of total extractables showed major components in the C7 - C20 carbon range with a pattern indicative of diesel.

11. GC/FID analysis of total extractables showed major components in the C9 - C25 carbon range with a pattern indicative of diesel.

12. GC/FID analysis of total extractables showed major components in the C9 - C20 carbon range with no discernable pattern.
## APPENDIX D

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		pH	pH		TOC	NH3	NH3	PO4	PO4	NO3	NO3
	Date	E.W.	.  F.W	E.W.	F.W.	E.W.	<b>F.W</b> .	E.W.	<b>F.W</b> .	NO2	NO2
L										F.W.	E.W.
	Aug. 5/92	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
	11	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
	12	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
	26	N.T.	N.T.	16.58	N.T.	N.T.	NT	NT	NT	NT	NT
	28	N.T.	N.T.	9.014	22.92	NT	NT	NT	NT	NT	NT
	Sept. 3	NT	NT	12 44	11 47	NIT		NIT		NIT	
	10	NT	NT	14 04	16.69	NT	NIT			N.T.	
	17	NT		14.10	17.00	N.T.				N. I.	N.T.
	22	N.T.		14.12	17.91	N.1.	N.1.	N.1.	N.1.	N.1.	N.T.
	20	N.1.	N.I.	16.99	25.26	N.1.	N.1.	N.T.	N.T.	N.T.	N.T.
	UCI. 15	N.I.	N.1.	16.44	20.5	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
	18	N.T.	N.T.	12.11	13.67	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
	22	N.T.	N.T.	21.62	27.46	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
	29	N.T.	N.T.	21.27	22.84	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
	Nov. 5	N.T.	N.T.	18.5	16.27	N.T.	N.T.	N.T.	N.T.	N.T.	N.T.
	19	N.T.	N.T.	55.45	44.94	N.T.	N.T.	N.T.	NT	NT	NT
	26	N.T.	N.T.	20.2	69.57	N.T.	N.T.	NT	NT	NT	NT
	Dec. 3	N.T.	N.T.	35.22	42.73	NT	NT	NT	NT	NT	NT
	10	N.T.	NT	39.03	41 26	NT	NT	NT	NIT	NIT	NIT
	22	NT	NT	46.33	42.52						IN.I.
	31	NT	NT	40.00	40.00			N.1.	N. I.	N. I.	N. I.
	lon 7/02	0.0	11.1.	49.3	40.00	IN. 1.	N.I.	N.I.	N.I.	N. I.	N.T.
	4 /	0.0	0.0	17.34	16.73	0.821	0.953	0.01	0.01	1.5	1.066
	14	8.5	8.7	16.17	17.02	1.281	0.359	0.01	0.01	1.07	1.307
	28	8.5	8.3	15.86	26.15	0.93	0.471	0.01	1.112	1.11	1.307
	reb. 4	7.2	8.1	20.04	17.18	1.163	1.096	0.01	0.01	1.38	1.596
	11	7.3	7.2	35.45	25.48	N.T.	4.954	0.01	0.01	2.03	1.114
	18	7.3	6.8	13.37	19.65	N.T.	8.919	0.159	4.211	0.3	1.499
	March 1	7	7.3	32.25	28	0.221	8.745	0.079	0.238	1.14	1.932
	8	7.3	7.7	36.79	27.94	0.132	11.35	0.079	0.397	N.T.	1,933
	12	7.3	7.5	33.16	33.27	0.067	11.2	0.079	1,191	1 64	2 077
	18	7.1	7.5	17.33	33.18	1.53	11.2	0.079	0.715	1 03	2174
	25	8	7.4	30.14	37.08	0.308	18.6	0.705	0.070	1.30	2 700
	April 1	7.1	75	30.29	26.49	0.241	16.85	0.730	0.079	0.15	2.799
	8	69	82	12 12	20.40	0.154	12.14	0.079	0.000	0.15	2.944
	15	74	77	30.06	24.00	0.104	0.000	0.079	3.576	1.52	3.305
	22	9.2	1.1	25.30	24.92	0.014	9.000	0.159	0.318	1.64	2.896
	20	0.0	0.5	35,33	21.92	0.286	7.013	0.079	0.159	1.69	2.318
	30	1.4	8.5	30.02	22.69	0.045	5.654	0.01	0.01	1.26	1.307
	May 6	8	8.3	44.73	17.64	3.004	9.115	2.225	2.702	1.89	3.137
	19	7.8	8.3	29.39	26.29	0.591	4.8	0.01	1.43	2.05	1.283
	31	7.6	7.7	18.16	23.98	0.897	4.1	0.01	0.318	0.51	3.329
	June 3	7.7	7.8	28.45	27.65	1.379	5.259	0.01	0.477	1.98	3.57
	10	7.5	7.8	19.87	23.18	0.832	11.22	0.01	5.8	0.75	3.088
	17	7.4	N.T.	29.99	N.T.	0.042	N.T.	0.079	NT	1.98	NT
	29	7.2	7.7	21.08	19.33	N.T.	0.109	10.01	5 165	1 45	NT
	July 7	7.8	8.6	23.93	17 23	0 042	NT	0.307	1 42	1 09	4 705
	20	6.9	71	444	16.6	13	0.3	1 74	1.40	0.1	4.725
	25	6.0	71	160	24.2	60.4	1500	1.74	4.44	2.1	11.0
	Aug 2	6.0	7.1	22.4	24.2	00.1	1590	40.6	2510	73.6	1490
	109.2	0.9	7.1	33.4	21.9	21	170	16.7	84.4	32.2	221
	10	0.9	<u></u>	17.3	15.9	4.1	61.6	0.99	77.2	7.4	5.2
	19	6.9	7.1	17	16.6	0.8	21.9	1.23	33.8	8	30.6
	Sept. 4	6.9	7.1	20.7	30	0.8	11.9	0.58	13.5	3.4	38.6
1	9	6.9	7.1	17.3	N.T.	0.3	N.T.	N.T.	N.T.	9.05	9.05
	15	6.9	7.1	N.T.	28.6	0.8	0.8	0.63	6.76	10.2	10.3
N.T. = Not Tested											
F.W. = To Feeder Wells, Influent											
E.W. = From Extraction Well, Effluent											
No	te: All Con	centrat	ions are	in mg/l.							