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# EVALUATION OF ANALYTICAL METHODOLOGIES FOR DIESEL FUEL

# CONTAMINANTS IN SOIL

BY

KRISTINA N. GRAHAM

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

MASTER OF SCIENCE

Department of Soil Science
University of Manitoba
Winnipeg, Manitoba

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DIESEL FUEL CONTAMINANTS IN SOIL


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Kristina N. Graham    1997 (c)

# ABSTRACT

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The widespread use of petroleum hydrocarbon fuels for transportation, heating and energy has led to the release of these fuels into the environment through accidental spills, long term leakage, or operational losses. As a result, many sites have been found to have soil and water which are contaminated with petroleum hydrocarbon fuels. As society becomes more cognizant of the negative repercussions of such contamination on soil and water quality, flora, fauna, and human health, it has become necessary to evaluate sites for potential contamination.


This study was undertaken because of an apparent lack of consistency among results obtained by analogous analytical methods for diesel fuel contaminants in soil as observed by those in industry and government alike. The goal of this study was to evaluate selected analytical methodologies for diesel fuel related contaminants in soil. The following hypothesis was tested:

*That new analytical methods[a] for diesel fuel related contaminants in soil perform at least as well as standard analytical methods[b] while possessing a number of significant benefits.*

[a] New analytical methods are defined as those which are not commonly used in commercial laboratories for such analyses, and are generally not identified for use by regulatory agencies. These methods include solid phase micro-extraction (SPME) methods, super-critical fluid extraction (SFE), and near infra-red spectroscopy (NIRS).

[b] Standard analytical methods are those which are currently being used in commercial laboratories in Manitoba for the analysis of diesel fuel related contaminants in soil, and are usually identified for use by regulatory agencies. These methods include sonication methods (SON & PROBE), shaker solvent extraction (SHAKE), soxhlet extraction (SOX), and magnetic stirring solvent extraction (STIR).

The methods were evaluated in three phases. Comparisons in Phases I and II are based on the criteria of accuracy and precision. Phase I assessment is a visual analysis of the data. Phase II is a statistical analysis using a linearity test and the student's $t$ test. Other parameters which affect the applicability of a method such as hazardous material generation, time and instrumentation needed, portability and specificity of the method are assessed in the Phase III evaluation.

After the Phase I and II evaluations it has been concluded that wide variability of results exists among commercially available analytical methods. The new methods tested in this study were shown to produce results which are no more variable than those produced by the standard commercial methods. Through the Phase II evaluation it is apparent that some of the new methods tested possess significant benefits which warrant the further investigation of these methods. These conclusions confirm the hypothesis and bring to light a number of recommendations for each stage of soil analysis including sampling, subsampling, analytical methods and data analysis.

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# 1. INTRODUCTION

The widespread use of petroleum hydrocarbon fuels for transportation, heating and energy has led to the release of these fuels into the environment through accidental spills, long term leakage, or operational losses. As a result, many sites have been found to have soil and water which are contaminated with petroleum hydrocarbon fuels. As society has become more cognizant of the negative repercussions of such contamination on soil and water quality, flora, fauna, and human health, there has been an increasing demand to evaluate sites for potential contamination.

The investigation of a potentially contaminated site is required to confirm and delineate the subsurface contamination. The investigation of a site involves a detailed historical inquiry, a geotechnical examination of the subsurface to understand potential routes of contaminant migration and laboratory analysis of the soil and water. The results of the laboratory analyses can provide quantitative data on the type and amount of contaminant present. These results will in turn be used by decision makers in industry and government to decide on the appropriate course of action for a particular site. The results of such laboratory analyses are used to define the extent and nature of contamination, to invoke legislation and guidelines, to evaluate remediation progress and to demonstrate regulatory compliance. The results of laboratory analyses are a

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critical tool for decision makers, used throughout the investigation and remediation process. The trigger for remedial action is often based on the laboratory analytical results. Similarly, allowable land uses will be determined on the basis of laboratory analytical results. Whether or not a home, school, park, or commercial building may be built on a formerly contaminated site will depend on the laboratory analytical results. For these reasons it is of utmost importance that the laboratory analyses be as accurate as possible, and that data users understand the limitations and inherent weaknesses of the data.

This study was undertaken because of an apparent lack of congruence among results obtained by standard analytical methods for diesel fuel contaminants in soil as observed by those in industry and government alike. The goal of this study was to evaluate selected analytical methodologies for diesel fuel related contaminants in soil. This goal was to be fulfilled through the following objectives:

    i) to observe a typical soil sampling procedure,

    ii) to research standard analytical methods,

    iii) to compare the results obtained by different methods in commercial laboratories,

    iv) to perform analyses by "new" methods (which are not currently being used in commercial laboratories in Manitoba),

    v) to compare all results obtained,

    vi) to pinpoint sources of variability and

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vii) to make recommendations on methods to be used for the analysis of diesel contaminated soils.

Using these objectives, the following hypothesis will be tested:

*That new analytical methods[a] for diesel fuel related contaminants in soil perform at least as well as standard analytical methods[b] while possessing a number of significant benefits.*

[a] New analytical methods are defined as those which are not commonly used in commercial laboratories for such analysis, and are generally not identified for use by regulatory agencies. These methods include solid phase micro-extraction (SPME) methods, super-critical fluid extraction (SFE), and near infra-red spectroscopy (NIRS).

[b] Standard analytical methods are those which are currently being used in commercial laboratories in Manitoba for the analysis of diesel fuel related contaminants in soil, and are usually identified for use by regulatory agencies. These methods include sonication methods (SON & PROBE), shaker solvent extraction (SHAKE), soxhlet extraction (SOX), and magnetic stirring solvent extraction (STIR).

Year I of the study focused on the first three objectives. The author observed and participated in the sampling of contaminated soil from a site in northern Manitoba. The samples were analyzed using three different standard methods in commercial laboratories, and also by the author using headspace solid phase micro-extraction (H-

SPME). Other SPME techniques were developed at this time. In Year II of the study further samples were obtained and analyzed by two standard methods in commercial laboratories, by headspace SPME, and by six additional methods. The additional methods employed in Year II include heated headspace SPME (HH-SPME) and direct liquid SPME (D-SPME), along with super-critical fluid extraction (SFE), the benchmark method of soxhlet extraction (SOX), magnetic stirring solvent extraction (STIR) adapted from a commercial method, and a novel application of near infra-red reflectance spectroscopy (NIRS). This thesis is intended to document these methods and the results obtained and to fulfill the remaining objectives of the study.

Table 1.1  Methods reference table.

| Method no. | Method description | Method abbreviation |
|---|---|---|
| 1 | Sonication | SON |
| 2 | Shaker | SHAKE |
| 3 | Sonic Probe | PROBE |
| 4 | Headspace SPME | H-SPME |
| 5 | Heated Headspace SPME | HH-SPME |
| 6 | Direct SPME | D-SPME |
| 7 | Supercritical Fluid Extraction | SFE |
| 8 | Soxhlet | SOX |
| 9 | Magnetic Stirring | STIR |
| 10 | Near-infrared Reflectance Spectroscopy | NIRS |

# 2. LITERATURE REVIEW

## 2.1 Diesel Fuel

### 2.1.1 Contamination of Soil with Diesel Fuel

Hydrocarbon fuels such as diesel are naturally occurring substances. Environmental contamination involving hydrocarbon fuels results when they are present at a location where they do not naturally occur, and in concentrations beyond those intrinsically present. Naturally occurring concentrations of $n$-alkanes can often be measured in organic rich soils, and will later be discussed as a potential analytical interference. Accidental, or controlled release of petroleum fuels may ensue at a number of points during procurement, refinement, transport, storage and use of the fuel. Release may happen in a single catastrophic event or over a long period of slow release. In either case, the resulting contamination has repercussions on the surrounding environment and its flora and fauna. To better understand the potential environmental effects, this chapter will examine the composition, toxicity and fate of diesel fuel.

## 2.1.2 Composition of Diesel Fuel # 2

**2.1.2.1 Sources of Variability.** Diesel fuel # 2 is composed of a suite of hydrocarbons which are obtained when crude oil is distilled. Diesel fuel # 2 is not designated according to its exact chemical constituents, but by the physical parameter of boiling point range (Block et al., 1991). Block et al. (1991) describe diesel fuel as "any petroleum distillate which boils between 300 °F and 700 °F" (149 °C and 371 °C). Millner et al. (1992) describe diesel fuel # 2 as petroleum distillates with boiling ranges between 160 °C and 360 °C. Generally this boiling range encompasses straight-run middle distillate, hydrodesulfurized middle distillate, and light catalytically and thermally cracked distillates (Millner et al., 1992). This broad definition of diesel fuel is often close enough to the specifications for heating oil # 2 that one product has been used for dual purpose marketing (Block et al., 1991). As a result of the inconsistent descriptions of boiling point ranges, a definitive carbon number range for diesel fuel is impossible to establish.

In addition to the variety of boiling point descriptions, a number of other factors may contribute to variability in diesel fuels. The source of the crude oil, the refinery process and shipment can all add to the variability of the mixture of hydrocarbons in diesel fuel. Furthermore, different diesel fuels have been produced for specific uses and customers. Arctic diesel with an increased low molecular weight component was created for use at low temperatures. Marine diesel is a low grade diesel with a greater amount of high molecular weight alkanes and aromatics for use in low speed ship propulsion. Large

consumers such as railway companies have chosen to use low quality diesel in order to realise cost savings. Non-petroleum additives such as alcohols, vegetable oils and coal fines have been used to enhance the fuel performance and cost (Block et al., 1991).

**2.1.2.2 Sources of Change.** In conjunction with a variable source mixture which comprises diesel fuel, the composition of the fuel will change over time as it is weathered. The rate and extent of the change in composition will depend on the weathering conditions including duration, temperature, and exposure to atmosphere, light and microbial population. Over time, a released fuel may be subjected to evaporation, dissolution, dispersion, photochemical oxidation, emulsification, microbial degradation, adsorption, sinking and sedimentation (Wang and Fingas, 1995). Studies on the effects of weathering on hydrocarbon mixtures such as light crude oil and kerosene have shown the changes that these mixtures can undergo. Low and intermediate molecular weight hydrocarbons, such as the volatile components are most readily lost to evaporation and microbial degradation. Subsequently there is an increase in the percentage of higher molecular weight compounds due to an overall volume reduction (Chaineau et al., 1995; Gerstl et al., 1994; Gruiz and Kriston, 1995; Mac Gillivary and Shiaris, 1994; Wang and Fingas, 1995).

Atlas and Bartha (1981) report that $n$-alkanes of intermediate carbon chain length ($C_{10}$-$C_{24}$) are the most readily degraded of diesel constituents. Low molecular $n$-alkanes tend to be toxic to micro-organisms, but are easily lost to volatilisation. Longer carbon chain

lengths are increasingly difficult to degrade, and when the molecular weight goes above *ca.* 500 (*ca.* $C_{36}$) the alkanes cease to be a carbon source. In addition, branching on the hydrocarbon backbone interferes with degradation, and may block it all together. Aromatic compounds, especially polycyclic aromatic hydrocarbons (PAHs), are degraded more slowly than alkanes. Alicyclic compounds are often insufficient as the sole carbon source for microbial growth, but may be broken down via cometabolism, or by complementary metabolic pathways (Atlas and Bartha, 1981). The end result of these transformations is a more viscous and recalcitrant contaminant, which may be significantly different from the original fuel product spilled. These changes in the composition of the fuel will affect both the toxicity and transport of diesel fuel in the environment.

**2.1.2.3 Diesel Fuel # 2 Composition.** Diesel fuel # 2 is composed of over 200 different compounds each with its own chemical and physical properties. Because of the above mentioned variability in diesel fuel composition, it is not possible to state the exact characteristics of this fuel. However, ranges of properties and the classes of compounds present can be discussed. Table 2.1 presents specifications for physical properties and those which normally occur. Table 2.2 shows chemical and physical properties which are useful for determining environmental fate of a contaminant.

Table 2.1  Typical and normally occurring physical properties of diesel fuel # 2 (adapted
from Block et al., 1991).

| Property | Specification | Normally Occurring |
|---|---|---|
| Specific Gravity | 0.830 to 0.876 | 0.85 to 0.87 |
| Flash Point (°C) | 57 (minimum) | 63 to 74 |
| Pour Point Summer (°C) | -12 (maximum) | -18 to -15 |
| Pour Point Winter (°C) | -18 (maximum) | -18 to -21 |
| Viscosity (cSt) @ 38 °C | 1.9 to 4.1 | 3.5 to 3.8 |
| Sulphur (wt %) | 0.50 (maximum) [a] | 0.42 to 0.48 |
| 10 % Initial Boiling Point | na [b] | 179 to 193 |
| 50 % Initial Boiling Point | na | 232 to 288 |
| 90 % Initial Boiling Point | 282 to 338 | 327 to 335 |
| Final Boiling Point | 316 to 366 | 352 to 357 |
| Cetane Number [c] | 42 (minimum) | 45 to 46 |

[a] reduced to 0.10 in 1993

[b] na = not available

[c] Cetane number is based on engine operation using test fuel compared to operation
when burning known mixtures of $n$-cetane.  The higher the cetane number, the better
the ignition characteristics (maximum cetane number = 100).

Table 2.2 Chemical Properties of Diesel Fuel # 2 used to predict Environmental Fate (adapted from Block et al., 1991).

| Parameter | Value |
|---|---|
| Aqueous Solubility | 0.2 mg/L |
| Vapour Pressure | 0.03 mmHg |
| Diffusion Coefficient in Air | $4.63 \times 10^{-2}$ cm$^2$/s |
| Henry's Law Constant | $4.2 \times 10^{-2}$ atm-m$^2$/mol |
| Log Organic Carbon - Water Partition Coefficient ($K_{oc}$) | 3.04 L/kg |
| Biodegradation Half-life ($t_{1/2}$) | 1 year$^{-1}$ |

Alkanes (or paraffins) (normal ($n$-), branched and cyclic), comprise the majority of diesel fuel at 65% to 85% (Block et al., 1991). The branched alkanes are predominantly monomethyl-, dimethyl- and trimethyl- substituted alkanes. Ratios of compounds in this category are used to identify the source and the extent of weathering of a fuel at a spill site. Cycloalkanes and bicycloalkanes are individually present in low concentrations in diesel fuel, and as they tend to exhibit poor GC analytical behaviour, are difficult to quantify (Block et al., 1991). Toxicity of this class of compounds is not high, yet alkanes have been identified as cancer promoting chemicals, or cocarcinogens (Millner et al., 1992).

Alkenes tend not to be present in diesel fuel, as they are not common in crude oil. However, alkenes may be produced by catalytic cracking processes, and these products may be incorporated into diesel fuel (Block et al., 1991). From a toxicological perspective, alkenes are thought to be similar to aromatic hydrocarbons, and are dealt with in the aromatic group (DEP, 1994).

Aromatic hydrocarbons represent approximately 10% to 30% of diesel fuel # 2. Low molecular weight aromatics are highly volatile, but diesel fuel itself is only moderately volatile. Often BTEX (benzene, toluene, ethyl-benzene and xylenes) compounds are used as marker compounds for environmental regulation of petroleum hydrocarbons, but only trace amounts of BTEX are present in diesel fuel #2. In Arctic diesel however, the flash point specifications are lower and significant concentrations of BTEX are present. In diesel fuel # 2, the most predominant aromatic compounds are naphthalene and methyl-substituted naphthalenes (Block et al., 1991; Millner et al., 1992). Polycyclic aromatic hydrocarbons, or PAHs, most common in diesel fuel are phenanthrene, fluoranthrene, pyrene, and to a lesser extent, triphenylene, benz[a]anthracene, anthracene, and chrysene. The last three of these compounds are listed by the U.S. EPA (Environmental Protection Agency) as potential carcinogens (Millner et al., 1992). A few highly carcinogenic PAHs such as benzo[a]pyrene are present only in trace amounts, but will add to the overall toxicity of the mixture (Stone, 1991).

It has been noted that due to the wide variability in PAH content, the environmental impacts of different diesel fuels vary by an order of magnitude or more (Block et al., 1991). Diesel fuel as a whole has been evaluated for its human health risks with respect to oral, dermal and inhalation exposures. Representative tests and results are shown in Table 2.3.

Table 2.3 Diesel fuel # 2 toxicity tests (adapted from Stone, 1991).

| Test | Organism | Value |
|------|----------|-------|
| Single Dose LD $_{50}$ | Rat | 5100 ppm |
| Subacute Dermal Toxicity | Rabbits | 1000 ppm |
| 90 day Inhalation Exposure - resulting in nephropathy and hepatocellular changes | Mice (male) | 0.05 mg/L |

## 2.1.3 Fate of Diesel Fuel in the Environment

Once released into the soil environment, the chemicals which comprise diesel fuel will partition differentially into various media depending on their chemical properties. Generally there are a number of fates for the compounds in the environment. Volatilisation is of importance, especially for the low molecular weight compounds (Wang et al., 1994). Loss of the contaminant to the atmosphere due to volatilisation will vary depending on environmental conditions such as ambient temperature and wind speed. The contaminant may also become sorbed to inorganic soil particles or to soil

organic matter. Organic matter consists of large, complex molecules which interact with and sorb the apolar hydrocarbons found in diesel fuel (Gerstl and Kliger, 1990). This sorption can cause immobilisation of the contaminant within the soil and a reduction in the effective toxicity (Voice et al., 1983). Conversely, when the contaminant becomes associated with dissolved organic matter, its mobility can be increased, as the contaminant will tend to move with the dissolved organic matter (Hassett and Milicic, 1985; Landrum et al., 1984; Lick and Rapaka, 1996; McCarthy and Zachara, 1989; Schwarzenback et al., 1993).

The various compounds within diesel fuel may move through the soil at different rates. Contaminant conductivity is influenced by the intrinsic permeability (texture, moisture content) of the media and by the fluid properties (density, viscosity) of the liquid (Gerstl et al., 1994). As the contaminant moves through the soil, it may have effects on the microbial population, macroscopic soil organisms, and the properties of the soil itself. Of particular interest in a permafrost region is the potential for the contaminant to change the freeze / melt cycle of a cryosolic soil by depressing the freezing temperature of the soil. In moving through the soil, components of diesel fuel may migrate to the groundwater where they may become dissolved in the water (Chiou et al., 1986; Lee et al., 1992) or may become associated with dissolved organic matter, or with microbiota in the water (Lyman et al., 1992). Once this happens the contaminant will move in the direction of flow of the ground water. This contaminated ground water may be tapped by a well and pose a risk to humans and animals, or the ground water may discharge at a

surface stream or lake. The surface water would be another corridor for contaminant transport, and may expose humans, wildlife and plants to the contamination. Through either direct exposure to the contaminant, or by exposure to contaminated media (such as soil, water, organic matter, or biota), plants, animals and humans are at risk of encountering diesel fuel related contaminants through a wide variety of pathways.

## 2.1.4 Remediation Criteria for Manitoba

In the province of Manitoba, any soils containing individual BTEX components in concentrations greater than 100 ppm are considered to be hazardous wastes. It is the responsibility of the waste generator to classify the waste based on analytical testing, as regulated under the Manitoba Regulation 282/87 of the Dangerous Goods Handling and Transportation Act. Soils which exceed the hazardous waste criteria must be dealt with at a licensed hazardous waste disposal facility, and transported by a licensed hazardous waste carrier. On-site treatment, or treatment at a non-licensed facility may be allowed with the approval of a Manitoba Environment Director. Soils which are not considered hazardous, but which require remediation (exceeding Level I remediation criteria), may be dealt with at a licensed hazardous waste facility, or a licensed soil recycling facility, or upon approval by the Director, may be dealt with on-site or at a waste disposal ground. Soils which are not classified as hazardous, and are below clean-up levels may remain on-site or, may be used as fill or cover material upon approval of the Director (Manitoba Environment, 1993a).

Site assessment must be performed by qualified professionals and site-specific conditions must always be taken into consideration. Site sensitivity ranking within the Manitoba Environment remediation criteria is not intended as a risk assessment model, but rather as general tool to be used for all petroleum hydrocarbon contaminated soil sites in the province of Manitoba. Currently soil remediation criteria do not exist for all of the individual components of diesel fuel. Total petroleum hydrocarbon (TPH) values for diesel fuel are listed under total semi-volatile hydrocarbons. The three levels of remediation criteria correspond to low, medium and high site sensitivity classifications. Site sensitivity must be based on assessment of the following parameters:

- Surrounding land use (within 150 m of site)

- Groundwater (depth, direction of flow, ownership and use)

- Surface water (users and drainage direction within 150 m of site)

- Underground structures (basements, etc., within 150 m of the site and buried utilities on or adjacent to site)

- Surficial geology (soil classification to bedrock)

- Special conditions (environmental or human factors requiring special attention)

- Evidence of surface contamination (physical evidence of possible contamination)

- Land use (current and proposed changes)

(Manitoba Environment, 1993b)


Generally, there are four land use sensitivity rankings corresponding to four remediation criteria levels. The highest sensitivity land use is appropriate for remediation to the

Level I criteria. The remediation criteria are outlined in Table 2.4 (Manitoba Environment, 1993b)

Table 2.4 Remediation criteria for soil (mg/kg or ppm) (adapted from CCME, 1997.) (*adapted from Manitoba Environment, 1997).

| Parameter | Level I | Level II | Level III | Level IV |
|---|---|---|---|---|
| Benzene | 0.05 | 0.5 | 5.0 | 5.0 |
| Toluene | 0.1 | 0.8 | 0.8 | 0.8 |
| Ethylbenzene | 0.1 | 1.2 | 20.0 | 20.0 |
| Xylenes (total-*o,m,p*) | 0.1 | 1.0 | 17.0 | 20.0 |
| Total Semi-Volatile Hydrocarbons * | 500 | 2000 | 2000 | 2000 |

In practical terms, the information above in Table 2.4 indicates that in Manitoba all soils outside of a hazardous waste facility must have less than 2000 ppm (mg/kg) of total semi-volatile hydrocarbons (also referred to as TPH). For land uses in which the site sensitivity is high, the level of total semi-volatile hydrocarbons in the soil must be below 500 ppm (mg/kg). This level of remediation is usually also required when selling a property to minimize the risk of liability to the buyer and the lending institution. Therefore, in the province of Manitoba, accurate analytical evaluation of TPH in soils over the concentration range of 500 to 2000 ppm is essential for regulatory decision making. The analytical procedures recommended by Manitoba Environment for measuring these parameters are U.S. EPA Method 3540 (Soxhlet) with GC method 8015

(GC-FID), or extraction Method 3550 (Sonication) with GC method 8015 (Manitoba Environment, 1993b).

## 2.2 Sampling

Any soil analytical procedure begins when the soil sample is taken. Retention of the analyte(s) of interest may be greatly affected by the way in which a sample is obtained and handled prior to analysis. Loss of analyte may occur due to volatilisation, which is an especially important consideration when taking into account highly volatile compounds such as BTEX. Volatilisation will occur the moment that the soil surrounding the sample is disturbed. When a sample is being obtained from below ground, disruption of the soil structure can result in increased pore space and disruption of equilibria which may have been established between contaminants sorbed to the soil particulates, pore water, and air. This can cause an immediate flux of the analyte from one matrix into another, depending on the characteristics of the analyte (e.g., vapour pressure, water solubility, polarity, Henry's law constant, octanol-water partition coefficient). Analyte volatilisation may also take place as the sample is being placed in the sample jar, especially when the soil structure is disrupted in the process. Volatilisation at this stage will depend not only on the analyte characteristics, but also on the ambient conditions at the time of sampling such as temperature and wind velocity. The amount of time in which the sample is exposed to the atmosphere will also affect the extent of volatilisation. This is a

parameter which will vary depending on the sampling procedure and the proficiency of the technician obtaining the sample.

Once the sample has been placed in the sample jar, loss of analyte may still occur through volatilisation. The analyte will partition into any airspace within the sample jar, and if the jar seal is compromised, there will be loss of volatile analyte to the atmosphere. A soiled sample jar rim has been shown to compromise a seal and is another important consideration in the sampling procedure (Hewitt et al., 1995). Depending on the analyte characteristics, loss of analyte to the glass sample jar or the plastic jar lid may occur. This loss due to sorption of the analyte to the sample vessel is especially of concern for the large and extremely apolar alkanes and PAHs found in diesel fuel.

Other losses of the original contaminants sampled may occur due to microbial degradation, photolysis, phototransformation and oxidation. Any change in the environmental conditions upon sampling the contaminated soil may result in the appropriate conditions for degradation, which were not present before the sample was removed. Changes such as increased temperature, light or oxygen may occur when a sample is obtained. The subsequent changes in the contaminant composition may lead to false characterisation of the contaminant, and poor decisions regarding the remediation of the site. There can be severe implications for human and environmental health risks if improper site characterisation takes place. The potential risk of analyte loss by

volatilisation, sorption or degradation all increase as the time between obtaining and analysing the sample increases (Hewitt et al., 1995). For these reasons it is vital to examine all details of the sample handling procedure when evaluating an analytical method.

## 2.2.1 Manitoba Sampling Guidelines

Manitoba Environment has described recommended procedures for subsurface evaluation of petroleum contaminated soils in Manitoba (Manitoba Environment, 1993b). The field investigation must be performed by qualified personnel capable of making important decisions regarding the number and placement of boreholes, based on the physical characteristics of the site. Borehole placements may be sited systematically, randomly or judgmentally. The judgmental approach requires technical judgement and prior knowledge of the site and its history. This method may have a relatively large bias, but requires the fewest number of samples to be obtained for a given site. A systematic approach involves use of a grid pattern for siting of boreholes, has less bias, but requires a greater number of samples than does the judgmental approach. A random approach to obtaining samples requires a method of generating true statistical randomness, and has the least relative bias, but requires the greatest number of samples for a given site (CCME, 1993).

Manitoba Environment recommends that judgmental or a combination of judgmental and systematic methods be employed for soil sampling. Initial investigation should include

tank sites, pump islands, loading or unloading connection points, and areas of visible staining (Manitoba Environment, 1993*b*).

Delineation of the petroleum hydrocarbon contamination must be precise to Level I remediation criteria (500 ppm TPH). Manitoba Environment (Manitoba Environment, 1993*b*) recommends that boreholes be augered with a mobile rig using a 50 mm diameter split spoon sampler. Boreholes must be logged, and any visible evidence of staining must be noted on the log sheet. Samples are to be taken at 0.75 m intervals, and at each stratiographic change, to a depth which will be determined on the basis of site conditions, particularly depth to bedrock. The soil held within the auger must be divided in half longitudinally, with one half used for laboratory analysis, and the other half used for field vapour screening. The vapour is measured after the soil has been deconsolidated by agitating the sample in a container, and allowing the sample to stand at 20°C for 10 min. A vapour analysing instrument capable of detecting petroleum hydrocarbons on a parts per million (ppm) scale, with either thermal conductivity, photoionization (PID), or flame ionization (FID) detection capability is suitable. Results of the screening must be documented on log sheets. The sample which is to be analysed in a laboratory must be properly packaged and stored to minimise the loss of volatile analytes. Decontamination of all sampling equipment must take place after each sample has been obtained.

### 2.2.2 Subsampling

For most laboratory analytical procedures, and for all of the ones employed in this study, the soil sample must be subdivided since only a portion is used for the analysis. The jar of soil obtained in the field is referred to as the sample. When the sample jar is opened, and a portion of the soil is removed, this is referred to as subsampling. The portion of soil removed from the sample jar is referred to as the subsample. The subsample may be placed in a new vial, referred to as the subsample vial. The manner in which this subsample is taken may affect the amount of volatile analyte lost at this stage of sample handling. The loss of volatile analyte depends on factors such as the amount of time that the sample is exposed to the atmosphere, the degree to which the soil structure is disturbed, the ambient temperature and the sample temperature. The quality of the subsample depends on where in the sample jar the subsample was obtained, and the homogeneity of the sample within the jar. At the top and around the edges of the sample jar, analyte loss may have occurred due to volatilisation and sorption. For this reason it is prudent to obtain subsamples from the interior of the jar, after having disposed of the top 1 to 2 cm of the soil sample.

The traditional scoopula method (described in section 3.3.2) removes the top layer of sample and then scoops out the desired amount of subsample with a metal scoopula. With this method there is disruption of the soil structure, the entire amount subsampled is exposed to the atmosphere throughout the procedure, and there is no precaution against

soiling of the subsample vial rim, which may lead to subsequent loss of volatile analytes (Hewitt et al., 1995).

An alternative subsampling technique is the modified syringe technique. It takes a core from the sample jar after the top layer of the sample has been removed (described in section 3.3.1). The core is an intact portion of the soil sample from the jar and is not exposed to the atmosphere, except at the bottom, during transfer. This means that there is reduced opportunity for loss of volatile analyte during subsampling (Hewitt, 1994). The contact of the soil with the plastic syringe during transfer does however, present a minor concern for potential loss of analyte due to sorption to the plastic syringe. The main advantage of this subsampling technique is that a rapid and efficient sample transfer is possible. Hewitt and co-workers found that the modified syringe technique resulted in reduced subsampling time compared to the scoopula method, and that the modified syringe technique was capable of delivering a subsample to the subsample vial with fewer incidents of dirty closures (Hewitt et al., 1995).

## 2.3 Analytical Methods

### 2.3.1 Ultrasonication Extraction Methods

Ultrasonication is an extraction technique described in the U.S. EPA Method 3550A. The procedure is to be used for extraction of non-volatile and semi-volatile organic compounds from solids including soils, sludges and wastes (EPA, 1992). In this

extraction method, ultrasonic waves are sent through the sample in pulses in attempt to physically disrupt the sample. This disruption may have enough energy to remove analyte from the sample matrix. The enhanced surface area created by the ultrasonic disruption also allows the organic solvent to come into contact with the analyte more readily. This in turn allows the solvent to solvate the analyte, extracting it from the sample matrix. The ultrasonic pulse may be deployed using either a water bath or a probe. When a probe or horn is used the ultrasonic pulse is delivered directly into the sample. When a water bath is used the ultrasonic pulse is delivered via the water bath to the sample medium in its container. For both techniques the choice of the extracting solvent determines the specificity and effectiveness of the extraction.

These two ultrasonic extraction techniques have been compared to other extraction methods in the literature. Marvin et al. (1992) compared extraction by ultrasonic probe to soxhlet extraction (as in Method 8) for PAHs from sediments and an urban dust standard. It was found that sequential ultrasonic extractions with two different solvents produced equivalent results to the soxhlet extraction, but required much less time. Each method had an extraction efficiency with *ca.* 15% variability. The soxhlet technique however, required 2 d, while the ultrasonic technique required only 45 min (Marvin et al. 1992). These authors also speculate that the ultrasonic extraction method may be analogous to supercritical fluid extraction (SFE) (used in Method 7), except that the ultrasonic technique eliminates some of difficulties of SFE such as restrictor clogging and the need for modifiers (Marvin et al. 1992).

An ultrasonic bath extraction technique was compared to two other extraction techniques by Morel (1996). In this study hydrocarbons were extracted from marine sediment samples by ultrasonic bath (used in Method 1), mechanical shaker (used in Method 2), and soxhlet (used in Method 8). Also compared were three different solvents and three separation and detection methods. It was found that if skilfully performed, all of the separation / detection methods produced comparable results. The parameter which had the greatest influence on results was the choice of solvent, not the extraction method. The author concluded that the 1 h ultrasonic extraction at 100 W might not have been a sufficient energy level, as the soxhlet and mechanical extractions were 1.5 to 3 times more efficient (Morel, 1996). Overall it was noted that a poor recovery of aromatic compounds was observed when extracting from wet sediment. Precision was thought to be most affected by mishandling of samples, and potentially nonhomogeneous samples. Other factors cited as influencing recovery were loss of analyte during the drying and solvent concentration procedures, incomplete analyte vaporisation in the GC, and variabilities in the GC quantification methods (Morel, 1996).

## 2.3.2 Shaker Extraction Method

The shaker extraction technique is used in Method 2 of this study and is based on the Alberta Environmental Centre (AEC) Method G108.0 for the qualitative and quantitative determination of petroleum hydrocarbons which are less volatile than gasoline, in soil (AEC 1992). In this method a predetermined amount of soil is shaken with an organic

solvent, the organic portion is decanted and an aliquot is analysed by GC-FID. Shaking the soil sample with an organic solvent is intended to expose the greatest possible amount of surface area of the sample to the solvent for solvation and extraction. The shaking action is applied to break down the soil sample structure, while keeping the surfaces bathed in solvent. The selectivity and effectiveness of this extraction will again depend largely on the choice of organic solvent.

When an analogous shaker method was compared to soxhlet (Method 8) and ultrasonication extraction techniques (Methods 1 and 3), it was found that the shaker and the ultrasonic technique were both more effective than soxhlet for the extraction of lighter PAHs (under 5 aromatic rings) (Morel, 1996). The shaker method (using acidified, freeze-dried sediment) was found to have excellent reproducibility (from 7% to 12%), and the most accurate GC-FID profiles. Morel (1996) concluded that qualitatively and quantitatively, the shaker method was the most convenient and accurate extraction method for a broad range of analyses (Morel, 1996).

### 2.3.3 Solid Phase Micro-extraction (SPME) Methods

Solid phase micro-extraction (SPME) methods are used in Methods 4, 5 and 6 of this study. SPME was developed by Pawliszyn and co-workers at the University of Waterloo (Belardi and Pawliszyn, 1989). SPME differs from most traditional extraction techniques in that it is based on non-exhaustive extraction in which an equilibrium is established. The SPME device consists of a syringe-like apparatus that houses a polymer coated (e.g.,

polydimethylsiloxane) fused silica fibre. This fibre is extended into either a liquid sample or the headspace above a solid or liquid sample. The analyte will then partition into the fibre coating from the sample matrix or from the headspace above the sample. The fibre is then withdrawn into the protective sheath and withdrawn from the sample vial. The tip of the SPME device is then inserted directly into the heated GC inlet, the fibre is exposed, the analytes are thermally desorbed, and chromatography proceeds as usual.

**2.3.3.1 SPME Principles.** The affinity which a particular analyte of interest will have for the SPME fibre coating depends on the properties of the coating and the partition coefficient of the analyte. For apolar compounds with octanol-water partition coefficients ($K_{ow}$) above *ca.* 1000 such as the hydrocarbons in diesel fuel, the 100 μm PDMS fibre coating is most effective (Webster et al., 1996). Schwarzenbach et al. (1993) summarise classes of hydrocarbons into $K_{ow}$ ranges. Typically, alkylated benzenes have $K_{ow}$ values ranging from $10^2$ to $10^5$; polycyclic aromatic hydrocarbons (PAHs) range from $10^3$ to $10^7$, and aliphatic hydrocarbons ($C_5$ to $C_{18}$) range from $10^3$ to $10^9$ (Schwarzenbach et al., 1993). Reported $K_{ow}$ values for specific diesel fuel hydrocarbons are listed below in Table 2.5.

Table 2.5  $K_{ow}$ values for selected diesel related hydrocarbons.

| Compound | $K_{ow}$ |
| --- | --- |
| ethylbenzene | 1 412[a] |
| (o-, m-, p-) xylenes | 1 318 to 1 412[a] |
| n-propylbenzene | 4 168 to 4 786[a] |
| naphthalene | 1 995 to 2 344[a,b] |
| 2-methylnaphthalene | 13 000[b] |
| anthracene | 22 000[b] |
| phenanthrene | 32 900[b] |
| pyrene | 150 000[b] |

[a] from Wasik et al., 1983.
[b] from Kenaga and Goring, 1980.

An equilibrium will be established between the concentration of analyte in the sample matrix and the amount in the fibre coating within a matter of minutes for most compounds. If, however, it is not possible to reach equilibrium within a few minutes, it is only necessary to expose the fibre to the sample for a constant amount of time as there is a linear relationship between the amount of analyte sorbed to the fibre coating, and the amount in the sample solution or headspace if the extraction time is constant. The relationship is dependent on the two constants $K$ the distribution constant of the analyte, and $V_s$, the volume of the fibre coating. The amount of analyte then which may be sorbed by the fibre coating, $n$, is determined by these constants and the variable $C$, which

is the concentration of the analyte in the sample solution, or in the headspace above the sample. This relationship is expressed in the following equation (Arthur et al., 1992a):

$$n = K V_s C$$

As compounds have varying $K$ values, the amount sorbed by the fibre will vary from one compound to another. This behaviour is analogous to the way that analytes will be differentially solvated by an organic solvent in traditional extraction procedures. In each case it is important that the appropriate solvent or fibre coating be chosen for the extraction. What makes these extraction techniques useful is that the partitioning behaviour of an analyte is constant from one trial to the next, provided that extraction conditions remain the same. Calibration of an unknown sample is based on the knowledge that concentration $x$ of diesel fuel in soil will give response $y$, and that this is a linear relationship over several orders of magnitude encompassing the concentration range of interest.

**2.3.3.2 Parameters Affecting SPME.** Parameters which may affect the partitioning of an analyte into the fibre coating are sample temperature, agitation and size (Zhang and Pawliszyn, 1993a). As $K$ values are temperature dependent, changing the temperature at which a sample is extracted may enhance the extraction process. However, increased temperature will also hinder the retention capacity of the fibre coating, as heating is the means of desorbing the analyte from the fibre coating within the GC inlet. Increased temperatures from 40 to 60°C generally provide the enhanced uptake of analyte without hindering sorption to the fibre coating (Pawliszyn, 1997; Webster et al., 1996). In this

study the heating of soil samples to 50°C has been used when sampling from the headspace above the sample in the heated headspace SPME (HH-SPME) condition (Method 5).

Agitation of the solid or liquid sample will shorten the time required to reach equilibrium. The agitation increases diffusion rates of the analyte(s) from the sample into the headspace above the sample and into the fibre coating (Pawliszyn, 1997; Webster et al., 1996). Agitation of the sample will also help to reduce the static volume of air or liquid surrounding the fibre, thereby reducing a limiting factor of the partitioning process (Louch et al., 1992).

Sample size may be an important factor for consideration when performing multiple extractions from one sample, or when dealing with low concentrations of analyte. In either case the analyte in the sample may be depleted sufficiently to affect the partitioning of the analyte into the fibre coating. At relatively high concentrations, SPME extraction will not deplete the sample significantly to affect further extractions. When dealing with very low concentrations of hydrophobic analytes the quantity of analyte available may be such that complete extraction is effected. When the sample size is increased, there is a greater quantity of analyte at the same concentration level, allowing for lower detection limits (Graham et al., 1996; Webster et al., 1996). Similarly, the volume of headspace into which the analyte may partition is relevant as the total volume available will

determine the amount of analyte available for partitioning into the fibre coating during extraction from the headspace (Webster et al., 1996).

SPME may also be affected by the water and salt content of the sample. It has been found that 10 to 40% moisture in a soil sample will enhance the partitioning of analytes into the fibre (Graham et al., 1994; Zhang and Pawliszyn, 1993b), as the moisture will displace some of the bound analyte from the soil matrix, and may open collapsed clay matricies. A saturated salt solution has also been used to assist in the uptake of the analyte by the fibre coating. The salt occupies analyte binding sites on the soil, thereby affecting the Henry's law constant, and releasing more analyte into the headspace (Zhang and Pawliszyn, 1993b).

**2.3.3.3 SPME Applications.** Researchers have found a growing number of analytical applications for SPME, including the analysis of volatile organics, hydrocarbons, PAHs, pesticides, phenols, and dioxins from environmental samples such as air, water, soil, sediment, sludge, food and pharmaceuticals (Arthur et al., 1992b; Buchholz and Pawliszyn, 1994; Choudhury et al., 1996; Graham et al., 1996; Page and Lacroix, 1993; Penton, 1994a; Sarna et al., 1994; Webster et al., 1996; Zhang and Pawliszyn, 1993a). SPME has also been investigated for the analysis of alcohol or drugs in complex fluids such as blood and urine (Chiarotti and Marsili, 1994; Zhang et al., 1994). Caffeine and flavour analyses have also been performed using SPME on foods and beverages (Hawthorne and Miller, 1992; Penton, 1994b; Yang and Peppard, 1994). On-line

monitoring of flowing samples (such as a stream or body fluids) has also been investigated (Motlagh and Pawliszyn, 1993).

Beyond residue analysis, SPME may be used in the determination of partition coefficients and may assist in understanding environmental fates of contaminants by measuring free contaminants in water (Dean et al., 1996; Martos et al., 1997; Poerschmann et al., 1997; Vaes et al., 1996). SPME has also been used to predict bioavailability of petroleum hydrocarbons and associated toxicity (Parkerton and Stone, 1998). Parkerton and Stone (1998) used the PDMS coated SPME fibre as a surrogate lipid. The amount of hydrocarbon contaminant picked up by the fibre was related to toxicity test results, narcotic toxicity in particular. Once the relationship has been fully established between amount of hydrocarbon and the associated toxicity, the SPME method might be a valuable field test method for toxicity testing. SPME is an extraction method based on the equilibrium established between the lipid-like fibre coating and the sample matrix rather than an exhaustive extraction; therefore, it might be a more realistic representation of the bioavailable contaminant level. If determination of toxicity is the ultimate concern of the analysis, information on the bioavailable concentration of contaminants may be more useful than the data representing the total amount of contaminant extractable under rigorous extraction conditions. The extraction technique which is able to represent the amount of contaminant that an organism would be exposed to might more accurately reflect the environmental hazards of a contaminated site. In this way SPME might be

used to bridge the two sciences of residue analysis and toxicity testing. This could in turn lead to an increased understanding of environmental and toxicological risk..

**2.3.3.4 SPME Comparisons.** SPME has been compared to other extraction techniques, such as purge and trap and liquid-liquid extraction for the determination of BTEX, volatile and semi-volatile organics in water and soil samples (ASL, 1995; Colby 1994a,b; MacGillivray et al., 1994). SPME has also been compared to solid phase extraction, and immunoassays for the analysis of the herbicide metolachlor in surface runoff and tile drainage water (Gaynor et al., 1996). To date however, there have been no direct comparisons in the literature of an SPME method to any of the other methods undertaken in this study.

## 2.3.4 Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction methods use $CO_2$, $N_2O$ or $H_2O$ above their critical temperatures and pressures. The supercritical state for $CO_2$ is reached above 1100 psi $(7.59 \times 10^6 \text{ N/m}^2)$ pressure and at or above 31°C (Black, 1996). When a fluid becomes supercritical, it maintains the mass transfer efficiencies of a gas and approaches the solvating power of a liquid as pressure is increased. Supercritical fluids are faster at extracting than are liquids because mass transfer is the rate determining step. Supercritical fluids have diffusivities which are an order of magnitude higher than those of liquid solvents, and viscosities which are an order of magnitude lower (Hawthorne, 1990). Extraction efficiencies of the supercritical fluids can be enhanced by adding small

amounts of organic solvents, referred to as modifiers. Commonly used modifiers include methanol, water, amines, acids and aromatic solvents. It has been proposed that modifiers enhance extraction efficiencies by either i) increasing the solubility of the analyte(s), ii) moving into active sites in the matrix once the analyte has vacated the site, thus preventing the analyte from readsorbing or partitioning back onto the site, or iii) interacting with the analyte / matrix complex and lowering the activation energy barrier of desorption (Yang et al., 1994). Modifier / matrix interactions have been shown to be more important than the modifier / analyte(s) interaction, indicating that modifier efficacy is matrix dependent (Yang et al., 1994).

The SFE method can be highly selective for certain analytes of interest as the solvent strength of the $CO_2$ can be increased with increased pressure. At a constant temperature less polar analytes are favoured at lower pressures, while more polar, higher molecular weight analytes are favoured at higher pressures. This allows for class specific extractions to be performed, even within a single extraction run, if pressure is varied over the extraction time (Hawthorne, 1990). SFE of hydrocarbon contaminated soil is typically performed (U.S. EPA, 1992) (Method 3560) at a temperature of 80°C and a pressure of 340 atm ($3.43 \times 10^7$ N/m$^2$). Hawthorne and Miller (1994) found that while these conditions worked well for lighter crude oil components (below *ca.* $C_{25}$ alkanes), an increase in temperature to 150°C increased the recovery of the heavier hydrocarbon fraction.

The SFE is performed when a sample is placed in the extraction cell of an SFE instrument and the temperature and pressure in the cell are raised to the set points. Extraction may occur in either static or dynamic mode, with the solvent either statically extracting for a set amount of time before being vented, or continuously venting the extractant, while maintaining the set pressure. In either case the solvent is vented into a capturing medium such as a collection solvent. This solvent is brought up to a known volume for quantitative analysis and an aliquot is analyzed (by GC-FID in this case) (U.S. EPA, 1992).

In the extensive exploration and validation work performed on this new extraction method, many studies have been undertaken to compare results obtained by SFE to results obtained by the bench-mark method of soxhlet extraction, or by sonication extraction. When polycyclic aromatic hydrocarbons (PAHs) were extracted by either soxhlet or SFE from environmental matricies such as soil, sediment, soot and air particulates, SFE results were found to be quantitative (ISCO, 1991; Yang et al., 1994). When PAH extraction by SFE was compared to results by sonication, the SFE results were between 80 and 120% of the sonication results for concentrations at or above 1 ppm (Bøwadt and Hawthorne, 1995). When eight polychlorinated biphenyls (PCBs) were extracted by either soxhlet or SFE in an inter- and intra- laboratory study, it was demonstrated that SFE results were competitive in both precision and accuracy to the soxhlet results, and no significant difference was found between the two methods (Bøwadt et al., 1995). When extracting alkanes from rock, a 21 min SFE was superior

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to a 48 h soxhlet extraction, and the SFE method allowed for selective extraction, where as the soxhlet extraction did not (ISCO, 1991). In a study of the extraction of TPH from soil contaminated with a range of hydrocarbon fuels from heavy crude to gasoline, it was found that SFE results were quantitative compared to soxhlet results, except in the case of gasoline and kerosene where SFE results were 134% of the soxhlet results (Eckert-Tilotta, et al., 1993). TPH extractions from soil by SFE and soxhlet extraction showed that while SFE recoveries of the volatile fraction were higher than those for soxhlet, the recoveries of higher molecular weight hydrocarbons were inferior (Burford et al., 1994; Hawthorne, et al., 1993). However, when the SFE temperature was raised to 150°C, and perchloroethylene was added as a modifier, SFE yields became 5 to 45% higher than soxhlet yields for the heavier hydrocarbon range (Hawthorne and Miller, 1994).

## 2.3.5 Soxhlet Extraction (SOX)

Soxhlet extraction as described in the U.S. EPA Method 3540 is for the extraction of non-volatile and semi-volatile compounds from solids such as soils, sludges and wastes. This method is applicable to the extraction of water insoluble and slightly water soluble compounds. The technique has been considered a benchmark standard for complete extraction of many analytes including hydrocarbons from soil. The technique has been used for many years, and is routinely employed to determine the total amount of contaminant present in a sample when evaluating different extraction techniques. In this manner, the value obtained by soxhlet extraction is used as 100 percent when determining recovery by another extraction method.

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Soxhlet extraction is considered a rigorous extraction technique for the extraction of organic contaminants from solids. Extraction occurs at elevated temperatures (60 to 80°C), and clean solvent is continually being washed over the sample for an extended amount of time (16 to 24 h). This method does not propose to ascertain the volatile fraction of diesel fuel. The procedure disregards volatile components as the apparatus is not sealed from the atmosphere during the lengthy soxhlet extraction (U.S. EPA, 1992) (Method 3540B).

The sample is mixed thoroughly with anhydrous sodium sulphate, placed in an extraction thimble in a soxhlet extractor, and extracted for 16 to 24 h using an appropriate organic solvent. The extract is then dried, concentrated, cleaned up, and exchanged into a different solvent if necessary. A known volume of the extract is then injected into the heated GC inlet for chromatographic determination by GC-FID (U.S. EPA, 1992) (Method 8015).

### 2.3.6 Magnetic Stirring Extraction (STIR)

The magnetic stirring extraction method was adapted from an in-house commercial laboratory method for total extractable hydrocarbons ($C_{10}$-$C_{30}$) in soil. The sample is acidified and then stirred the sample with an organic solvent using a magnetic stir bar and plate. While there is no heating or rigorous physical disruption of the sample, the stirring action is used to provide enhanced solvent exposure to the soil. The selectivity

of this method is determined solely by the selection of the extraction solvent. This method is not intended to analyse for hydrocarbons smaller than $C_{10}$. While this eliminates the more volatile end of the hydrocarbon spectrum, there are many compounds in diesel fuel above $C_{10}$ in size which do undergo some degree of volatilisation. In this method the extraction occurs in an unsealed vessel and therefore there will be loss of even slightly volatile analytes in the stirring process. This loss of volatile components may be a significant source of error associated with this method. No previous comparisons of this method with any other method evaluated in this study have been found in the literature.

### 2.3.7 Near-infrared Reflectance Spectroscopy (NIRS)

Near-infrared reflectance spectroscopy (NIRS) is based on the measurement of stretching vibrations and overtones of certain bonds such as O-H, N-H and C-H which may be observed in the near-infrared region of 780 to 2500 nm. In this manner, the NIR spectra gives information about the molecular composition of the material being analysed (Malley and Nilsson, 1996). The absorption of the NIR light is exponential, following the Beer-Lambert law, and may be related to the concentration of the measured parameter (Benson, 1995).

$$\text{Log } I_i \text{ / } I_r = Kt$$

where $I_i$ is the intensity of the incident light, $I_r$ is the intensity of the reflected light, $K$ is the absorption coefficient and $t$ is the concentration of the measured parameter. Prior calibration of the method is required to perform statistical predictions of unknown

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concentration levels using statistical operations such as step-wise multiple linear regression, principal component analysis or partial least squares regression (Malley and Nilsson, 1996).

NIRS has been widely used in the agricultural, food processing, pharmaceutical, textile, paper and petrochemical industries for over 25 years. Over 5000 publications have dealt with the use of NIRS in these industrial applications (Malley and Nilsson, 1996). In 1965 Bowers and Hanks first demonstrated the use of NIRS for the measurement of moisture, organic matter and particle size in soils (Bowers and Hanks, 1965). Since then other soil parameters such as organic carbon, nitrogen, lignin, cellulose, clay, pH, iron, aluminium, potassium and phosphorus have been characterised in a wide variety of soils using NIRS (Malley, 1997a). Other environmental applications of NIRS have included the measurement of suspended C, N and P in lake water (Malley et al., 1996), detection of fungi and moulds in plant tissues (Nilsson et al., 1994; Roberts et al., 1987; Roberts et al., 1988, Roberts et al., 1991) and analysis of lipids and proteins in freshwater fish tissues (Mathias et al., 1987). NIRS has also been used for characterisation of sediments and lake water which can be used in modelling of biological and chemical processes (Korsman et al., 1992; Palmborg and Nordgren, 1995).

The NIRS method can be performed on a small amount of sample within the sample vial. The absorbance is measured and stored within a few seconds, without destruction of the sample. Reduced sample handling decreases the risk of analyte loss during the analytical

procedure, and eliminates analyst exposure the potentially harmful contaminants of interest. For the statistical calibration of obtained spectra a large number of spectral analyses need to be performed, and a prior calibration on the samples is required (by another method of analysis). The technique is, however, field portable, and produces reliable results in a short amount of time. The actual analysis requires little technical training; however, the statistical calibration and interpretation of results requires a high level of expertise.

Literature indicates that NIRS has not previously been applied to the characterisation of hydrocarbon contaminated soils or sediments. For that reason no comparison of this NIRS method to other analytical methods for hydrocarbon contaminants in soil had previously been made. The NIRS method for characterising lipid content in fish tissues was compared to a reference method involving a hexane extraction. The precision of the NIRS method was found to be four times that of the reference method in the study of Mathias et al. (1987).

## 2.4 Spiking

Spiking or adding the contaminant of interest or a related compound to the matrix being extracted is a common method of determining extraction efficiency. Although this procedure can be instructive in some ways, caution must be taken to avoid extrapolating the results beyond their true relevance. Contaminants can sorb to soil by different

mechanisms. Initially a contaminant will become associated with the outer surfaces of soil particles. These exterior binding sites are somewhat more assessable to solvents than interior sites and therefore contaminant binding may be more readily reversed. Over longer periods of time the contaminant will become associated with the interiors of soil particles such as interlayers of clay particles or aggregate structures. This binding is less easily reversed (Gamble, 1998). When soil is spiked and then extracted not long afterwards, there has been no opportunity for long term sorption, and recovery of the spiked analyte can be quite great, but not very reflective of recovery of an aged contaminant. Therefore, spike recovery data is only of limited usefulness when attempting to evaluate the efficiency of an extraction technique which is to be used on "real-world", aged samples (Hawthorne, 1996). For these reasons, only minimal use was made of spiked samples in this study. The spiked sample data was used in this study for the express purpose of helping to determine accuracy and precision of the commercially available methods (1 and 2), in the second year of the study.


## 2.5 Interferences


Interferences are considered here to be factors which can affect the results obtained from the analysis of hydrocarbon contaminated soils. These issues may not be of concern with every analytical method under investigation in this study, but should nonetheless be considered when evaluating analytical methods for hydrocarbons in soil. Understanding

the factors which can influence analytical results is important not only to the analyst but also to the data users.

## 2.5.1 Spill Characteristics

The characteristics of the release of the fuel into the environment are important for understanding the chemical composition of the original contamination, the potential changes the contaminant may have undergone, and the binding of the contaminant to soil and organic matter. The chemical composition of the original contaminant is a starting point for understanding what was released into the environment and what may be extracted from the contaminated soil samples. The source and type of fuel released is an important source of information. As discussed in section 2.1.2, marine diesel, arctic diesel and locomotive diesel are all chemically different. These differences can provide insight into the probable behavior of the contaminant in the environment and will give an indication of what might be found in the soil analysis. Other factors which affect the original contamination such as the duration and season of the release are relevant in understanding the potential for loss of volatile fractions, original toxic effects to soil organisms and initial movement of the contaminant. The time that has passed since the release of the contaminant is also a very important factor which will help to determine the amount of degradation, and sorption to expect. Over time, the contaminant will migrate and transform through biological and chemical means. This can result in a very different suite of hydrocarbons from what was originally released. In such cases more attention may have to be paid to the higher molecular weight,

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complex hydrocarbons such as PAHs and polycyclics. This should ideally be reflected in the analytical methods employed, and the overall site assessment strategies.

## 2.5.2 Soil Type

The characteristics of the soil sample being analyzed can influence the sorption of contaminants, the potential for loss of volatile analytes, and interference of naturally occurring soil lipids. With increased surface area of smaller soil particles found in loamy and clayey soils, there is an increased potential for contaminant sorption. These high surface area matricies may also be more difficult to extract from as the aggregates tend to be quite stable. This makes contact between a solvent and the bound contaminant more difficult, and the contaminant more difficult to extract from these matricies as opposed to lower surface area matricies such as sandier soils. On the other hand, while sandier soils may be easier to extract from, there is also an increased potential for loss of volatile analyte, as the soil matrix is easily disrupted, and does not retain the analyte as well as higher surface area soils.

It has been shown that naturally occurring soil lipids, which are found in high concentration in soil organic matter, are structurally similar to aliphatic hydrocarbons such as those found in diesel fuel. When analyzed by standard GC-FID methods, the two compound classes may be virtually indistinguishable. Where the soil under investigation has a high amount of organic matter, it can be extracted along with the diesel contamination and falsely elevate the total petroleum hydrocarbon level reported.

It is therefore important to consider the analytical technique employed when dealing with a high organic matter containing soil.

## 2.5.3 Drying Agents

Drying agents such as sodium sulphate or magnesium sulphate are often mixed with the soil sample to dry the sample, and to create a mealy texture which is much easier for a solvent to penetrate for analyte extraction. In mixing the sample with the drying agent, the sample is often exposed for several seconds or minutes to the atmosphere while being disaggregated, warmed and mixed. This creates ideal conditions for volatile analytes to be lost to the atmosphere which can also create health concerns for the technician if the task is not performed in a fume cupboard under adequate ventilation. The efficacy of the drying agent is affected by the matrix itself. As the surface area and the water holding capacity of a soil increases, the efficacy of a drying agent can decrease. It has also been demonstrated by Buford et al. (1993) that many drying agents retain analytes of interest from the soil sample. This reduces the detectable amount of analyte and can skew results.

## 2.5.4 Quantification

Quantification of the data is a critical step in obtaining reported results, yet it appears that very little attention is paid to this step. There is no one standard diesel fuel used for calibration of results, and this can be a serious source of variability among methods and over time. Often the diesel used for standards is obtained from commercial fuel

stations from which there is no assurance of control of chemical composition of the fuel obtained from one day to the next. Suppliers, refineries, additives and grade of the fuel obtained can all change over time. If the standard used for calibration of an unknown sample changes, calibrations will be inconsistent over time.

When quantifying a mixture such as diesel fuel, the range of compounds included in the calibration defines which compounds are included and which are excluded from the quantification. For TPH analyses, the range is defined in terms of carbon chain length. All those compounds outside of the predetermined boundaries will not be included. Even with an issue as simple as this, there is a lack of continuity among methods. Standard methods in this study had TPH ranges of $C_8$ - $C_{30}$, $C_{10}$ - $C_{30}$, $C_{11}$ - $C_{29}$, and $C_{11}$ - $C_{30}$. This fundamental difference in quantification is not easily compensated for when comparing data obtained by the different methods.

In addition, the method by which the baseline was established on the GC trace (or chromatogram) itself can have wide implications for the quantification of analytes. Should an analyst or computer program be inconsistent in the manner in which the data is integrated or the baseline is drawn, the resulting quantification of sample results will be inconsistent. This apparent detail to the overall assessment of a contaminated site can have vast implications to the reliability of the data generated. For this reason, the analysts must have a clear understanding of the significance of this issue and follow standard operating procedures for the quantification of data.

The detection limits reported for a particular method must also be understood by the data users. It can affect the precision of the data and the confidence the user should have in the data. At very low limits of detection, there must be some concern for the signal to noise ratio (S/N) under which the analysis was run. At a very low signal to noise ratio, results may be suspect at levels near the detection limit.

# 3. MATERIALS AND METHODS

## 3.1 Site Histories

The diesel fuel contaminated soil samples used in this study were obtained in conjunction with the Geotechnical Division of Manitoba Hydro from three different sites in northern Manitoba. The samples were taken for the purpose of delineating the concentrations and boundaries of hydrocarbon fuel related contaminants at decommissioned former generating stations and tank farms. The results of the commercial analyses will be utilised by Manitoba Hydro in future decisions regarding these sites. The historical and geological details of each site will be presented independently. The information presented in the historical and geological descriptions of the three sites has been graciously provided by Mr. Derek Wilson, P.Eng., of the Geotechnical Department at Manitoba Hydro.

### 3.1.1 Churchill, Manitoba

The site referred to as Churchill (CH) is a decommissioned diesel fuel generating station tank farm. The site is located *ca.* 5 km east of the town of Churchill, west of the airfield on Parcel 6, Plan 5329 (National Lands Title Office). Railway tracks owned by

Canadian National are directly west of the tank farm. To the north of the site is a gravel road and a storage building which is no longer in use. A small pond is located to the east of the site providing potential contaminant receptors. The landscape consists of discontinuous permafrost in the tundra with wet muskeg to the south and west of the site. Individual sample soil data is presented in the Appendix.

The early history of the site is not well known; however, it is known that the tank farm was built in the 1950s, holding two 1,136,500 litre tanks used for diesel storage, and a 340,950 litre tank which may have been used for gasoline storage. Earthen dikes *ca.* 1 m high, which surrounded all tanks, are still in place. The tank farm was last used in the late 1970s for waste fuel storage. Ownership of the land has been with the Manitoba Hydro Electric Board (M.H.E.B.), and Her Majesty the Queen (Canada) (H.M.Q.) since 1968. Prior to this date no records of ownership are held in the Lands branch of the Department of Mines and Natural Resources (Manitoba Hydro, 1997).

Table 3.1 Churchill tank farm ownership history (Manitoba Hydro, 1997).

| Owner | Certificate title # | Date | Land description |
|---|---|---|---|
| M.H.E.B. | E34254 | 95/09/01 | Pcl. A, Plan 32634 |
| M.H.E.B. | 144878 | 70/03/06 | Pcl. 6, Plan 5329 |
| H.M.Q. | 140212 | 68/11/18 | Pcl. 6, Plan 5329 |
| H.M.Q. | Old System [a] | 68/08/19 | Plan 5329 |

[a] Grant number 4132, vol. 16 registered in the Lands Branch of the Department of Mines and Natural Resources.

The tank situated in the northwest corner was removed in the 1980s. All other tanks and piping were removed by Public Works and Government Services Canada in 1994. Records indicate that a fuel spill occurred at tank no. 4 on November 11th, 1981, but was contained within the diking. Approximately 25% of the spill was recovered immediately as free phase material. The remainder, absorbed by the snow, was recovered the following spring. There is anecdotal knowledge of other fuel spills at the site; however, dates and amounts are not available (Manitoba Hydro, 1997).

### 3.1.2 Granville Lake, Manitoba

The site at Granville Lake, Manitoba (GV), is a decommissioned diesel generating station and associated fuel storage facility used for the purpose of supplying electrical services to the community of Granville Lake. The site is located *ca.* 735 km north of Winnipeg, Manitoba, on a point of land 50 m from the lake shore. Currently there are residences

located *ca.* 25 m south of the former tank farm. An outdoor hockey rink is now situated over the southern one-third of the former property. A water treatment plant is located 50 m northwest of the former location of diesel unit 3. A pipeline to this plant runs north-south, 10 m east of the former property. The diesel generating station first provided service in 1975. The generating capacity of 60 kW was provided by three generators and two 45,000 litre (10,000 gallon) fuel storage tanks, contained by earthen dikes. While there are no records of spills having occurred at the site, there are records of fuel, oil and coolant leaks until March 1985. Most leaks were attributed to cracked fittings and pipes on units 1 and 2. In March of 1985 the station was taken out of service and the site was connected to the integrated electricity system by a land transmission line. At this time the fuel storage tanks were salvaged, generator equipment and buildings removed, and dikelines eliminated (Manitoba Hydro, 1996).

### 3.1.3 Cranberry Portage, Manitoba

The site of Cranberry Portage (CB) was utilised by Manitoba Hydro as a diesel electrical generating station and tank farm from November 1962 until October 1975. Prior to this the site was operated under the DEW Line project. A diesel fuelled boiler plant and a helicopter hanger were on the site. Anecdotal evidence states that there were long term fuel line leaks associated with the boiler. The fuel is said to have been collected in a steel drum and periodically disposed of into the nearby storm sewers (Manitoba Hydro, unpublished data).

## 3.2 Sampling

A grid system was employed for sampling of all sites. A benchmark location of known co-ordinates and elevation was used as a reference marker, and the grid was established with respect to this location. Grid lines were spaced either 10 or 20 m apart as found to be appropriate by the on-site engineers. Drilling and sampling were performed by a professional crew from Paddock Drilling Ltd. of Brandon, MB. Professional geological engineers of the Geotechnical Engineering Department at Manitoba Hydro performed on-site characterisation of the soil samples (Appendix), and preliminary characterisation of the contaminants using a portable *Photovac MicroTIP* Photoionization Detector (PID) device (Hazco Canada, Inc.). Holes were drilled at the grid intersections with an RM-30 (track mounted) drill rig equipped with hollow stem augers and 60 x 7.6 cm O.D. sample split tubes located within the lead auger. If no sample was obtained by this method, a split spoon was hammered ahead of the augers. All holes were continued to bedrock. The 60 x 6.5 cm core was split horizontally and replicate samples from each half were tightly packed into sterile 120 mL glass jars with Teflon lined screw cap lids. Packing of the samples was performed using stainless steel scoopulas and knives, and latex gloves were worn by the samplers to prevent contamination. Samples were packed as quickly, and with as little void volume as possible to minimise loss of volatile analytes. The samples were labelled and transferred to a cooler with ice packs for transport. If the samples were stored overnight before transfer they were kept in a refrigerator at 4°C until time of shipment. The samples were transported to the laboratories by air and

parallel analyses were performed on the samples using each of the methods under investigation. All utensils used for packing the sample into jars were wiped clean with a paper towel after each sample. The split tubes were cleaned with water from a high pressure washer after each sample was obtained. The auger was cleaned in this manner after each hole was completed. All boreholes were backfilled with any surplus excavated material and commercial bentonite (*Wyo-ben*, Enviro plug: medium; Paddock Drilling, Brandon, MB).

## 3.3 Subsampling

### 3.3.1 Syringe Technique

The subsampling technique employed for all analytical methods except where stated otherwise (Method 3, described in section 3.3.2), involved the use of a modified plastic syringe which was used to take a core from the sample jar (Figure 3.1). The tip of a (3 cc Becton Dickinson : Methods 4-10) plastic syringe was cut off using a scroll saw. A 120 mL glass jar containing the soil sample was brought to near room temperature, the screw cap was removed, and the top 1 to 2 cm of sample was discarded. The syringe barrel was depressed into the sample and a core was removed. The filled barrel was inserted into the subsample vial, the plunger depressed, and the soil plug was delivered quickly and efficiently, without soiling the rim of the vial. The subsample vials were sealed with a plastic screw cap and Teflon lined septa and stored in darkness at 4°C until the time of analysis.

Figure 3.1 Modified syringe subsampling device.



## 3.3.2 Scoopula Technique

The screw cap was removed from a 120 mL glass jar containing the soil sample and the top 1 to 2 cm of sample was discarded. The subsample was then obtained from the sample jar using a clean metal scoopula to scoop out a portion of the sample in a spoon-like fashion. The subsample was then placed in the extraction vessel and extraction takes placed as described.

### 3.3.3 Evaluation of Subsampling Techniques

An evaluation of the two subsampling techniques was undertaken to validate the modified syringe technique. The modified syringe technique was compared to the more traditional scoopula method. The scoopula method was performed by allowing the sample to warm to near room temperature, then uncapping the jar and discarding the top 1-2 cm of soil. The stainless steel scoopula was then used to transfer *ca.* 5 g of sample to the subsample vial. When sufficient sample had been transferred, the subsample vial rim was wiped clean and a screw cap lid with Teflon lined septum was applied. The amount of time required to obtain equivalent subsamples was measured using a stopwatch.

### 3.4 Analytical Methods

### 3.4.1 Method 1: Sonication (SON)

Method 1 was based on the U.S. Environmental Protection Agency (EPA) Method 3550 and 3580/8000 for total extractable hydrocarbons described as $C_{11}$ - $C_{30}$ (U.S. EPA, 1992). This method of extraction and analysis was performed in a commercial laboratory, where it is routinely used. The sample was stored for a maximum of 7 d at 4°C, in darkness. A 25 g portion was obtained by a modified syringe technique after the top 1 cm of sample had been discarded. The subsample was weighed into a culture tube and mixed with anhydrous sodium sulphate. A 1:1 mixture of hexane and acetone (10 mL) was added and the mixture was shaken for one hour on a wrist action shaker. The sample was sonicated for 5 min and then centrifuged. The solvent was decanted,

and an aliquot was injected into a Hewlett Packard gas chromatograph (GC) equipped with a flame ionization detector (FID), and a J&W Scientific DB-1 column. Samples were run in duplicate only when the matrix allowed for adequate homogeneity of contaminant distribution. Analyte recovery was assessed based on the percent recovered from matrix spikes. A standard soil was spiked with automotive grade diesel and water was added to 20% moisture. One of these tests was carried out for every 20 samples run. Other quality assurance and quality control (QA/QC) measures employed at this laboratory are outlined in Table 3.1. Quantification was based on the total area under the curve, and data was not adjusted according to the percent recovery of matrix spikes.

Table 3.2  QA/QC measures used with analytical Method 1.

| Technique | Frequency | Tolerances |
|-----------|-----------|------------|
| Standard Soil Blank | 1 per batch | no detectable peaks |
| Control Standard | 1 per day | ± 15% difference |
| Verification standard | 1 in 10 | ± 15% difference |

## 3.4.2  Method 2: Shaker (SHAKE)

Method 2 followed the Alberta Environmental Centre (AEC) method A108.0 for total extractable hydrocarbons in soil, described as $C_8$ - $C_{30}$. This method was carried out

in a second commercial laboratory where it was routinely being used. The sample was stored at 4°C to a maximum of ten days before analysis. A subsample was taken using a modified syringe technique to obtain *ca.* 20 g of soil. The subsample was then supersaturated with water, and shaken with dichloromethane (DCM), at a ratio of 2:1 (soil : DCM) for 1 h, on a wrist action shaker. The subsample was centrifuged and an aliquot of the extract was analysed by GC-FID (AEC, 1992). The samples were run on a Hewlett-Packard gas chromatograph using the following temperature program: 40°C (1 min), 10°/min to 325°C (10 min). The QA/QC analysis performed with this method were tests for accuracy and % relative standard deviation (RSD) based on spike recovery. Every twentieth sample was spiked in duplicate with automotive grade diesel fuel. From these analyses accuracy and % RSD are determined in the following manner:

$$\frac{\text{Ave \% Rec. MS} + \text{Ave \% Rec. MSD}}{2} = \text{\% Accuracy}$$

$$\frac{\text{Ave \% Rec. MS} - \text{Ave \% Rec. MSD}}{\text{\% Accuracy}} = \text{\% RSD}$$

where:

Ave % Rec. MS = matrix spike, and Ave % Rec. MSD = matrix spike duplicate.

Using a time slice technique, recoveries are grouped according to molecular weight, then totalled for $C_8$ - $C_{30}$. The data is not adjusted to reflect the determined percent

recoveries of spikes samples. Reported detection limits for this method were 1 ppm for all molecular weight groups.

### 3.4.3  Method 3: Sonic Probe (PROBE)

Method 3 is based on the U.S. EPA Method 3550 (U.S. EPA, 1992), and was the final method performed in a commercial laboratory setting in this study. This method aimed to quantify hydrocarbons in the range of $C_{11}$-$C_{29}$, inclusive. Samples were stored at 4°C for up to 14 days before analysis. A subsample was obtained by metal scoopula and then extracted using DCM as a solvent, and a Sonicator 300 Watt disrupter sonic probe with a 13 mm horn and 6 mm microtip. The extract was then analysed by GC-FID on a Hewlett Packard 5890 GC, using a DB-5 column, autosampler, and the HP Chemstation software package. The GC temperature program was as follows, with an injector temperature of 200°C, and a detector temperature of 300°C; 40°C (1 min), 20°/min to 250°C (5 min). Quantification was based on the addition of peaks in the ranges listed: $C_{10}$, $C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$, $C_{20}$, $C_{22}$, $C_{24}$, $C_{26}$, $C_{28}$. Percent recovery was determined using an EPA standard diesel fuel in soil. Data was not adjusted to reflect percent recovery. QA/QC was ascertained by running a control sample every ten samples, and a surrogate compound ($C_{30}$) in every sample. The limit of detection for this method was reported to be 5 mg/kg (ppm).

### 3.4.4 Method 4: Headspace Solid Phase Micro-extraction (H-SPME)

Solid phase micro-extraction was performed using a Supelco Canada, Inc., (Sigma-Aldrich Canada Ltd., Mississauga, ON, Canada) 100 μm polydimethylsiloxane (PDMS) coated fibre assembly (cat. no. 713-0126), with the manual fibre holder (cat. no. 5-7330). All fibres were pre-conditioned for 1 h at 200° C. Fibre blanks were run intermittently to check for fibre bleed or analyte carry-over. The subsample (*ca.* 5 g) was transferred by the modified syringe technique to a 40 mL clear glass vial with a Teflon lined septum and a screw cap closure. The sample was stored at 4°C in darkness until time of analysis, when it was brought up to room temperature (*ca.* 21°C) for analysis. The septum piercing needle was inserted into the subsample vial through the septum and the fibre was extended and exposed to the sample headspace for 15 min. After this time the fibre was withdrawn into the septum piercing needle, the apparatus removed from the sample jar, and the fibre inserted directly into the heated GC (SRI 8600) inlet (200°C), where the analytes were thermally desorbed from the fibre coating. Analysis was then performed by temperature programmed GC-FID. Chromatography was carried out in the department of Soil Science at the University of Manitoba using a portable SRI 8610 GC (Chromatographic Specialties Inc., Brockville, Ontario) equipped with an FID. A J&W Scientific (Chromatographic Specialties, Brockville, ON) DB-5 30 m column with a 0.1 μm film was used. Prepurified hydrogen and helium at flow rates of 6.7 and 3.2 mL/min respectively were used along with compressed air provided by the GC air compressor at a flow rate of *ca.* 3mL/min. Data was collected on a portable Toshiba 4900 computer using Peak Simple II or Peak

Simple for Windows (version 1.16) software. The GC temperature program was as follows: 40°C (2 min for SPME or 0.45 min for all syringe injections), 5°/min to 250°C (3 min), 10°/min to 280 °C (2 min). These analyses were performed in triplicate, and total area counts were averaged over the entire run time.

### 3.4.5 Method 5: Heated Headspace Solid Phase Micro-extraction (HH-SPME)

The SPME and GC run conditions follow those described in Method 4. The difference in this method is that the sample was heated for extraction. The entire subsample vial excluding cap, was immersed in a 50°C water bath and allowed to acclimate before extraction occurred. These analyses were performed in triplicate and total area counts were averaged. These subsamples had already been analyzed by Method 4.

### 3.4.6 Method 6: Direct Solid Phase Micro-extraction (D-SPME)

Samples already extracted by headspace SPME (Methods 4 and 5) had 20 mL of HPLC grade water added through the septa using a plastic syringe. The vials were shaken in darkness, using a wrist action shaker, for 16 h at room temperature. The samples were then returned to 4°C storage, and the sediment was allowed to settle for 10 d. At the time of analysis, the separated samples were brought up to room temperature, uncapped, and a 1.5 mL aliquot of water extract was taken by auto pipette and transferred into 2 mL glass auto sampler vials with screw cap lids and Teflon lined septa. The liquid samples were loaded into a Varian 8200 cx SPME autosampler. The SPME adsorption was performed using a Supelco 100 μm PDMS coated fibre assembly

(Supelco cat. no. 713-0126), in an auto sampler casing (Supelco cat. no. 713-0127). Extraction time was 15 min and vibration of the sample carousel was achieved during extraction using the "Woodpecker device" developed in-house (Thomas et al., 1998). Once the extraction time had elapsed, the fibre was automatically withdrawn from the vial and inserted into the Varian Star 3400 cx GC equipped with an FID. Chromatography was performed as described in Method 4. Data was collected using the Varian Star Chromatography Software package (version 4.02) on an Opus 486 computer.

### 3.4.7 Method 7: Supercritical Fluid Extraction (SFE)

Extractions were performed on an ISCO SFX 2-10 Supercritical Fluid Extractor following U.S. EPA method 3560 with some modifications. A known amount of sample (*ca.* 5 g) was mixed with *ca.* 3 g of anhydrous sodium sulfate within the subsampling vial. A layer of anhydrous sodium sulfate was added to the stainless steel 10 mL extraction vessel, the sample mixture was added, and another layer of anhydrous sodium sulfate was added to fill the void volume in the vessel. $CO_2$ was used to extract the samples at a temperature of 80°C, under 340 atm (3.43 x $10^7$ N/m$^2$) pressure for 30 min in dynamic mode. The extract was collected in a vented glass tube containing 3 mL of dichloromethane (DCM), with an 8.5 inch 50 μm restrictor heated to 100°C. The extract was run through solvent-wetted glass columns of anhydrous sodium sulfate to remove any residual water. The column was rinsed with at least 3 mL of solvent to ensure that all extracted analyte had passed through.

The volume was brought up to 5 mL with DCM, transferred to 12 mL glass vials with Teflon septa and screw cap lids and stored at 4°C in the dark until analysis by GC-FID.

### 3.4.8 Method 8: Soxhlet (SOX)

Approximately 5 g of sample was mixed with *ca.* 3 g of anhydrous sodium sulfate in the subsample jar. The sample was transferred to a cellulose extraction thimble and soxhlet extraction was performed following EPA method 3540B, modified to accommodate a reduced sample size. As the soil sample analyzed was reduced by 50% (from 10 g to 5 g), the total solvent volume was also reduced by 50% (from 300 mL to 150 mL). A 1:1 mixture of acetone and hexane with a total volume of 150 mL, with boiling chips added, was used for extraction. The transformer connected to the power supply was set at 50% power creating a steady, even boil. Extraction proceeded for 16 h and the extract was allowed to cool. All solvent and hexane washings were poured through anhydrous sodium sulphate on filter paper in a glass funnel to remove any residual water. The extracts were then concentrated by rotary evaporation at 60°C to near dryness. The volume was then brought up to 5 mL with hexane and the solution transferred to 12 mL glass vials with screw cap lids and Teflon lined septa and stored at 4°C in the dark until analyzed by GC-FID, as described in Method 4.

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### 3.4.9 Method 9: Magnetic Stirring (STIR)

This method is based on an in-house commercial laboratory method for total extractable hydrocarbons in soil ($C_{10}$-$C_{30}$). Approximately 5 g of sample was acidified using 75 μL concentrated HCl (reagent grade), mixed with *ca.* 3 g of sodium sulfate, and transferred to a hexane-rinsed 50 mL Erlenmeyer flask. Reagent grade hexane (25 mL) was added, and the sample was stirred for 1 h with a Teflon coated 15 mm oval magnetic stir bar at 60 % maximum speed to produce a vortex 1 cm deep. The mixture and 10 to 15 mL of hexane rinsings were filtered through solvent rinsed Whatman IPS filter paper (15 cm diameter). The extract volume was reduced to near dryness by rotary evaporation at 40°C, brought up to 5 mL with hexane, and stored in darkness at 4 °C in 12 mL glass vials with screw cap lids and Teflon lined septa. A 1 μL aliquot of the extract was then injected into the GC inlet for analysis by FID as described in Method 4.

### 3.4.10 Method 10: Near-infrared Reflectance Spectroscopy (NIRS)

Near-infrared reflectance spectroscopy was performed on *ca.* 5 g samples which had been sub-sampled by the modified syringe technique and stored at 4° C in darkness until time of scanning. Samples were contained in a 40 mL glass vial when scanned using an NIRSystems Model 6500 visible/NIR spectrophotometer (NIRSystems, Silver Spring, MD) equipped with a Rapid Content Sampler®. The analyses were performed by Ms. Laurie Wesson working with Dr. Diane F. Malley, at the Freshwater Institute, Winnipeg, MB. Using the Near infrared Spectral Analysis Software (NSAS), provided

with the instrument, absorbance at wavelength intervals of 2 nm was recorded over the wavelength range 1100 to 2498 nm as log 1/R, where R is reflectance. The samples were read three times, usually sequentially. The sample was removed from the detector, shaken, and replaced in order to obtain representative scans of the material. Prior to each scan of a sample, a ceramic reference was scanned and the reference spectrum was automatically subtracted from the sample scan. Each sample or reference scan took about 40 s.

### 3.4.10.1 Development of NIR Calibrations.

The sample set consisted of 26 contaminated soil samples each scanned in triplicate. The triplicate spectra were averaged to give one spectrum per sample. The results of the laboratory analysis for each sample were added to the NIR spectral file. The spectra were then sorted from lowest to highest hydrocarbon values. The spectra were then divided into two sets, the odd-numbered spectra as a calibration set and the even-numbered spectra as the prediction set. Each set represented the full range of concentrations. Using the calibration set, a large number of calibration equations were developed over wavelengths of 1100-2498 nm using the stepwise multiple linear regression (MLR) option in the NSAS software. Separate calibration equations were computed using the raw optical data (log 1/R) smoothed over four and ten wavelength points, and using the first or second derivatives of the smoothed log 1/R data, with several combinations of segment (smoothing) and derivative ("gap") sizes. Each calibration equation developed from the calibration set was used to predict hydrocarbon values for the spectra in the

prediction set. For each trial, the NIR-predicted values for the prediction set were correlated to their reference chemistry values. The process was completed when one calibration equation was selected as giving the best results. The best calibration is the one with the highest $R^2$ and lowest SEP (standard error of performance).

## 3.5 Extraction Efficiency

The use of spike recovery data is still widespread in commercial environmental analyses to report extraction efficiencies of the method in use. Although questions have been increasingly raised about the usefulness of these tests, it was decided that spiked samples should be sent to the commercial laboratories for analysis. The information gained from this aspect of the study was used to determine the potential loss of analyte during the various analytical procedures post-extraction. The recovery of a spiked analyte is not related in this study to the actual achievable recovery of a real world, aged and weathered hydrocarbon contaminated sample.

### 3.5.1 Spiking Method

Uncontaminated sand samples (1200 g) (obtained from MB Hydro) in thick polyethylene bags were spiked in three concentrations with diesel fuel, obtained from the Petro Canada gas station at 2012 Pembina Highway, Winnipeg, Manitoba. The diesel was stored in a clean 4 L brown glass bottle at room temperature until used (*ca.* 4 wk). Concentrations of 10,000, 1,000 and 75 ppm (mg/kg) were produced by

adding 14.2 mL, 1.42 mL and 71.1 μL of diesel fuel respectively, made up to a total volume of 20 mL with DCM, to the sand portions. The mixture was poured onto the sand, the bag was twisted closed, retaining air space for mixing. The sand was well mixed, and all areas were seen to have been wetted with the solvent - diesel mixture. Glass sample jars (120 mL) were then filled using a glass beaker and firmly packed leaving as little headspace as possible. The jar rim was cleaned and the screw cap lid applied. The jars were stored in the dark at 4 °C until they were sent to the laboratories for analysis (*ca.* 12 h).

# 4. RESULTS AND DISCUSSION

## 4.1 Prelude

This project was undertaken to evaluate several analytical techniques which might be used for diesel fuel derived contaminants in soil. Over the course of the project, changes which were beyond the control of the participants in the study meant that one method had to be eliminated from the study. In particular, the changing ownership of one of the commercial laboratories resulted in a change of analytical methodology employed at that institution. This meant that Method 3 was no longer commercially available in the second year of the study. As a result, Method 3 was utilized only in year 1. Furthermore, a number of additional methods were added to the study in the second year. Method 6 (SPME - direct) was examined in the first year, and the resulting modifications were employed as Method 6 in Year 2. In addition, Dr. Diane F. Malley of the Freshwater Institute (Winnipeg, Manitoba) graciously provided the opportunity and facilities to examine NIR (Method 10) in the context of the project. Consequently the data will be discussed in terms of the Year 1 (1995) results and the Year 2 (1996) results. While the two sampling periods are not replicates of one another, important information was gained through the Year 1 study which was used to the benefit of the Year 2 study design.

## 4.2 Year 1 Results

The data included in this section are those obtained by Methods 1, 2 and 3, all of which were carried out by commercial laboratories as a part of their routine analyses. Methods 4 and 5 results were obtained by the author through work performed in the Department of Soil Science at the University of Manitoba. These results will be presented and compared to one another to the extent possible in the context of environmental evaluation through chemical analysis of diesel fuel contaminated soil. The comparisons are based on the criteria of accuracy and precision (ascertained through visual and statistical analysis). Accuracy is defined as how close the result is to the actual concentration, and precision is defined as the ability to obtain the same result consistently with multiple extractions of a sample. Other parameters which affect the applicability of a method (hazardous material generation, time & instrumentation needed, portability and specificity) were also evaluated. These criteria were assessed in three phases. The visual assessments were performed in Phase I, the statistical assessments in Phase II, and the other parameters in Phase III.

This study was designed to investigate potential sources of variability among results obtained by different analytical methods during the course of subsurface contaminant geotechnical investigations. As the onset of any analytical procedure occurs at time of sampling, the normal sampling procedures were used to obtain samples for this study.

These samples were obtained as a part of an actual investigation carried out by Manitoba Hydro. The determination of which samples are to be analyzed for TPH content in the commercial laboratory setting was performed, as usual, by the chief geological engineer on site. These data, along with the site investigation logs, containing soil information, was forwarded to the author by the geotechnical staff at Manitoba Hydro as they became available. It is within this context of an actual site investigation that the study samples were acquired and comparison of the various results obtained by different analytical methods were made. Constraints of sample availability, financial costs of analysis, and of procuring the sample in a remote northern site were all present. The site investigations performed by Manitoba Hydro geotechnical staff with the assistance of a professional drilling team in a remote northern community ran at considerable cost; therefore, time was also a factor for consideration at all times. In Year 1 of the study the author and Mr. Leonard P. Sarna (Department of Soil Science at the University of Manitoba) assisted in obtaining the majority of the samples for analysis. In Year 2 (GV and CB) all samples were graciously provided by Manitoba Hydro staff using the same procedures as in the Year 1 sampling. Where gaps in the data sets occur it must be realized that this was not out of poor design, but rather out of substantive constraints of performing analyses on actual samples obtained through Manitoba Hydro site investigations.

## 4.2.1 Phase I Assessment

The results presented in Table 4.1 from Methods 1 (SON), 2 (SHAKE) and 3 (PROBE) are derived from standard methods performed in commercial laboratories, which, at the time of analysis were using these analytical procedures on a routine basis. These methods are used to characterize hydrocarbon contamination of soils for compliance with Manitoba Environmental regulations. The results of these analyses are used by industries and regulators to make decisions on land use suitability and regulatory compliance. The results are used regularly to define contaminant boundaries and severity, demonstrate clean-up, and make remediation decisions. Reliable qualitative results are of paramount importance in this decision making process. The standard methods, such as Methods 1, 2 and 3, are used exclusively for the reason that they are expected to provide the most reliable and accurate information possible. These methods are developed to be robust enough to produce adequately reliable results from one commercial laboratory to another. Under these assumptions, the methods are employed and the resulting data is often utilized without any measure of assurance of their accuracy or reliability. From the comparisons performed in this study, it becomes evident that there are instances of great variability among results obtained by different methods which are supposed to produce similar results. The coefficient of variance (CV) reported in the data tables has been calculated by dividing the standard deviation by the average. Large coefficients of variation reflect the variabilities of the data sets and will also make the determination of statistical significance between data sets more difficult.

Table 4.1 Year 1 results obtained by Methods 1, 2 and 3 for TPH (mg/kg, or ppm).

| Hole no. | Depth | Sample code | Soil type | Method 1 | Method 2 | Method 3 | CV |
|---|---|---|---|---|---|---|---|
| CH 209 | 0.00-0.51 | CH 1 | SM[a] | 1200 | 5200 | | 88% |
| CH 211 | 0.00-0.51 | CH 2 | SM | 140 | | 130 | 5% |
| CH 213 | 1.52-2.03 | CH 3 | CL[b] | 280 | | 95 | 70% |
| | 1.18-1.52A | CH 4 | CL | 3000 | 9500 | 710 | 104% |
| | 1.45-1.55 | CH 5 | CL | 41000 | | 2100 | 128% |
| | 1.77-2.03 | CH 6 | CL | 29 | | 39 | 21% |
| CH 219 A[c] | 0.7-0.9A | CH 7 | SM | 6500 | 10000 | | 30% |
| CH 219 | 1.05-1.19 | CH 8 | SM | 2200 | 2900 | 150 | 82% |
| | 1.25-1.50 | CH 9 | SM | 19000 | | 930 | 128% |
| | 1.60-1.80 | CH 10 | CL | 8000 | 15000 | | 43% |
| CH 222 | 0.45-0.65 | CH 11 | SM | 11000 | | 360 | 132% |
| | 1.52-1.74 | CH 12 | CL | 4700 | | 270 | 126% |
| | 2.03-2.28 | CH 13 | CL | 26 | 30 | | 10% |
| | 1.52-1.76 | CH 14 | CL | 270 | | 63 | 88% |
| CH 199 A | 0.30-0.50 | CH 15 | SM | 11000 | 6200 | 790 | 85% |
| | 0.50-0.80 | CH 16 | SM | 31000 | 24000 | 690 | 85% |
| | 1.20-1.50 | CH 17 | CL | 64 | 160 | 14 | 94% |
| CH 198 A | 1.20-1.50 | CH 18 | CL | 53 | 120 | 38 | 62% |

[a] SM = silty sand
[b] CL = low plasticity clay
[c] A = auger sample

Upon viewing the numerical data, it is apparent that the values reported by Methods 1 and 2 are in greater agreement to one another than to those obtained by Method 3. In all cases except one, the result obtained by Method 3 was lower than those obtained by either Method 1 or 2 for the same sample. As Method 3 results are consistently low in this study it is postulated that Method 3 is biased low. Further visual and statistical assessments will appraise the validity of this statement. Other remarks which can be made about these results after a visual assessment are that there are some instances of great variability among the methods in relative agreement (Method 1 and 2). For

example, sample CH 1 is reported at 1200 ppm by Method 1, which would meet level II remediation criteria for Manitoba soils. However, the result reported by Method 2 is 5200 ppm which would not meet the level II criteria of 2000 ppm. In the cases of samples CH 15 and 16, the Method 2 results reported are lower than the Method 1 reported results. For this reason, it appears that neither Methods 1 nor 2 are biased high or low. Visually however, there appears to be an alarming lack of accuracy in predicting the amount of contaminant present in a contaminated sample by these three standard methods. Due to the nature of this portion of the study, it is not possible to say which method is providing the most accurate answer as the actual concentration of TPH in these real world samples is not known. The spiking portion of the project will be able to address the accuracy and bias questions to some extent.

Another means of visually assessing the data is to plot the results obtained by one method against the results obtained by another method. The resulting line fit and slope will indicate how close the results of one methods are to the others. In the case of a perfect match, the line would have a slope of 1, and the adjusted $R^2$ value would approach 1 (0.999). As the results from one method are plotted against those of another method apparent outliers may be encountered. These data points which may skew the slope and $R^2$ values must be carefully considered for the role which they may play in determining the similarities of two methods. Data may be tested for outliers using box plots or some other method (Howell, 1992). However, it must be understood that there is no set definition for the determination of an outlier. This

implies that the selection of the outlier analysis method can lead to the subjective determination of outliers (Hunter, 1998). Such subjective tests must be carefully applied when discarding data is a result. For these reasons outlier analysis was not undertaken in this study.

When results from Methods 1 through 5 were individually plotted against one another, the only two methods which produced a slope close to 1 (between 0.6 and 1.4) were Methods 1 and 2. The slope obtained was 0.8627, and the $R^2$ value was 0.6808 (see Figure 4.1). This indicates that Methods 1 and 2 have produced fairly similar results overall in Year 1. The other Methods examined in Year 1 did not produce results similar to one another in Year 1. It should be noted that the sample size for Methods 4 and 5 was very small in Year 1, and this would make correlations more difficult.
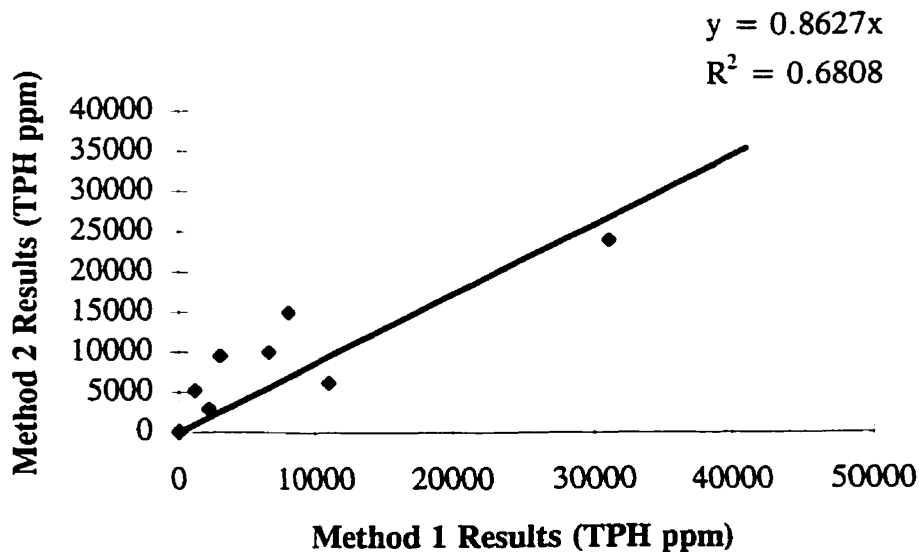


Figure 4.1  Method 1 results versus Method 2 results for TPH (mg/kg or ppm) for Year 1 (CH) samples.

Calibration of Method 4 and 5 results was retroactively performed using the calibration equations for each method developed in Year 2. The application of these equations was most desirable as in Year 1 of the study there were very few results which were reproduced across all of the methods in question. Because of this low number of complete replicates, it was not possible to select an adequate number of results to create a calibration curve for Methods 4 and 5. For this reason the calibration equations derived in Year 2 were applied to the Year 1 data. This method for calibration will be detailed in section 4.3.2.

As all of the numerical data was visually assessed, it became apparent that there were two possible categories which seemed to be well defined in high and low groups based on Method 1 results. The low group consists of results in Method 1 between 0 and 999 (mg/kg or ppm), and the high group consists of results in Method 1 which are greater than 1000 (mg/kg or ppm). Method 1 results were chosen as the benchmark results as this is a standard analytical method which was performed in a commercial laboratory setting, and the greatest amount of data was available for this method. The high and low categories were chosen as the results seemed to have an obvious split at these groupings with seven samples below 300 (mg/kg or ppm), and the remaining 11 samples were all above 1200 (mg/kg or ppm). These groupings are also significant as they overlap the Manitoba remediation criteria for TPH in soil. The level I criteria

being 500 (mg/kg or ppm) and the level II, III and IV criteria being 2000 (mg/kg or ppm).

In Figures 4.2 and 4.3, it can be seen that Method 3 results are consistently lower than any of the other results presented. Method 4 and 5 results are variable at the higher concentrations with respect to the reported results of Methods 1 and 2. At the lower concentration levels however, Method 4 and 5 results are consistently higher than the results reported by Methods 1 and 2.
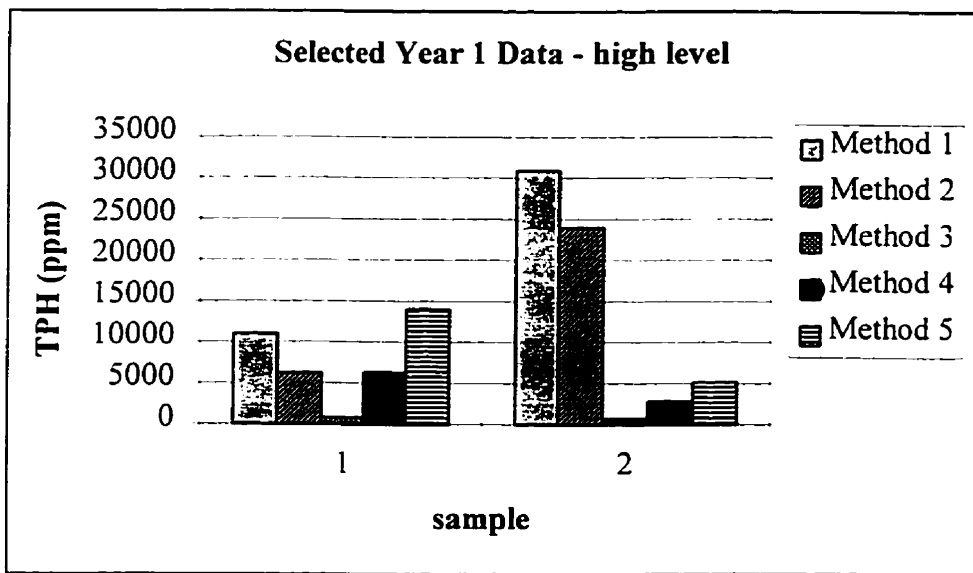


Figure 4.2 Selected Year 1 Data at high reported concentrations.
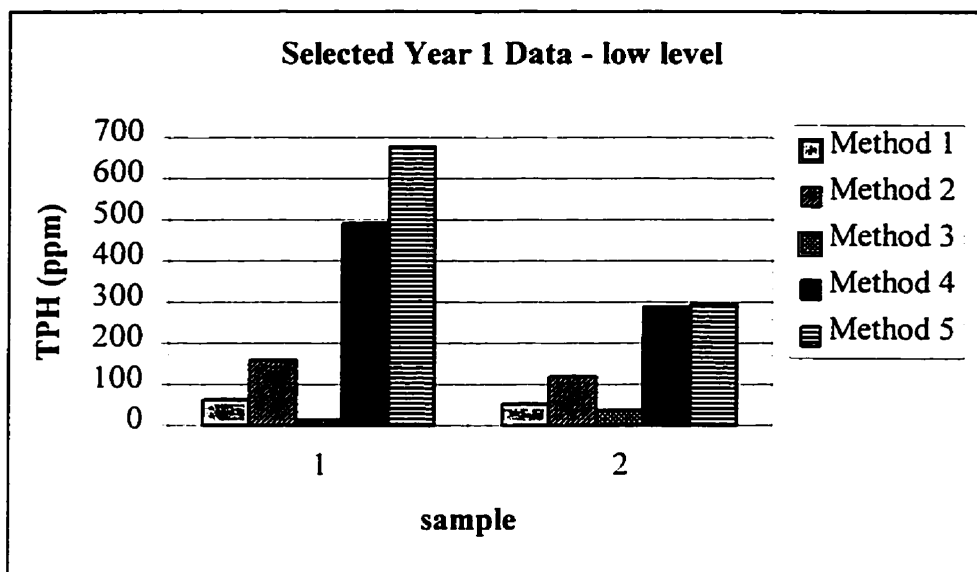
Figure 4.3 Selected Year 1 Data at low reported concentrations.

### 4.2.2 Phase II Assessment

For the statistical assessments, student's $t$ tests were performed on the data for pair wise comparisons. The tests were chosen to be two tailed because one method can produce a result which may be either higher or lower than the result produced by another method. An alpha ($\alpha$) value of 0.05 or lower is considered to be significant (indicating that the two methods being compared have produced significantly different data sets). This means that the chance of having this difference randomly occur is 5 in 100, and is a widely accepted value for significance in student's $t$ tests. When the two tailed, paired student's $t$ test was performed on the data obtained by each method, there was only one pair of methods that appeared to be significantly different from one another at the 0.05 level. Method 3 was significantly different from Method 1, with an $\alpha$ value of 0.03. It should be mentioned that the number of samples available for the

statistical comparison was as low as 5 for some methods, providing few degrees of freedom and potentially large standard deviations with which it is difficult to obtain statistically significant differences.

Table 4.2  Student's $t$ test $\alpha$ values for results from Year 1 (CH) samples. Only those numbers at or below 0.05 show significant differences between methods.

|          | Method 2 | Method 3 | Method 4 | Method 5 |
|----------|----------|----------|----------|----------|
| Method 1 | 0.50     | 0.03     | 0.19     | 0.34     |
| Method 2 |          | 0.12     | 0.41     | 0.68     |
| Method 3 |          |          | 0.12     | 0.13     |
| Method 4 |          |          |          | 0.14     |

The student's t test was performed on two groups of results; low (0-999 ppm) and high (1000+ ppm) as found by Method 1. There was no significance found in the low category, however, there was significance found between Methods 1 and 3 in the high group. It should be noted that the high group had more data than did the low group, providing better potential for finding significant differences.

Table 4.3  Student's $t$ test $\alpha$ values for results from low (0-999 ppm; from Method 1) Year 1 (CH) samples. Only those numbers at or below 0.05 show significant differences between methods.

|          | Method 2 | Method 3 | Method 4 | Method 5 |
|----------|----------|----------|----------|----------|
| Method 1 | 0.18     | 0.11     | 0.18     | 0.26     |
| Method 2 |          | 0.17     | 0.20     | 0.29     |
| Method 3 |          |          | 0.19     | 0.27     |
| Method 4 |          |          |          | 0.48     |

Table 4.4 Student's $t$ test $\alpha$ values for results from high ($\geq$1000 ppm; from Method 1) Year 1 (CH) samples. Only those numbers at or below 0.05 show significant differences between methods.

|          | Method 2 | Method 3 | Method 4 | Method 5 |
|----------|----------|----------|----------|----------|
| Method 1 | 0.52     | 0.02     | 0.19     | 0.36     |
| Method 2 |          | 0.12     | 0.50     | 0.75     |
| Method 3 |          |          | 0.16     | 0.14     |
| Method 4 |          |          |          | 0.14     |

In these Year 1 comparisons it was found that while there was only one case of statistically significant differences between two methods, wide variability in results was observed. Difficulties in creating a calibration set from the data of Year 1 led to the decision to use Year 2 calibration data for Methods 4 and 5 in Year 1. Both of the above stated situations were a result of few samples having been replicated across each method under investigation. This situation was rectified in Year 2 of the study. The major observation from this part of the study is that variability among commercially available methods is quite high (200-300%).

Method 3 results are in almost all cases substantially lower than the results obtained by the other two standard methods. The extraction technique in Method 3 makes use of an ultrasonic probe. This vigorous extraction technique can lead to the erosion of the probe tip which can result in reduced extraction efficiency as the probe tip wears, resulting in low reproducibility of data (Sarna, 1997). In addition, subsampling in

Method 3 was performed using the traditional scoopula technique. This technique has been shown to result in increased loss of volatile hydrocarbon analytes compared to the modified syringe subsampling technique because of the longer time required to transfer the sample (Hewitt et al., 1995). The loss of volatile analytes may be a factor in the observed lower responses of Method 3; however, internal laboratory problems with instrumentation and quality assurance / quality control measures are likely the most important factor, as reported by the laboratory using this method.

### 4.2.3 Phase III Assessment

The Phase III assessment is based on other parameters which affect the practical application of a method. These parameters include hazardous material generation, time & instrumentation needed, portability and specificity. When hazardous materials are used or generated in the course of performing a soil analysis, there are increased costs and concerns with performing the method, especially on a wide-spread basis. Hazardous organic solvents (such as chlorinated solvents) may be difficult and costly to obtain and dispose of. Extra precautions must be taken by the technician to insure his or her safety. Safety equipment such as ventilation systems, and protective wear requires certain infrastructure and ongoing costs. While these may be in place in accredited laboratories, it may be difficult to achieve in remote locations or in underdeveloped countries.

The time required by instruments and personnel to perform an analysis affect turn around time and cost of analysis. Lower turn around time may mean monetary savings for the data user, especially in a situation such as Manitoba Hydro's where many people on the drilling crew are retained often at remote northern sites. A quick and reliable answer may produce significant cost savings by eliminating unnecessary drill holes and soil analyses. Reduced analytical costs which are passed on to the consumer may mean that more soil analysis can be performed. This may result in a better characterized site, which can lead to more effective decision making. Consequentially, the number of surprises and delays encountered on a project may be reduced.

Instrumentation needed to perform an analysis affects many other relevant parameters such as the cost of the analysis, the skill level required of the technician, and the portability of the method. Instruments used in an analysis include extraction instruments and glassware, gas chromatographs or other detection devices, and data handling systems.

The potential for an analytical method to be performed in a field setting defines portability here. The benefits of having a potentially portable method are related to turn around time and cost. If a method can be performed in the field, and turn around time is low, near real-time monitoring may be achieved. However, even if this is not the goal, the benefit of having results obtained in the field are great. This would allow the investigation team to respond rapidly to unexpected results, avoiding delays and

backtracking. For example, the result from one sample may lead the investigator to sample in another direction than was originally planned, and this could be done immediately, rather than coming back to the site at a later time. Costs could be reduced by the reduced response time, and on-site analysis would eliminate the costs involved with transferring samples to a remote laboratory. The case of many northern sites, sample transport is done by air which can be costly. In addition, increased time between sampling and analysis can increase the likelihood of loss of analyte. This is especially of concern with volatile and semi-volatile compounds.

Although current methods used for TPH evaluations in soil do not identify specific compounds, as more is learned about the range of toxicity of compounds in hydrocarbon fuels it may be desirable to quantify certain compounds of interest within the contamination. For example, as health risks of a certain PAH which may be present in diesel fuel are recognized, it would be beneficial to be able to identify the compound using the same analytical technique as is used for identifying the total amount of hydrocarbon present. This would give the investigator a more meaningful picture of the contamination and its significance in the ecosystem. For this reason it would be an asset to be able to select for certain compounds using an analytical method and to identify and quantify them.

Methods 1, 2 and 3 were compared under these above mentioned criteria. Method 1 utilizes 10 mL of non-chlorinated organic solvents, while Methods 2 and 3 require

between 20 and 200 mL of a chlorinated solvent. Under this criterion Method 1 appears to be superior. The time required to perform the work-up and extraction for Method 1 is 1 h 15 min. Method 2 work-up and extraction requires approximately 1 h and 25 min, Method 3 requires *ca.* 1 h. Given that the skill of the technician performing these tasks influences the speed and efficiency of the work-up, it was not possible to say that the time requirements for these three methods differed significantly. The instrumentation required for each of these methods is very similar. These methods used standard GCs with FID detection and computerized data handling. Methods 1 and 3 required a sonication device, while Methods 1 and 2 used a wrist action shaker and related glassware. In all cases, relatively large and expensive instruments, solvents and standard lab set ups are required. Portability of the methods for the above reasons would be difficult. The specificity of the methods may be varied by adjusting the solvents used. This technique is of limited capacity for selecting specific compounds as it may only preferentially extract groups of compounds. The use of a more specific detection system such as a mass spectometer would allow for compound identification. None of these options were used in this study.

## 4.3  Year 2 Results

The results presented in this section are those of Methods 1 and 2 which were carried out in commercial laboratories where these analyses are routinely performed. Method 1 however, was performed in a new location, but by the same corporation which had

performed these analyses in Year 1. Method 3 was no longer commercially available and was therefore not included in the Year 2 comparisons. Methods 4 through 9, also included in this section, were performed at the University of Manitoba, Department of Soil Science by the author. Method 10 was performed at the Freshwater Institute, Winnipeg, MB. The soils utilized in this part of the study are those from Granville Lake and Cranberry Portage Manitoba. These soils provided a variety of textures ranging from clay to sand. Soil characterization data is available in the Appendix.

### 4.3.1 Methods 1 (SON) and 2 (SHAKE)

**4.3.1.1 Phase I Assessment.** Table 4.6 provides the data obtained by Methods 1 and 2 for the Granville Lake samples which are predominantly clayey in texture. The results obtained by these two methods on the GV samples appear to have some variability, particularly around the decision making values of 500 and 2000 ppm total petroleum hydrocarbons in soil at level I and level II remediation criteria respectively. In most cases the results vary by *ca.* 200% of one another, however, it does not appear that one method yields values consistently higher or consistently lower than the other method.

Table 4.5  Total petroleum hydrocarbon (mg/kg, or ppm) data obtained by Methods 1 and 2 for Granville Lake (GV) samples.

| Hole no. | Depth | Sample code | Soil type | Method 1 | Method 2 | CV |
|---|---|---|---|---|---|---|
| GV 01 | 0.50-0.75 | GV 1 | CH$^a$ | 300 | na$^b$ | |
| | 0.75-1.0 | GV 2 | CH | 310 | 101 | 72% |
| | 1.25-1.5 | GV 3 | CH | 790 | 1365 | 38% |
| GV 12 | 1.25-1.5 | GV 4 | CH | 1600 | 4119 | 62% |
| | 1.75-2.0 | GV 5 | CH | 470 | 1502 | 74% |
| | 2.20-2.4 | GV 6 | CH | 480 | 914 | 44% |
| GV 17 | 2.39-2.49 | GV 7 | ML$^c$ | 3800 | na | |
| GV 34 | 1.50-1.75 | GV 8 | CI$^d$ | 4700 | 2254 | 50% |
| | 1.75-2.00 | GV 9 | CI | 3700 | 1248 | 70% |

$^a$ CH  =  high plasticity clay
$^b$ na  =  not available
$^c$ ML  =  low/non plastic clay
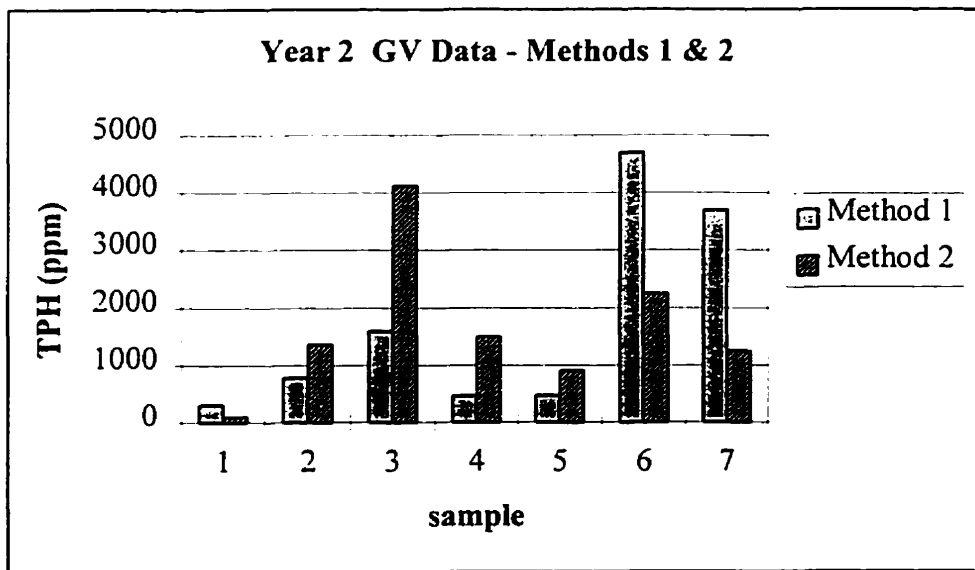$^d$ CI  =  intermediate plasticity clay



Figure 4.4  TPH in Granville Lake (GV) samples by Methods 1 and 2 (Year 2).

The results obtained by Methods 1 and 2 on the CB samples show greater variability between the methods than those for the GV samples. One reason for this variability may be the nature of the CB sample matrix. The predominantly sandy samples have a very coarse texture. This means that while the sample may be easier to extract as it is easier to contact the matrix surfaces which hold the contaminant, it is also more likely that loss of volatile analytes will be a greater problem since the volatile hydrocarbons will be more easily exposed to the air than they will be in the clayey GV samples.

Table 4.6 Total petroleum hydrocarbon (mg/kg, or ppm) data obtained by Methods 1 and 2 for Cranberry Portage (CB) samples.

| Hole no. | Depth (m) | Sample code | Soil type | Method 1 | Method 2 | CV |
|---|---|---|---|---|---|---|
| CB 04 | 2.28-2.85 | CB 1 | ML[a] | 67 | 11494 | 140% |
|  | 3.80-4.27 | CB 2 | SP[b] | 7000 | 3411 | 49% |
|  | 4.92-5.30 | CB 3 | ML | 13 | 1 |  |
|  | 6.85-7.25 | CB 4 | SP | 6000 | 2147 | 67% |
| CB 05 | 6.85-7.22 | CB 5 | ML | 7.5 | 2776 | 141% |
| CB 06 | 3.80-4.17 | CB 6 | SP | 190 | 41 | 91% |
| CB 08 | 8.55-9.15 | CB 7 | SP | 410 | 1 | 141% |
|  | 10.28-10.65 | CB 8 | SM[c] | 4.1 | 1 | 86% |
| CB 15 | 3.05-3.55 | CB 9 | SP | 71 | 668 | 114% |
| CB 16 | 1.87-2.25 | CB 10 | SP | 10000 | 652 | 124% |
|  | 2.62-3.05 | CB 11 | SP | 0.5 | 41 | 138% |
|  | 3.05-3.42 | CB 12 | SP | 5.2 | 1 | 96% |

[a] ML = low/ non plastic silt
[b] SP = clean sorted sand
[c] SM = silty sand
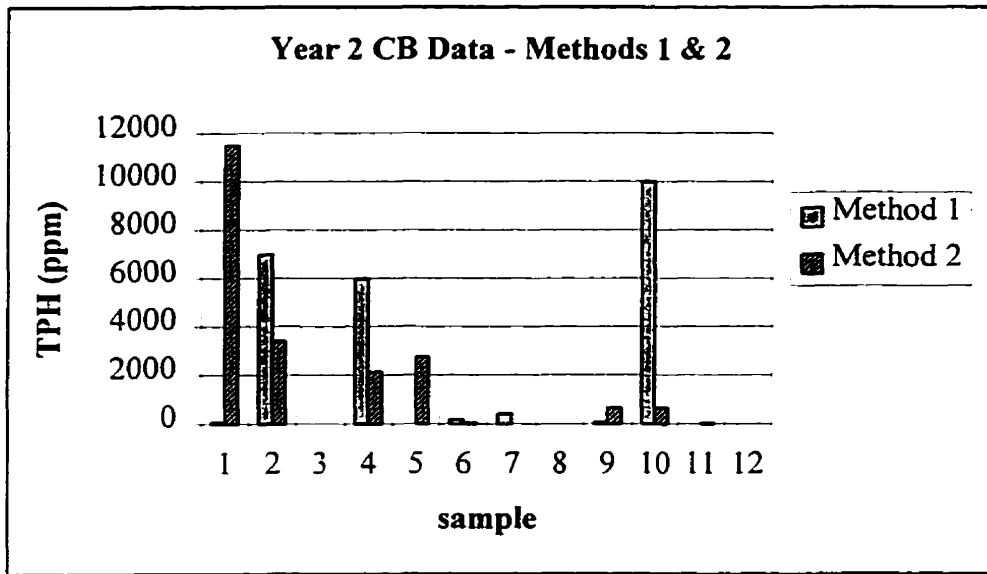
Figure 4.5  Data obtained by Methods 1 and 2 in year 2 from Cranberry Portage (CB) samples. Where results do not appear on graph, value is too low to be shown. Refer to Table 4.6 for data.

When all of the results obtained by Methods 1 and 2 in Year 2 (GV and CB) are plotted against one another, the slope is not close to one (0.3034), indicating that the results are not very similar. However, when only the GV data for these methods are plotted, the slope of the line is closer to one (0.6088), indicating that for the clayey GV samples there is better agreement between the results. The $R^2$ value however, is still very poor at -0.4403, indicating that the fit of the line to the data is weak.

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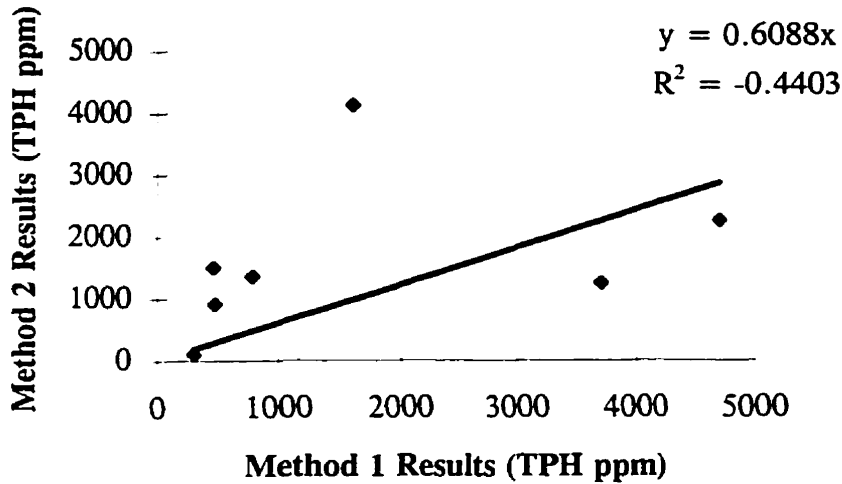Figure 4.6  Method 1 results versus Method 2 results for TPH (mg/kg or ppm) for Year 2 GV samples.

**4.3.1.2 Phase II Assessment.** Upon performing a two tailed student's $t$ test, Methods 1 and 2 for these data are not significantly different from one another at the 0.05 level (see Table 4.13). When the data is divided into low level ($< 1000$ ppm by Method 1) and high level ($> 1000$ ppm by Method 1) there were no statistically significant differences found between results from Methods 1 and 2 using the student's $t$ test.

When the two tailed student's $t$ test was performed on the methods using the complete CB data and the data grouped by concentration levels, there were no significant differences in any case at the 0.05 level (see Table 4.15). The student's $t$ test may not be able to detect differences when one high data point within a method is canceled out by one low data point, as is the case within each of the methods. For this reason,

significant difference may be impossible to detect in this case. Results for some of the samples are very high with one method and much lower with the other method; however, one method is overall neither consistently high nor low. For this reason it is not possible to state if a methodological bias was present.

The outcome of this comparison is that while results obtained by Methods 1 and 2 often differ by 200% or greater in some of the sandy samples (up to 37 000%), overall there is no statistical significance between the results obtained. As there were instances of extreme variation found in the sandy samples and not in the clayey samples, it may be concluded that soil characteristics have an effect on the reproducibility of results obtained in this study. The practical implication of this finding is that while the variability of soil type may be an important consideration for sample handling and data variation, it is not formally taken into account in either of the methods. When dealing with coarse textured sample matrices, special sample handling procedures may help to minimize sample loss and reduced precision.

**4.3.1.3 Phase III Assessment.** The Phase III assessment for Methods 1 and 2 was dealt with in the Year 1 study in section 4.2.3.

**4.3.2 Method 4 (H-SPME), 5 (HH-SPME) and 6 (D-SPME), Results**

Methods 4, 5 and 6 are all SPME methods and for that reason will be dealt with together in this section. Normally, calibration of SPME results from a complex matrix

such as soil is performed by spiking the contaminant onto a like matrix in known concentrations, extracting by SPME, and relating the obtained FID response (in area counts) to the known concentration. A linear relationship between the area counts and the concentration is expected. The resulting equation may then be used to relate FID responses from unknown samples to the corresponding equation. A number of problems that exist in applying this calibration method have been identified during the course of this study. Firstly, the relevancy of results obtained from freshly spiked standard material in relation to the real world aged samples which are to be analyzed is questionable. Hydrocarbon samples have been shown to change in composition due to volatilization, transformation, and degradation (Block et al., 1991). A calibration performed with spiked samples is based on a different set of compounds than those in the samples to be analyzed. Secondly, sorption models tend to support two types of sorption. The more easily desorbed contaminant is from surface sites on the matrix while the less easily desorbed (and perhaps sorbed) compounds are thought to be sorbed at sites which are in the interior of the complex structure of the matrix particle (Gamble, 1998). Thirdly, when purchased, commercial standards containing diesel fuel #2, at 10,000 ppm are dissolved in methanol, and methanol or some other solvent is used for dilutions. Solvents, particularly methanol, at high concentrations in the sample tend to interfere with SPME (Eisert, 1997). Lastly, the use of uncontaminated soil which is identical to the contaminated soil would be a preferred spiking matrix. When this is not available, as in the case of this project, a surrogate matrix must be

sought which introduces an additional source of error. For these reasons an alternative mode for calibrating the results obtained by Methods 4, 5 and 6 was sought.

Results obtained by Methods 1 and 2 were investigated as reference concentrations to be used for calibration of other method responses. This strategy was seen to be justifiable as these two methods are regulatory methods approved for use in Canada and the U.S., and were performed in commercial analytical laboratories. Methods 1 and 2 extract TPH from soil in two different ways and the results are comparable. No better method of defining the actual concentrations of TPH in these samples was available. For these reasons it can be argued that Method 1 and 2 results represent actual levels in the samples; they are current industry standards and, imprecise though they may be, are appropriately used in calibrating the other methods. Year 2 samples whose results by Methods 1 and 2 were in relative agreement (within 175% of one another) were averaged. The average concentration reported by Methods 1 and 2 were then related to the FID response (area counts) obtained by the analysis of the same sample by the various other methods. Where an acceptable linear fit was produced it was judged to be a valid calibration technique for the method of interest.

As presented in Figures 4.7, 4.8 and 4.9 this method of calibration produced reasonably linear relationships with $R^2$ values of 0.9409, 0.7677 and 0.9845 over 6 data points when the y-intercept was forced through zero. The equation obtained in this case was used to calibrate the sample responses from Methods 4, 5 and 6. This

result was then adjusted to account for the actual subsample mass by multiplying the result by 5 (target mass) and then dividing by the actual subsample mass (e.g., 4.987) to increase accuracy of the data. The data obtained by this procedure over Methods 4, 5 and 6 are presented in Tables 4.8 and 4.9 as total petroleum hydrocarbons present in parts per million.
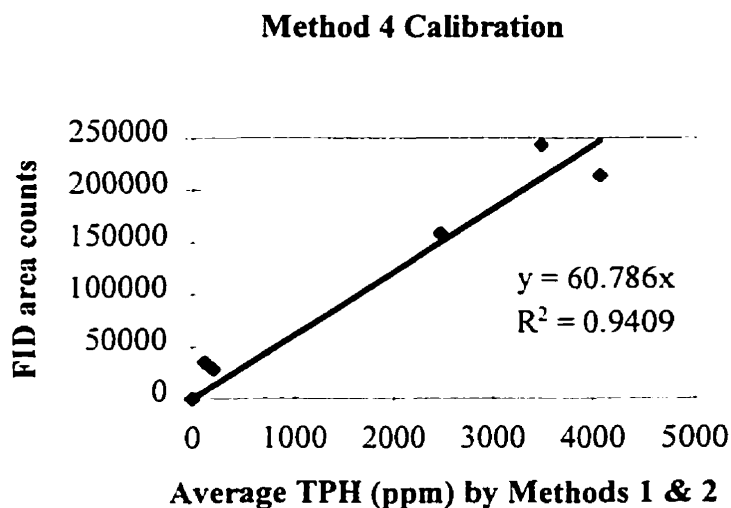
**Method 4 Calibration**



Figure 4.7  Calibration of Method 4 data based on averaged results obtained Methods 1 and 2.
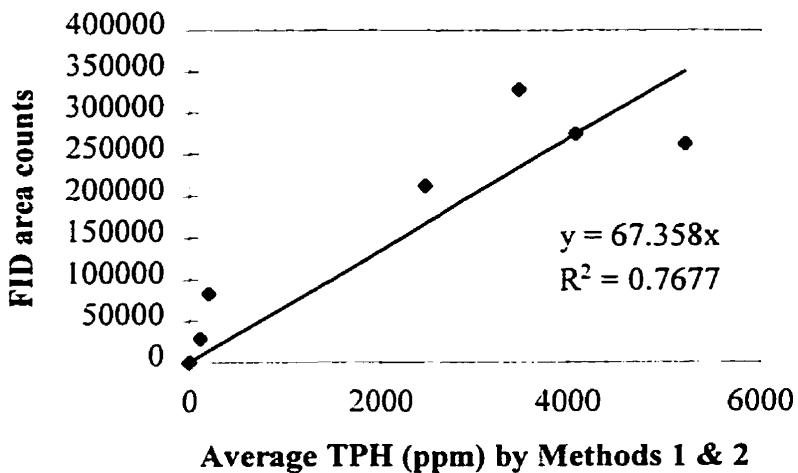
**Method 5 Calibration**



Figure 4.8 Calibration of Method 5 data based on results from Methods 1 and 2.
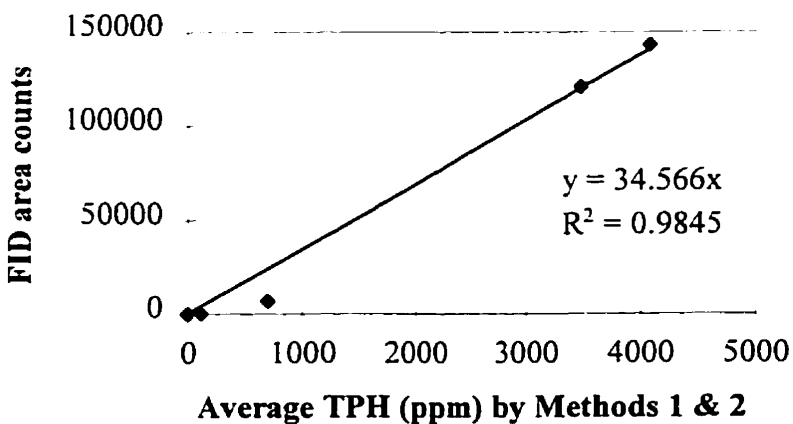
**Method 6 Calibration**



Figure 4.9 Calibration of Method 6 data based on results from Methods 1 and 2.

**4.3.2.1 Phase I Assessment.** Upon visual assessment of the data it is apparent that Method 6 results in the sandy samples (Cranberry Portage) are not in high agreement with the results obtained by Methods 4 and 5. In the clayey GV samples Method 6 results appear to be somewhat closer to the results obtained by Methods 4 and 5.

Table 4.7 Total petroleum hydrocarbon (mg/kg, or ppm) data obtained by Methods 4, 5 and 6 for Granville Lake (GV) samples.

| Sample code | Soil type | Method 4 | Method 5 | Method 6 | CV |
|---|---|---|---|---|---|
| GV 1 | CH $^a$ | 370 | 1304 | 0 | 120% |
| GV 2 | CH | 440 | 1156 | 0 | 110% |
| GV 3 | CH | 2789 | 4055 | 4929 | 27% |
| GV 4 | CH | 654 | 1834 | 1331 | 46% |
| GV 5 | CH | 613 | 2138 | 1761 | 53% |
| GV 6 | CH | 752 | 1999 | 200 | 94% |
| GV 7 | ML $^b$ | 4360 | 4800 | 3266 | 19% |
| GV 8 | CI $^c$ | 3680 | 4490 | 3214 | 17% |
| GV 9 | CI | 2340 | 2825 | 4449 | 34% |

$^a$ CH = high plasticity clay
$^b$ ML = low/non plastic silt
$^c$ CI = intermediate plasticity clay

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Table 4.8  Total petroleum hydrocarbon (ppm) data obtained by Methods 4, 5 and 6 for Cranberry Portage (CB) samples.

| Sample code | Soil type | Method 4 | Method 5 | Method 6 | CV |
|---|---|---|---|---|---|
| CB 1 | ML [a] | 2921 | 3860 | 6051 | 38% |
| CB 2 | SP [b] | 2743 | 4099 | 1029 | 59% |
| CB 3 | ML | 35 | 34 | 0 | 87% |
| CB 4 | SP | 3622 | 4213 | 4277 | 9% |
| CB 5 | ML | 2460 | 3245 | 2494 | 16% |
| CB 6 | SP | 662 | 458 | 0 | 91% |
| CB 7 | SP | 1676 | 2667 | 1270 | 38% |
| CB 8 | SM [c] | 1 | 1 | 0 | 88% |
| CB 9 | SP | 287 | 1173 | 0 | 126% |
| CB 10 | SP | 588 | 1432 | 0 | 107% |
| CB 11 | SP | 104 | 326 | 0 | 116% |
| CB 12 | SP | 1 | 2 | 0 | 94% |

[a] ML = low/ non plastic silt
[b] SP = clean sorted sand
[c] SM = silty sand

The data sets were further visually assessed by plotting the results of one method against the results of another method. A resulting line with a slope of 1 and an $R^2$ value approaching 1 would indicate a perfect fit of the two data sets. When Method 4 was compared to Methods 1, 2, 5 and 6 a number of the resulting slopes approached 1. However, after a more in-depth evaluation where the GV and CB data sets were individually compared for each method it was found that without exception the GV data sets produced a closer relationship than did the CB data sets for these comparisons. When Method 4 (H-SPME) was plotted against Methods 1 and 2 individually the resulting slopes were 0.3951 and 0.4178 for the full data set. In contrast the GV data sets produced slopes of 0.8636 for Methods 1 and 4, and 0.678

for Methods 2 and 4. This indicates that it may be more difficult to obtain accurate results for sandy samples such as those found in the CB data set. Nonetheless, Method 4 may be an equivalent analytical method to the standard methods for clay samples.
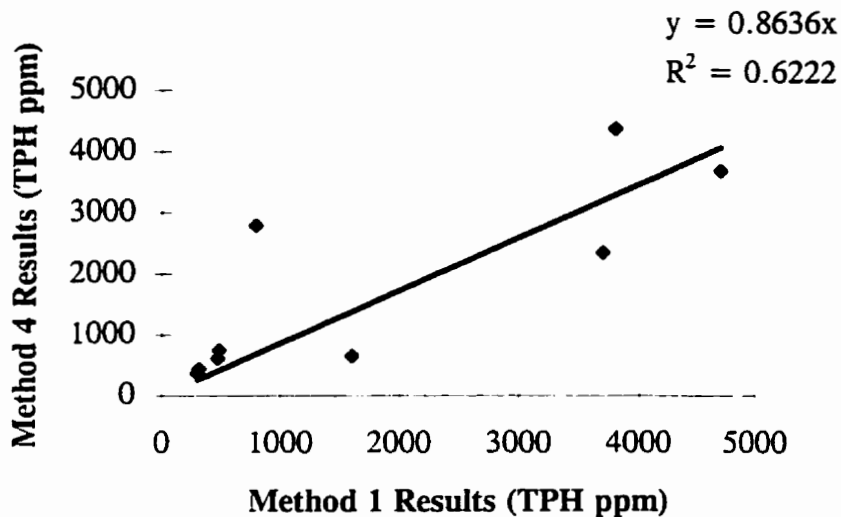


Figure 4.10  Method 1 results versus Method 4 results for TPH (mg/kg or ppm) for Year 2 GV samples.
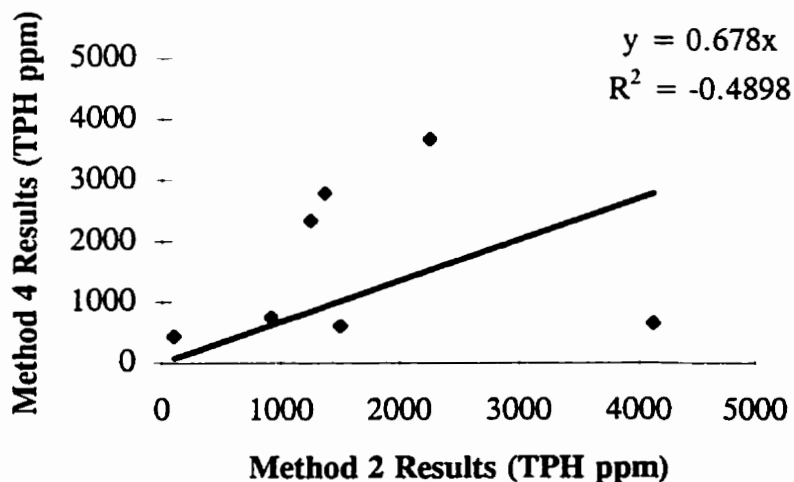


Figure 4.11  Method 2 results versus Method 4 results for TPH (mg/kg or ppm) for Year 2 GV samples.

When Method 4 was assessed in this manner against the other SPME Methods of 5 (HH-SPME) and 6 (D-SPME) the resulting slopes were very close to 1. The slopes for the CB data were quite good at 1.3298 with an $R^2$ value of 0.9372 for Method 4 versus 5. CB data for Method 4 versus 6 produced a line with a slope of 1.1372, and an $R^2$ value of 0.6988. The GV data produced slightly better slopes at 1.2708, and 1.1014, yet the $R^2$ values were poorer at 0.6182 and 0.5774 respectively. This suggests that there is little scatter of the sand (CB) sample data, yet the methods are less equivalent for sand samples than they are for clay samples in these trials.



Figure 4.12 Method 4 results versus Method 5 results for TPH (mg/kg or ppm) for all Year 2 samples.

Figure 4.13  Method 4 results versus Method 6 results for TPH (mg/kg or ppm) for all Year 2 samples.

When Method 5 was compared to the standard Methods 1 and 2, the overall relationships were poor; however, when the GV data sets were examined, the resulting slopes showed a good relationship.  Method 1 versus Method 5 for GV data only, produced a line with a slope of 1.0852.  Method 2 versus Method 5 for GV data again showed a close relationship with a line slope of 1.1162.  The $R^2$ values were very low, however, which indicates that the data do not fit the lines produced very well (see Figures 4.14 and 4.15).  The inference from this is that Method 5 may be equivalent to the standard Methods 1 and 2 for clay samples.
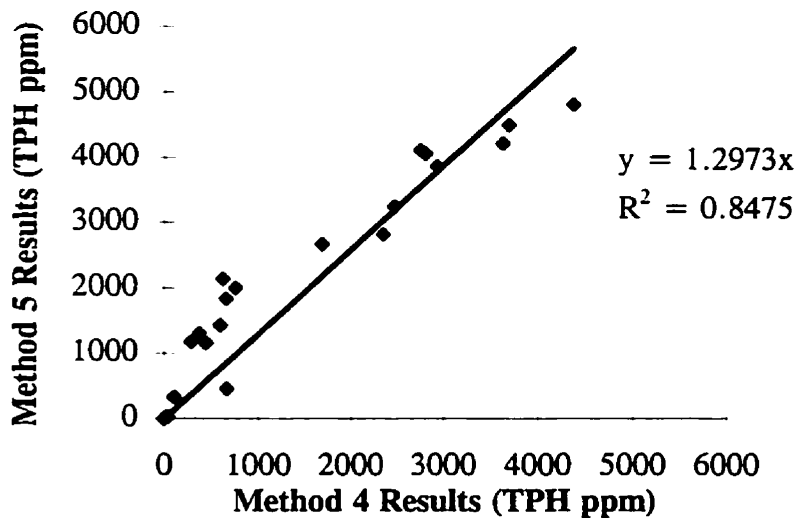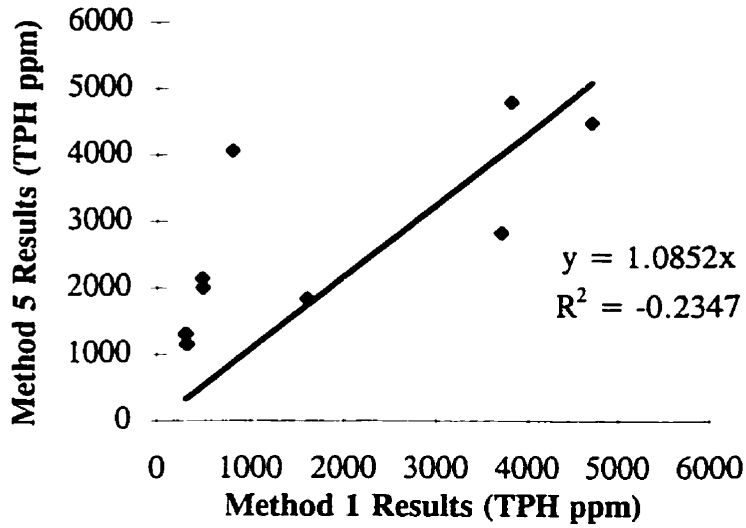
Figure 4.14 Method 1 results versus Method 5 results for TPH (mg/kg or ppm) for all Year 2 samples.
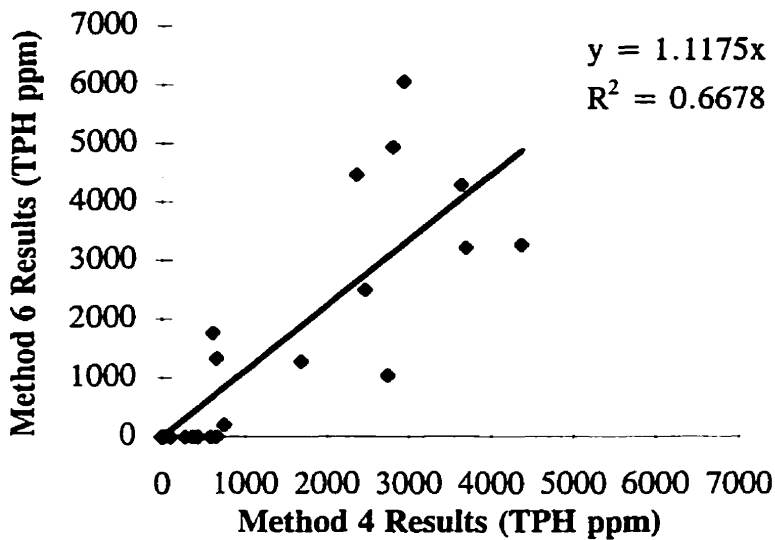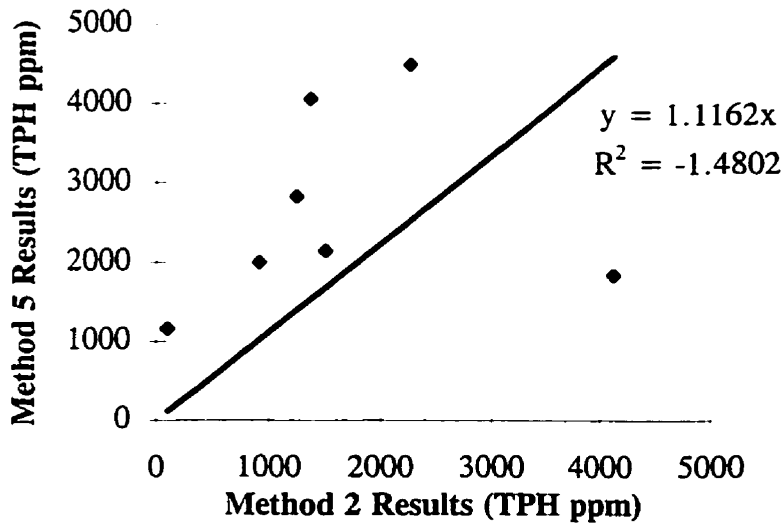


Figure 4.15 Method 2 results versus Method 5 results for TPH (mg/kg or ppm) for all Year 2 samples.

When Method 5 was compared to Method 6 (D-SPME) the resulting slopes were close to 1 for the total data (0.9442), as well as for the separate GV and CB data sets (0.9896, 0.8945) respectively. In all these cases however, the $R^2$ values are quite low, but the poorest line fit is for the GV data set. This indicates that there is a good relationship between the two SPME methods which applies to both clay and sand samples.



$$y = 0.9442x$$
$$R^2 = 0.3459$$
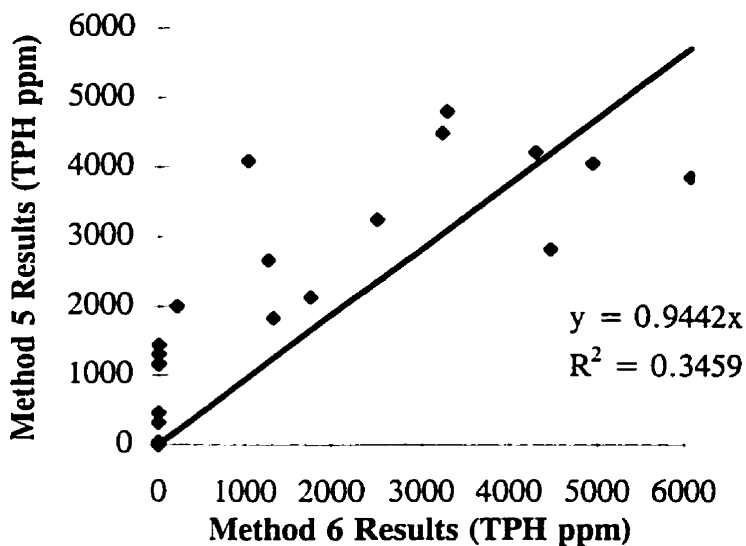
Figure 4.16  Method 6 results versus Method 5 results for TPH (mg/kg or ppm) for all Year 2 samples.

Method 6 was compared to standard methods 1 and 2. Similar to previous comparisons, the resulting slopes were poor, but when the GV and CB data were examined the GV data produced a line with a slope close to 1. Method 1 versus Method 5 for GV data produced a line with a slope of 1.0852, while the full data line

had a slope of 0.537. Method 2 versus Method 6 for GV data produce a line with a slope of 0.9743, while the full data set had a line slope of 0.6307. This implies that Method 6 may be an equivalent analytical method to the standard methods 1 and 2 for clay samples, but this relationship does not hold for the sand (CB) samples. In both graphs presented below outliers are evident, but they have not been excluded in attempt to retain all data. The exclusion of such outliers would inevitably improve $R^2$ values.
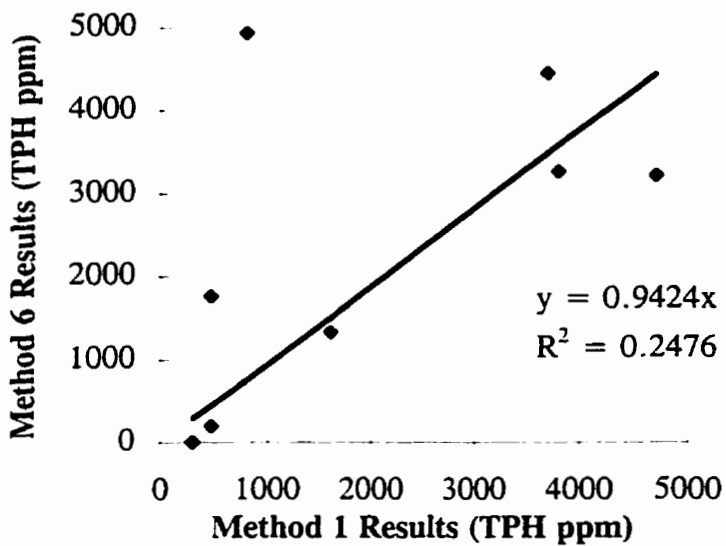


Figure 4.17   Method 1 results versus Method 6 results for TPH (mg/kg or ppm) for Year 2 GV samples.

Method 6 Results (TPH ppm)

5000 —

4000 —

3000 —

2000 —

1000 —

0

$y = 0.9743x$

$R^2 = -0.3832$

0    1000   2000   3000   4000   5000

**Method 2 Results (TPH ppm)**
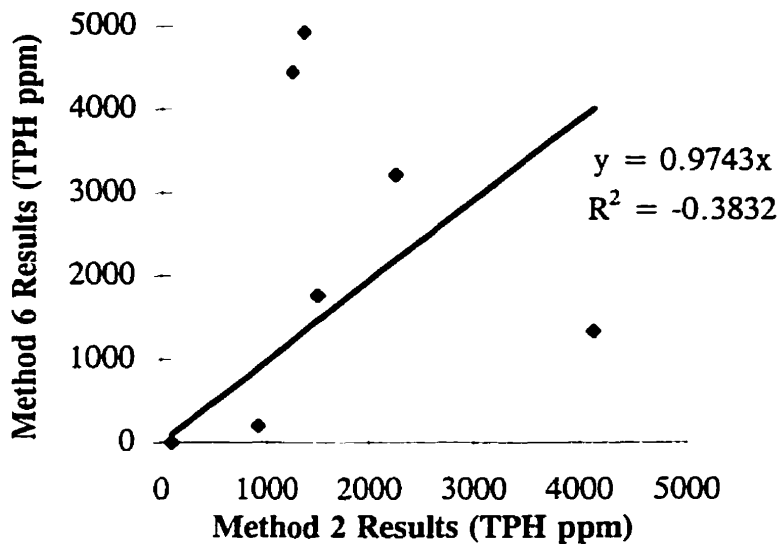
Figure 4.18   Method 2 results versus Method 6 results for TPH (mg/kg or ppm) for Year 2 GV samples.

**4.3.2.2  Phase II Assessment.**  When a two tailed paired student's $t$ test was performed on the results obtained by the above methods, it was found that in the clay samples, Methods 1 and 5 and Methods 4 and 5 are significantly different from one another at the 0.05 level.  Within the sand samples (CB) Methods 4 and 5 were significant at the 0.05 level.  When the complete data set was tested, Methods 4 and 5 are significant and Methods 5 and 6 are significant.  In no case was Method 4 found to be significantly different from Method 6.  The importance of this analysis is that it shows that for this data set, the SPME methods (4, 5, and 6) are not significantly different from the standard methods 1 and 2, with the exception of Methods 5 with Method 1 for the clay samples (see Tables 4.13, 4.14 and 4.15).

**4.3.2.3 Phase III Assessment.** Methods 4, 5 and 6 were assessed under the criteria outlined previously. None of these methods uses hazardous organic solvents for extraction. Method 6 (D-SPME) uses water, and all methods make use of the re-usable SPME fibre for extraction. The fibres are relatively inexpensive as they may be used for 100 extractions or more. Disposal of the fibre does not pose a hazard, nor does it have added costs. These methods are equivalent for solvent use, and are superior to the previous methods under this criteria.

Work-up and extraction times required for Methods 4, 5 and 6 are 20 min, 20 min, and 16 h 20 min respectively. The headspace SPME methods (4 and 5), have much shorter work-up times than does Method 6 which is D-SPME. This method it should be noted could be adjusted to require less shake time, or if the method were to be used on water samples, no shake time would be required at all, bringing the time required down to 20 min. Presently, Method 4 and 5 require much lower extraction and work-up time than the previous methods evaluated.

Instrumentation required for Methods 4 and 5 involved the pen sized SPME holder and the portable GC and computer. Method 5 also made use of a simple water bath for heating of the sample. Method 6 was performed using a wrist action shaker, a full sized GC and computer, with an SPME autosampler. Methods 4 and 5 make use of inexpensive and robust instrumentation. Method 6 uses more expensive and laboratory oriented instrumentation.

The simple procedures and instruments and lack of solvents used in Methods 4 and 5 make them ideal candidates for use in the field setting, as the systems are quite portable. Method 6 did not make use of the same instrumentation and is consequentially less portable. Nevertheless, Method 6 could easily be modified to fit the portability of the other SPME methods as the extraction technique is still based on the simple SPME extraction procedure. The small extraction device used for SPME and the portable GC and computer used in Methods 4 and 5 mean that these methods may easily be transferred to appropriate field conditions where a power supply and shelter were available. Under this criterion Methods 4 and 5 are superior to previous methods.

For specificity of extraction to be applied to the SPME methods it would involve choosing a different fibre coating to extract the desired range of compounds from the sample. A variety of different fibre coatings and thicknesses are becoming available commercially from the manufacturer (Varian Canada Inc., Missassauga, ON). The advantage to SPME extraction is that it is a non-exhaustive extraction and therefore allows for multiple extractions of a single sample if necessary. The use of specialized detection systems such as a mass spectrometer would allow for the confirmation of specific compounds. The three SPME methods (Methods 4, 5 and 6) all have the potential for compound specific extraction and detection.

### 4.3.3 Method 7 (SFE), 8 (SOX) and 9 (STIR) Results

Methods 7, 8 and 9 are exhaustive solvent extractions performed under varying conditions. These methods were carried out by the author in the department of Soil Science, at the University of Manitoba. Subsamples were taken using the modified syringe technique. Calibration of the results was performed in the traditional manner with the extractant GC-FID responses being compared to those of stock solutions of diesel at known concentrations. Calibration was also performed by the method described in section 4.3.2 in which results within 175% from Methods 1 and 2 were used as the basis for the calibration. The results produced by the two different calibration methods were similar. This result justifies the use of the alternative calibration method, using Method 1 and 2 results. To increase continuity of treatment among methods, the alternative calibration results were chosen in the final analysis.

These calibration curves had good linear fits with $R^2$ values of 0.9761 and 0.9116 over 6 data points with the y-intercept at zero. The resulting equations were used to obtain a concentration level for the unknown samples and the data was adjusted as described above, for the actual subsample size. The total petroleum hydrocarbons present are reported in Tables 4.9 and 4.10 below in parts per million.

**Method 7 Calibration**



$y = 2.747x$
$R^2 = 0.9761$
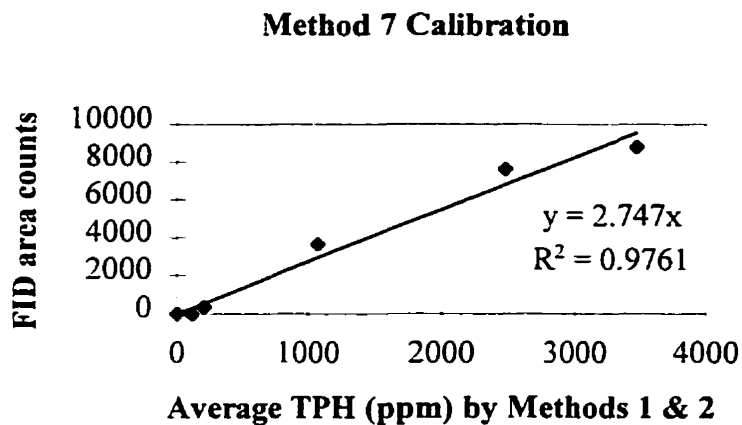
Figure 4.19  Calibration of Method 7 data based on results from Methods 1 and 2.

**Method 8 Calibration**



$y = 4.9638x$
$R^2 = 0.9116$
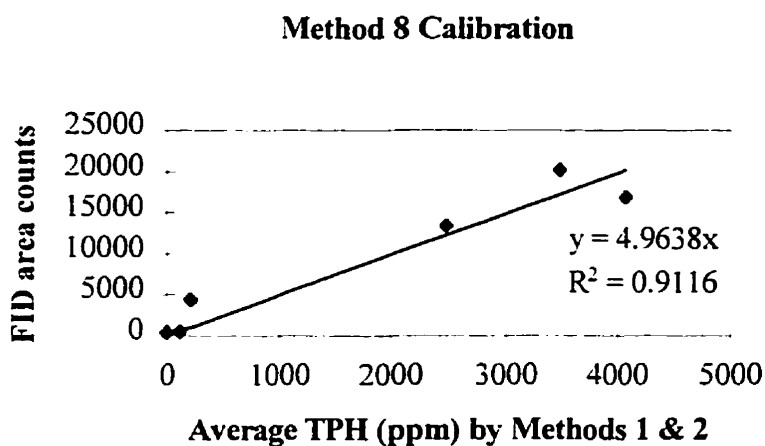
Figure 4.20  Calibration of Method 8 data based on results from Methods 1 and 2.

**Method 9 Calibration**
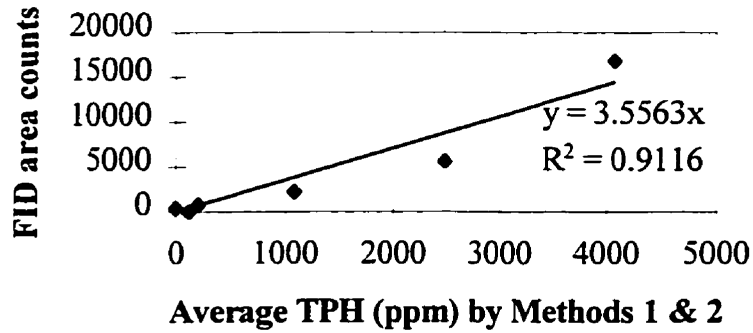


Figure 4.21  Calibration of Method 9 data based on results from Methods 1 and 2.

**4.3.3.1 Phase I Assessment.** From these data it may be noted that there appears to be relatively good agreement in general among the results obtained by these methods. Methods 7 and 8 do have a few results which appear to be anomalously high, but overall the results appear to be similar.  Method 8 appears to be reporting higher results than the other two methods for some of the low concentrations, as in the case of samples GV 2, GV 6, CB 6, CB 7, and CB 11.

Table 4.9 Total petroleum hydrocarbon (ng/kg, or ppm) data obtained by Methods 7 (SFE), 8 (SOX) and 9 (STIR) for Granville Lake (GV) samples.

| Sample code | Soil type | Method 7 | Method 8 | Method 9 | CV |
|---|---|---|---|---|---|
| GV 1 | CH[a] | 802 | 2013 | 854 | 84% |
| GV 2 | CH | 140 | 892 | 269 | 120% |
| GV 3 | CH | 1335 | 2212 | 756 | 84% |
| GV 4 | CH | 1670 | 1825 | 1862 | 36% |
| GV 5 | CH | 347 | 129 | 232 | 21% |
| GV 6 | CH | 464 | 662 | 339 | 68% |
| GV 7 | ML[b] | 2585 | 3482 | 2033 | 60% |
| GV 8 | CI[c] | 3196 | 4063 | na[d] | 105% |
| GV 9 | CI | 2768 | 2703 | 1861 | 46% |

[a] CH = high plasticity clay
[b] ML = low/non plastic silt
[c] CI = intermediate plasticity clay
[d] na = sample was lost for the Method 9 treatment

Table 4.10 Total petroleum hydrocarbon (mg/kg or ppm) data by Methods 7 (SFE), 8 (SOX) and 9 (STIR) for Cranberry Portage (CB) samples.

| Sample code | Soil type | Method 7 | Method 8 | Method 9 | CV |
|---|---|---|---|---|---|
| CB 1 | ML[a] | 15757 | 8044 | 8952 | 18% |
| CB 2 | SP[b] | 3482 | 2532 | 988 | 53% |
| CB 3 | ML | 120 | 90 | 0 | 90% |
| CB 4 | SP | 1280 | 3400 | 5058 | 62% |
| CB 5 | ML | 8326 | 3433 | 1303 | 67% |
| CB 6 | SP | 0 | 105 | 0 | 173% |
| CB 7 | SP | 14 | 201 | 136 | 103% |
| CB 8 | SM[c] | 5 | 101 | 116 | 85% |
| CB 9 | SP | 310 | 221 | 0 | 89% |
| CB 10 | SP | 352 | 278 | 50 | 74% |
| CB 11 | SP | 15 | 108 | 28 | 117% |
| CB 12 | SP | 0 | 114 | 0 | 173% |

[a] ML = low/non plastic silt
[b] SP = clean sorted sand
[c] SM = silty sand

When the data sets from Methods 7, 8 and 9 were independently plotted against the data sets of all previous methods many visual assessments could be made. Method 7 (SFE) was compared to the two standard methods (1 and 2), and good correlation was found between Methods 1 and 7 in the GV data set, and between Method 2 and 7 for all data sets. Overall Method 2 versus Method 7 had a slope of 1.0868. The GV data set produced a line slope of 0.5986, while the CB data set produced a better fit with a line slope of 1.1757. As the overall line slope was close to 1, and the data fit the line well with an $R^2$ value of 0.8349 it is possible to state that Method 7 produced results that are equivalent to those produced by Method 2 for all soil types. The good correlation with Method 1 results for GV samples indicates that Method 7 may be equivalent to Method 1 for clay soil analysis.



$$y = 0.6147x$$
$$R^2 = 0.8772$$

Figure 4.22  Method 1 results versus Method 7 results for TPH (mg/kg or ppm) for GV Year 2 samples.

Figure 4.23  Method 2 results versus Method 7 results for TPH (mg/kg or ppm) for all
     Year 2 samples.

Method 7 was compared to the three SPME methods (Methods 4, 5 and 6). All of

these methods compared well to Method 7 results. When broken down into GV and

CB data sets, in all instances the CB data sets produced line slopes that were closer to

1 than the GV data set line slopes. Overall, Method 7 produced equivalent results

within these analysis to those produced by Methods 4, 5 and 6 for all soil types. It is

curious to note that the relationships are stronger in the CB samples than in the GV

samples for these analyses, as it was opposite in prior method comparisons. This may

be explained by the study design. Each of these methods were subsampled by the

author in the same manner, thus greatly reducing sample handling differences.

Differences in sample handling may account for loss of volatile analyte, especially from a porous matrix such as sand. At the same time, the porous matrix may be easier to extract from since the analyte may not be held as tightly, and is easier to access. As a result, the differences in sample handling techniques between laboratories appears to affect results more greatly in sandy samples than in clay samples.
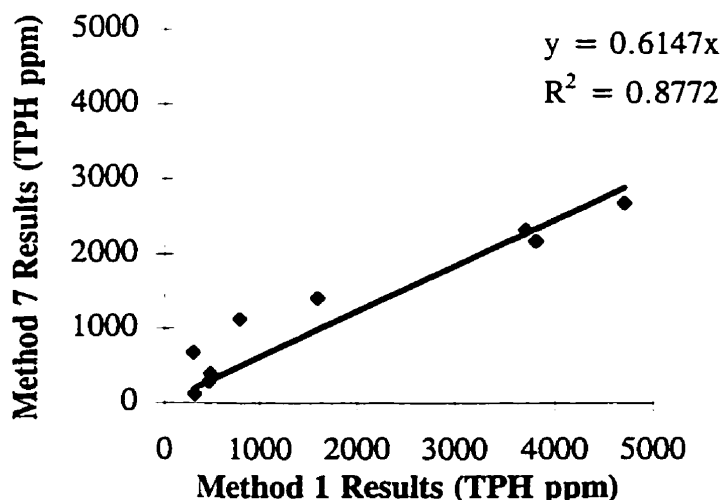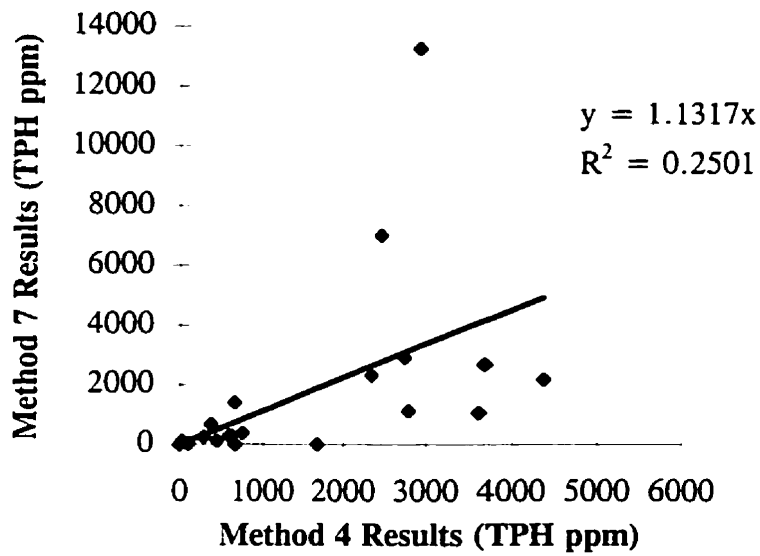


Figure 4.24 Method 4 results versus Method 7 results for TPH (mg/kg or ppm) for all Year 2 samples.

Figure 4.25  Method 5 results versus Method 7 results for TPH (mg/kg or ppm) for all
Year 2 samples.
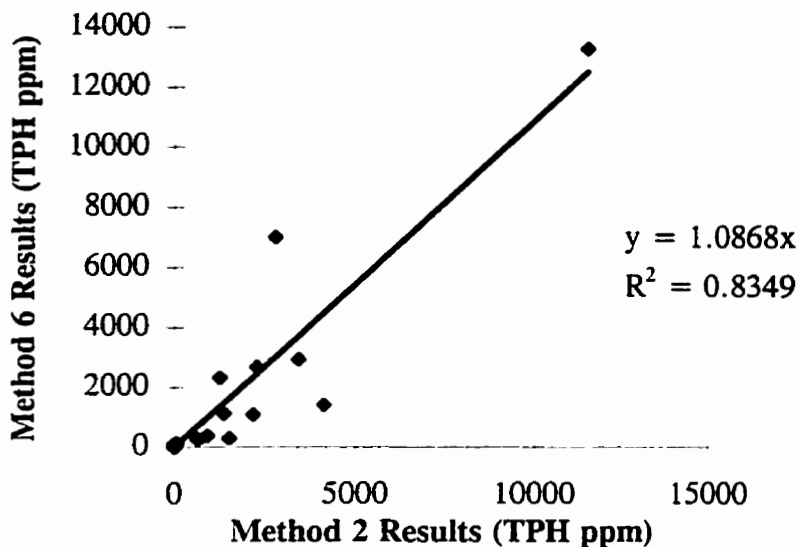


Figure 4.26  Method 6 results versus Method 7 results for TPH (mg/kg or ppm) for all
Year 2 samples.

Method 8 (SOX) was compared to methods 1 and 2.  In the Method 1 comparison only the GV data set had a good correlation.  In the Method 2 comparison there was an overall good relationship for the entire data set.  It is noteworthy that when the data sets were divided by soil type, the CV data had a better fit (slope $= 1.1458$, $R^2 = 0.9154$) than did the GV data (slope $= 1.2750$, $R^2 = -0.1979$).  From this comparison it may be postulated that Method 8 is equivalent to Method 1 for clay samples and is equivalent to Method 2 for all soil types.
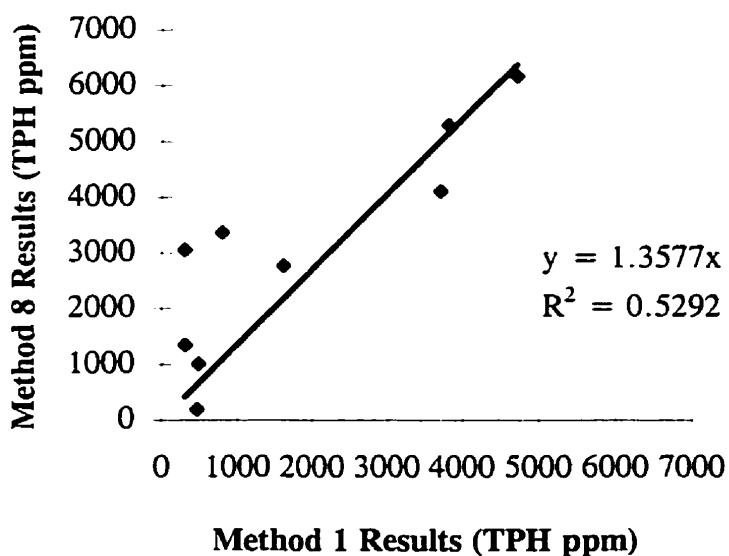


Figure 4.27  Method 1 results versus Method 8 results for TPH (mg/kg or ppm) for Year 2 GV samples.
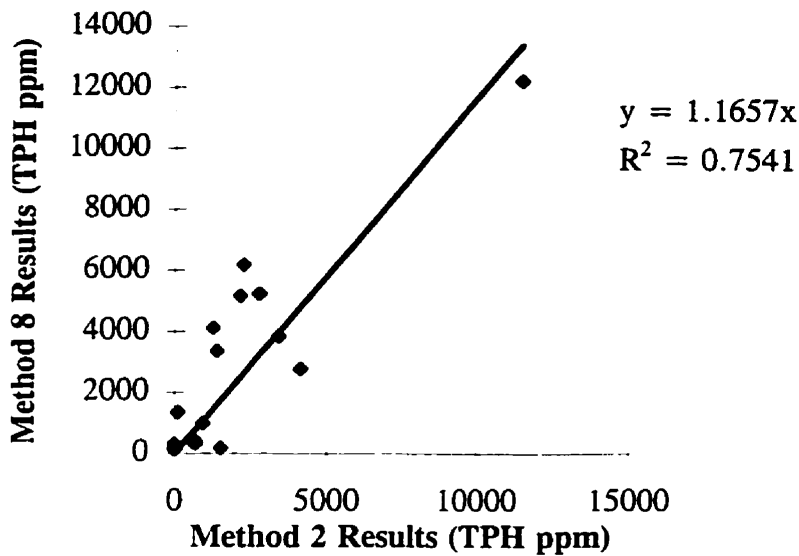
Figure 4.28  Method 2 results versus Method 8 results for TPH (mg/kg or ppm) for all
Year 2 samples.

When Method 8 is compared to the three SPME methods (Method 4, 5 and 6) all have

good overall relationships, except for Method 4 which produced a line slope of 1.7133,

with an $R^2$ value of 0.5717. The GV data sets show a better relationship than do the

CB data sets in each case. This evaluation indicates that Method 8 is equivalent to

Methods 5 and 6, but has better correspondence with the clay samples than with the

sand samples. Method 8 may also be considered analogous to Method 4 for clay

samples. The slopes of the lines show that methods 7 and 8 produce higher values

generally compared to those of Methods 1 and 2. This may indicate that Methods 1

and 2 may not be as exhaustive as Methods 7 and 8.

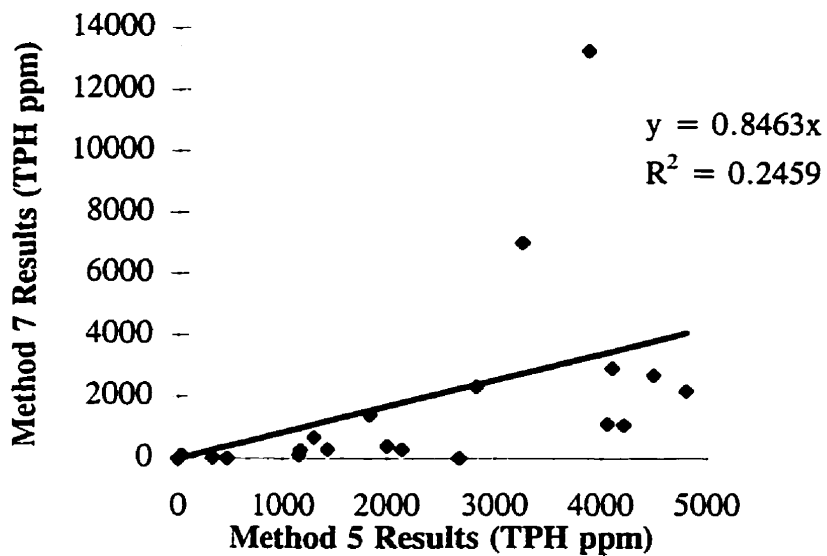Figure 4.29  Method 4 results versus Method 8 results for TPH (mg/kg or ppm) for Year 2 GV samples.



Figure 4.30  Method 5 results versus Method 8 results for TPH (mg/kg or ppm) for Year 2 GV samples.
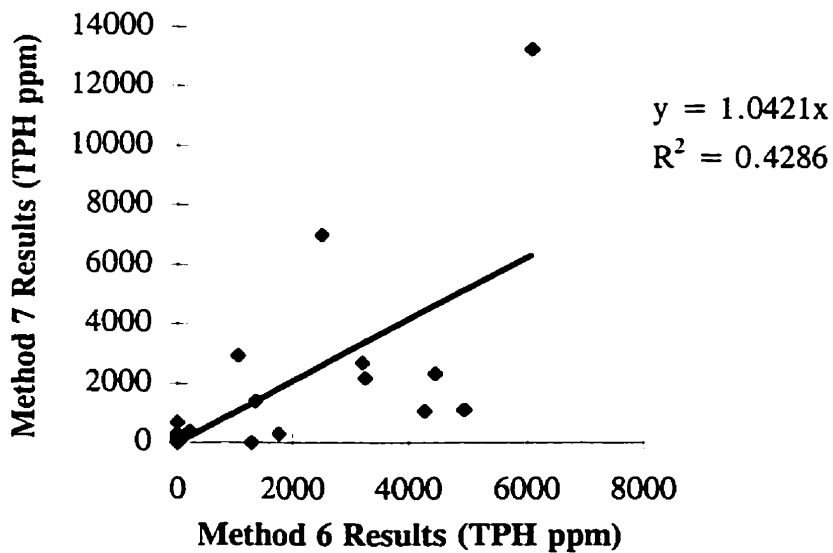
Figure 4.31   Method 6 results versus Method 8 results for TPH (mg/kg or ppm) for Year 2 GV samples.

Method 8 (SOX) was compared to Method 7 (SFE) and had a good overall relationship. The GV data set however, did not produce an equivalent relationship with a line slope of 2.2529, and an $R^2$ value of 0.8052. The CB data set had a close to equivalent relationship with a line slope of 0.9192, and an $R^2$ value of 0.8650. As a result Methods 7 and 8 may be viewed as equivalent for sand samples. For the clay samples, while there appears to be a clear relationship between the two methods it is not an equivalent one.

14000 –

12000 –

10000 –

8000 –

6000 –

4000 –

2000 –

0

Method 8 Results (TPH ppm)

$y = 1.0303x$

$R^2 = 0.6694$

0    2000   4000   6000   8000   10000  12000  14000

**Method 7 Results (TPH ppm)**
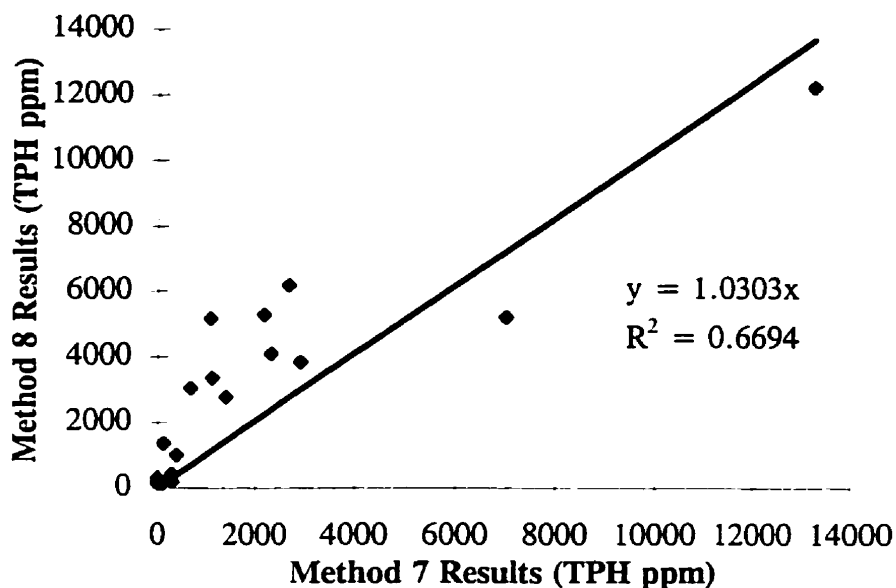
Figure 4.32  Method 7 results versus Method 8 results for TPH (mg/kg or ppm) for all Year 2 samples.

Method 9 was compared in this manner to the previous methods. When compared to Methods 1 and 2, no correlation was found with Method 1. Method 2 correlated well with Method 9 when all data was evaluated (slope = 0.7235, $R^2$ = 0.7607). Upon breaking down the data into GV and CB groups there is no relationship found in the GV set (slope = 0.3782, $R^2$ = 0.2138), while there is a good relationship in the CB set (slope = 0.0.7863, $R^2$ = 0.8192). These results indicate that Method 9 may be equivalent to Method 2 results for sand samples, but is not equivalent to Method 1 in any case.
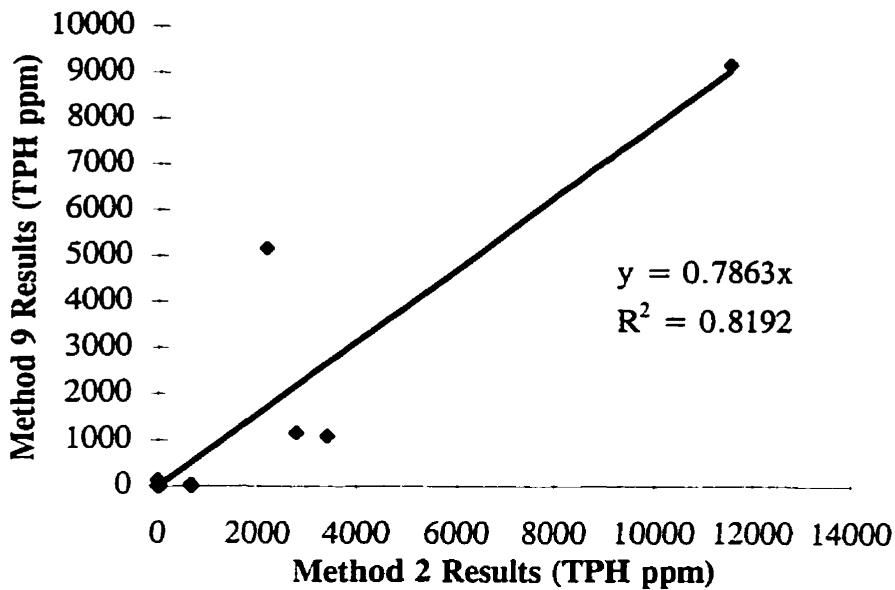
Figure 4.33   Method 2 results versus Method 9 results for TPH (mg/kg or ppm) for Year 2 CB samples.

Method 9 was compared to the SPME methods 4, 5 and 6.  Method 4 compared well to Method 9 with the full data set (slope = 0.7865, $R^2$ = 0.2562), but the CB data set produced a better relationship than did the GV data set.  Method 5 had a significant relationship only in the CB comparison.  Method 6 had an overall good comparison to the Method 9 data (slope = 0.7614, $R^2$ = 0.5088).  Again the CB data set was the only one to show a near equivalent relationship.
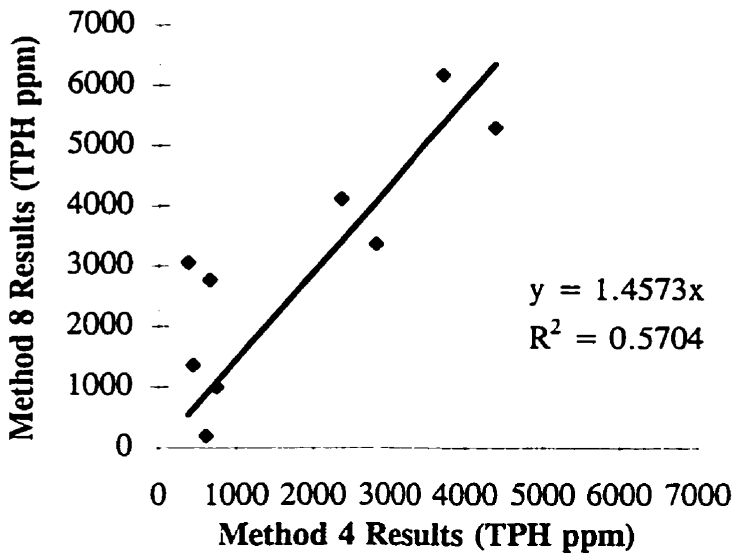
115

Figure 4.34  Method 4 results versus Method 9 results for TPH (mg/kg or ppm) for Year 2 CB samples.
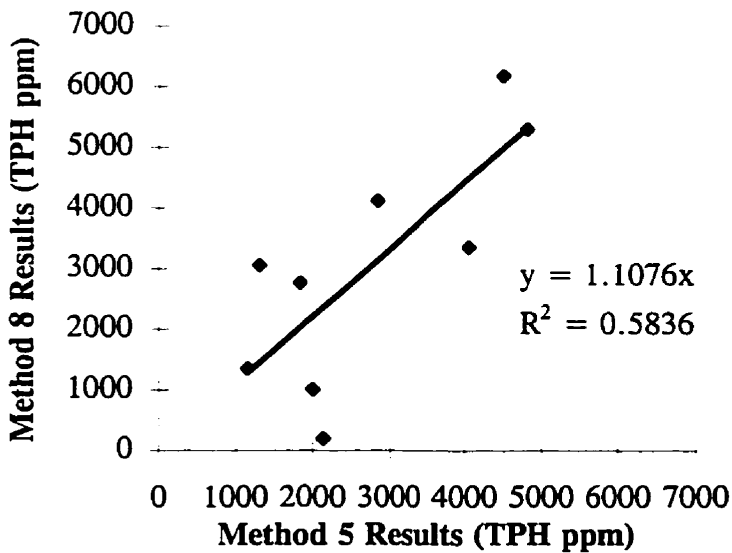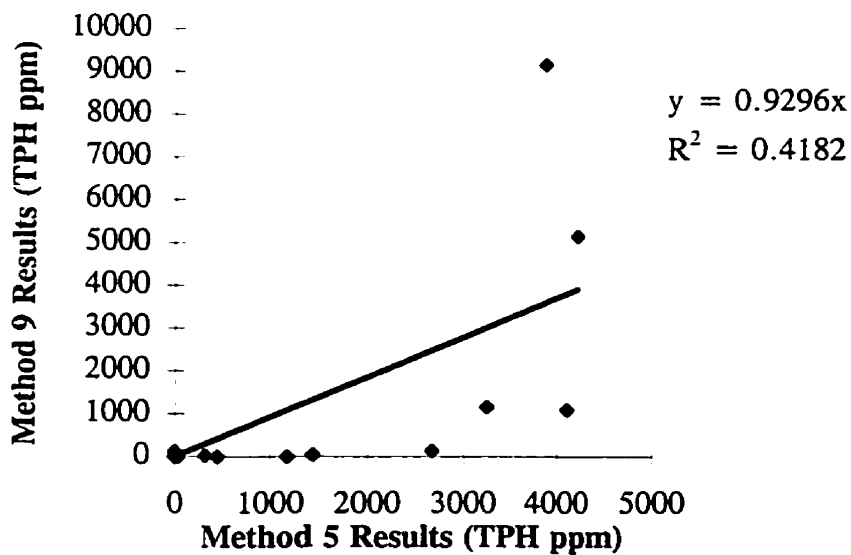


Figure 4.35  Method 5 results versus Method 9 results for TPH (mg/kg or ppm) for Year 2 CB samples.
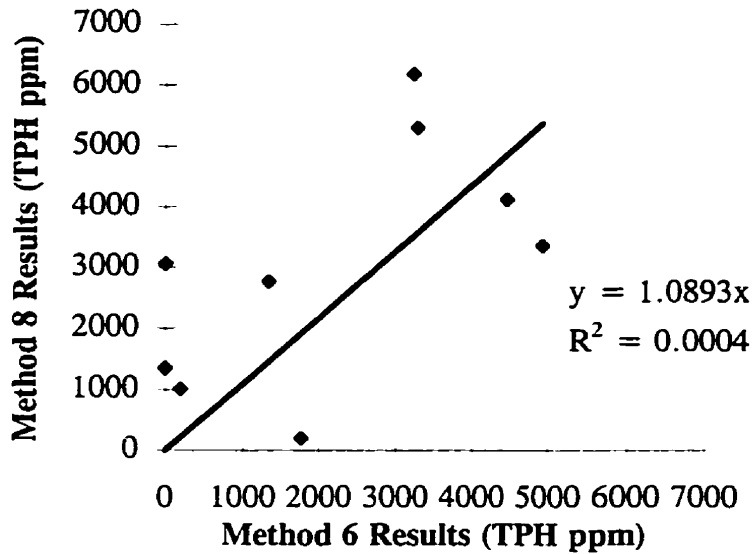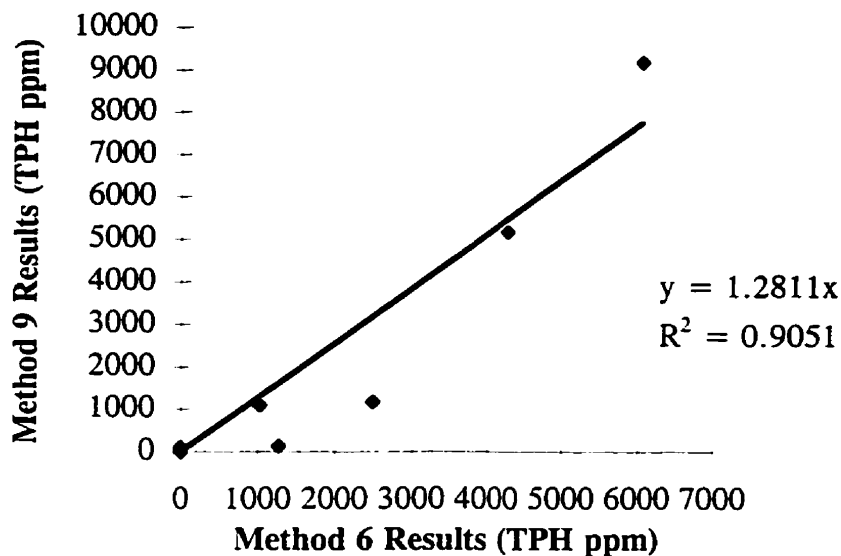
Figure 4.36 Method 6 results versus Method 9 results for TPH (mg/kg or ppm) for Year 2 CB samples.

Method 9 was compared to the other two in-house solvent extraction methods; Method 7 (SFE), and Method 8 (SOX). For the full data set, Method 7 results had a good fit with Method 9 results. Both GV (slope = 1.0911, $R^2$ = -0.0732) and CB (slope = 1.2231, $R^2$ = 0.6421) data sets also produced lines with slopes close to 1. When Method 8 was plotted against Method 9 data, the slope produced was near to 1 for the full data and the CB data sets; however, it was not for the GV data set. These relationships suggest that Methods 7 and 9 may produce equivalent results for all soil types, but Methods 8 and 9 are only equivalent for sandy soil types.
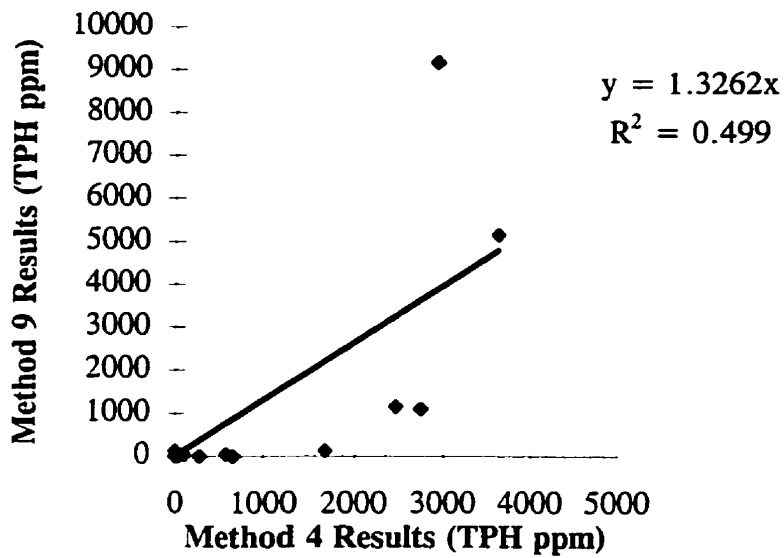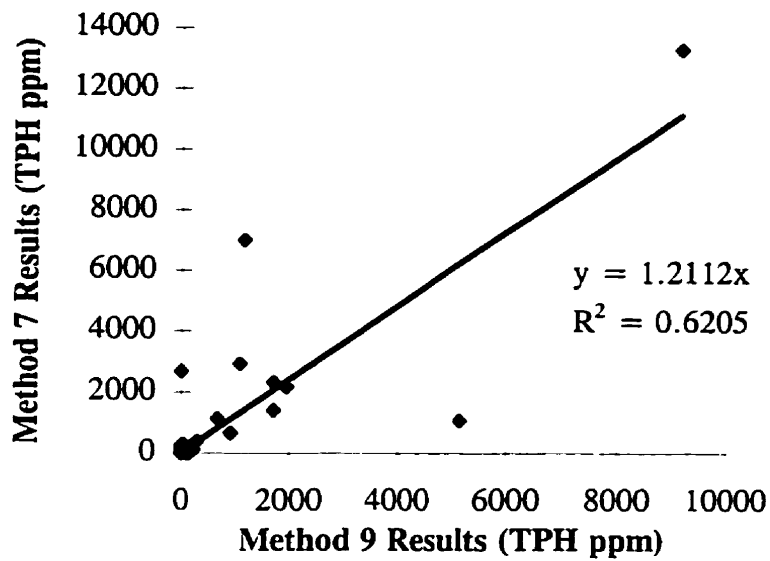
Figure 4.37  Method 9 results versus Method 7 results for TPH (mg/kg or ppm) for all
Year 2 samples.
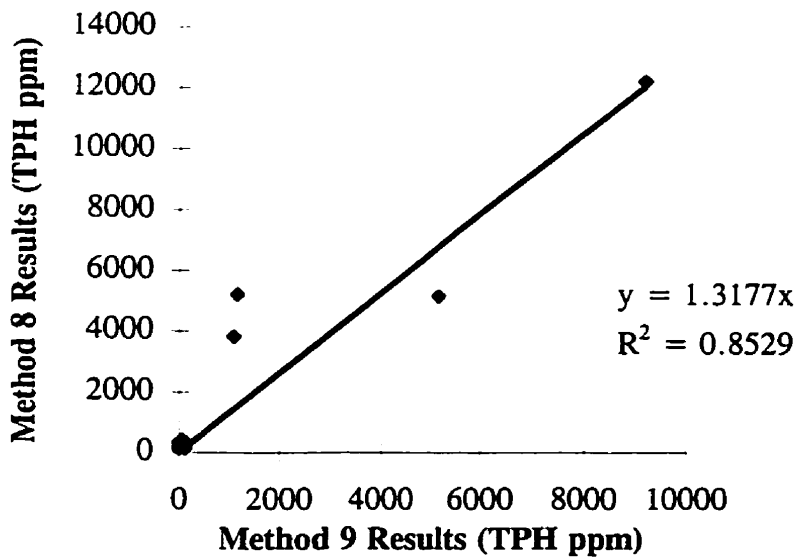


Figure 4.38  Method 9 results versus Method 8 results for TPH (mg/kg or ppm) for
Year 2 CB samples.

**4.3.3.2 Phase II Assessment.** When a two tailed, paired student's *t* test was performed on the data, it was found that in the clayey Granville Lake samples, Method 8 was significantly different from Methods 5, 7 and 9 at the 0.05 level (see Table 4.15). Methods 7 and 9 were each significantly different from Method 5 for these samples. In the sandier Cranberry Portage samples, however, it was found that Methods 7, 8 and 9 were not significantly different from any other method under investigation. When the combined data set was tested, only Method 9 was significantly different from Method 5 at the 0.05 level; although, Method 8 and 9 were borderline significantly different from one another with an $\alpha$ value of 0.0627.

**4.3.3.3 Phase III Assessment.** Hazardous materials are used in the extraction procedures of Methods 7 (SFE), 8 (SOX) and 9 (STIR). The solvent used in Method 7 is supercritical carbon dioxide, and a small amount (3 mL) of chlorinated solvent. The concern regarding use of the $CO_2$ is the high pressure that the gas is under. High grade pressurized $CO_2$ may be costly to obtain and there are inherent risks when dealing with pressurized gasses. Method 8 used in excess of 150 mL of non-chlorinated solvents. Method 9 requires a small amount of concentrated acid, and at least 40 mL of chlorinated solvent. Of these methods Method 7 utilizes the least environmentally harmful substances, yet the safety hazard is among the highest, requiring skilled and knowledgeable technicians.

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The time required for work-up and extraction in Method 7 is 45 min, and the operator must be monitoring the extraction procedure to deal with clogged restrictor tubes as they arise. Method 8 requires over 16 h for extraction and work-up, but the operator need not be present to monitor the system. Concentration of extract is however a labour intensive step, requiring *ca.* 30 min of the technician's time per sample. Method 9 requires about 1 h 45 min for extraction and work-up. Again the operator need not be present for the extraction process; however, the concentration step can be time consuming.

Instrumentation required for Method 7 includes an expensive SFE device. Method 8 extraction requires specialized glassware, and laboratory infrastructure for water and ventilation systems. Method 9 requires only standard glassware, a GC and fume hood ventilation. Of these methods it would seem likely that only Method 7 (SFE) would be amenable to transport into a field setting. The infrastructure required of methods 8 and 9 would be prohibitive to allowing easy field application of these methods.

Method 7 may be altered to allow for compound class specific extraction with the use of modifier solvents, and temperature and pressure adjustments. Methods 8 and 9 might allow for some specificity of extraction with adjustments to the solvents used. All of these methods could have compound identification capacity with the use of a specialized detector such as a mass spectrometer (MS).

### 4.3.4 Method 10 (NIRS) Results

This is the first attempt to predict the concentrations of petroleum hydrocarbons in contaminated soil by NIRS. Statistics used to evaluate the calibration are RPD, the ratio of the standard deviation (SD) of the reference chemistry values for the prediction set and the standard error of prediction (SEP), and the RER, ratio of the range of the reference chemistry values for the prediction set and the SEP. In the analysis of agricultural commodities, RPD is usually greater than 3 and often greater than 5, and RER is usually greater than 10. In this case, although the $R^2$, RPD, and RER are not as high as desirable, or as high as obtained for other constituents in soils (Malley 1997b; Malley et al. 1997), the results are very encouraging. The accuracy of the NIR results is dependent upon the quality of the hydrocarbon analytical data. The next step in exploring the feasibility of using NIRS for the prediction of petroleum hydrocarbons in soil would be to attempt to obtain soil samples with highly accurate reference chemical analytical data.

NIRS has been used frequently for the determination of hydrocarbons and their properties (Workman, 1996); however, most of these applications are on liquid hydrocarbons or on industrial process mixtures. For example, whole oil content and oil impurities are estimated by NIRS in water soluble cooling lubricants in the metal working industry (Timm et al., 1997). Additives to gasoline are monitored by NIRS in the process stream during gasoline manufacture (Pasquini et al., 1997). In addition to

the quality of the reference data used in the calibration, other factors may influence the results. The soils measured here are "as is", i.e., wet. Water is the strongest absorber in the NIR region, and water may obscure absorption of wavelengths of other constituents near its peaks. Secondly, the sample set used in this study represented three different locations, and a variety of soil types, and soil depths. Thirdly, the nature of the petroleum hydrocarbons being detected at each site may have differed. Nevertheless, the results here indicate that NIRS is potentially a useful method for the rapid detection of petroleum-hydrocarbon contaminated soil.

Table 4.11 Description of reference values in calibration and prediction files for the hydrocarbon prediction. Values are parts per million (ppm), wet weight basis.

| | Calibration (TPH by method 4 in ppm) | Prediction (TPH in ppm) |
|---|---|---|
| Mean | 1880 | 1570 |
| Standard Deviation | 1820 | 1470 |
| Minimum | 1 | 1 |
| Maximum | 6260 | 4360 |
| Range | 6260 | 4360 |
| Number of Spectra | 13 | 13 |

Table 4.12 Accuracy of prediction, mathematical treatments and wavelengths for calibrations for hydrocarbon in soil. Wavelength range for all calibrations, 1100-2498 nm.

| Statistic | TPH (ppth) | Description |
|-----------|------------|-------------|
| $R^2$ | 0.677 | |
| SEP | 0.837 | standard error of prediction |
| RPD | 1.76 | ratio of standard deviation to SEP (SD/SEP) |
| RER | 5.21 | mathematical treatments |
| Math. | D1OD | D1OD = first derivative |
| Seg./Gap | 2/2 | segment = degree of smoothing, i.e. number of wavelength points averaged |
| | | gap = derivative size, i.e. distance in wavelength points between the beginning and end of the derivative |
| 1 | 1100 | the wavelengths used in the calibration equation |
| 2 | 2360 | |
| 3 | 1460 | |
| 4 | 2180 | |

**4.3.4.1 Phase I Assessment.** In the phase I visual assessment of Method 10 plotted against all other method results independently, there are only a few instances in which the results appear to be alike. Method 4 results are similar to those obtained by Method 10, but this is not surprising, as the calibration of Method 10 results was based on the Method 4 results. Overall this comparison resulted in a line with a slope of 0.691, and an $R^2$ of 0.333. When the two soil types GV and CB were examined independently, the slopes were very similar (0.692 and 0.690 respectively). Only the $R^2$ value was improved in the CB sample set at 0.425 compared to the $R^2$ for the GV set at 0.140. The only other comparison which produced a slope close to 1 was in the GV sample set between Method 7 and Method 10. The line had a slope of 1.107, but the data fit was poor with an $R^2$ value of 0.052.

**4.3.4.2 Phase II Assessment.** When a two-tailed, paired student's $t$ test was performed on the full data sets, significant differences at the 0.05 level was found only between Method 10 and Method 6 results ($\alpha = 0.0038$), and Method 10 and Method 8 results ($\alpha = 0.0464$). The statistical analysis was performed independently on the two soil sets. In the GV (clayey) soil Method 10 results were significantly different from Method 6 results ($\alpha = 0.0201$), Method 9 results ($\alpha = 0.0102$), and close to significance with Method 8 results ($\alpha = 0.0713$). In the CB (sandy) soil set, only Method 6 came close to being significant from Method 10 results with $\alpha = 0.0864$. From this statistical assessment it can be concluded that while there are few significant differences in the data sets obtained by these different analytical methods, the Phase I assessment shows that there are also few comparisons in strong agreement. Method 4 appears to be most comparable to Method 10; however, Method 10 data is based on calibration using Method 4 data.

Table 4.13 Student's $t$ test $\alpha$ values for results from all Year 2 samples (GV and CB). Only those $\alpha$ values at or below 0.05 represent significant differences between methods.

| Method # | 2 SHAKE | 4 H-SPME | 5 HH-SPME | 6 D-SPME | 7 SFE | 8 SOX | 9 STIR | 10 NIRS |
|---|---|---|---|---|---|---|---|---|
| Method 1 | 0.88 | 0.46 | 0.61 | 0.70 | 0.85 | 0.38 | 0.35 | 0.37 |
| Method 2 | | 0.43 | 0.64 | 0.74 | 0.94 | 0.04 | 0.06 | 0.20 |
| Method 4 | | | 0.00 | 0.55 | 0.69 | 0.02 | 0.47 | 0.49 |
| Method 5 | | | | 0.04 | 0.43 | 0.34 | 0.03 | 0.00 |
| Method 6 | | | | | 0.86 | 0.02 | 0.20 | 0.56 |
| Method 7 | | | | | | 0.01 | 0.21 | 0.55 |
| Method 8 | | | | | | | 0.00 | 0.05 |
| Method 9 | | | | | | | | 0.77 |

Table 4.14 Student's $t$ test α values for results from Year 2 Granville Lake (GV) samples. Only those numbers at or below 0.05 show significant differences between methods.

| Method # | 2 SHAKE | 4 H-SPME | 5 HH-SPME | 6 D-SPME | 7 SFE | 8 SOX | 9 STIR | 10 NIRS |
|---|---|---|---|---|---|---|---|---|
| Method 1 | 0.91 | 0.96 | 0.05 | 0.56 | 0.10 | 0.01 | 0.13 | 0.98 |
| Method 2 | | 0.96 | 0.15 | 0.48 | 0.37 | 0.21 | 0.06 | 0.41 |
| Method 4 | | | 0.00 | 0.41 | 0.12 | 0.01 | 0.11 | 0.71 |
| Method 5 | | | | 0.16 | 0.00 | 0.50 | 0.00 | 0.02 |
| Method 6 | | | | | 0.10 | 0.16 | 0.07 | 0.61 |
| Method 7 | | | | | | 0.00 | 0.25 | 0.21 |
| Method 8 | | | | | | | 0.01 | 0.07 |
| Method 9 | | | | | | | | 0.01 |

Table 4.15 Student's $t$ test α values for results from Year 2 Cranberry Portage (CB) samples. Only those numbers at or below 0.05 show significant differences between methods.

| Method # | 2 SHAKE | 4 H-SPME | 5 HH-SPME | 6 D-SPME | 7 SFE | 8 SOX | 9 STIR | 10 NIRS |
|---|---|---|---|---|---|---|---|---|
| Method 1 | 0.90 | 0.47 | 0.84 | 0.55 | 0.96 | 0.80 | 0.67 | 0.36 |
| Method 2 | | 0.41 | 0.78 | 0.28 | 0.49 | 0.12 | 0.38 | 0.28 |
| Method 4 | | | 0.00 | 1.00 | 0.42 | 0.20 | 0.81 | 0.57 |
| Method 5 | | | | 0.17 | 0.77 | 0.48 | 0.55 | 0.09 |
| Method 6 | | | | | 0.32 | 0.07 | 0.64 | 0.76 |
| Method 7 | | | | | | 0.50 | 0.36 | 0.39 |
| Method 8 | | | | | | | 0.04 | 0.21 |
| Method 9 | | | | | | | | 0.69 |

**4.3.4.3 Phase III Assessment.** When Method 10 is evaluated under the Phase III assessment, it is apparent that the method has many favorable attributes. This method makes use of no solvents whatsoever. The analysis is performed within approximately 40 seconds, and is non-destructive to the sample. Therefore multiple analyses are

easily performed. Instrumentation required involves the NIRS sampler which fits easily onto a benchtop, and a computer for data handling and statistical analysis. It should be noted that the skill of the person handling the data must be quite high since various statistical tests must be performed, and the most appropriate model must then be applied to the data for calibration. The relative simplicity of the instrumentation and procedure make this method an ideal candidate for field use. The only potential drawback of this method is the need for a calibration data set which should be based on the same or similar kinds of samples since the matrix can play an important role in NIRS analyses. If such a calibration set is not available at time of testing, it would be difficult to achieve calibration of the spectra on-site and actual results in close to real time. The method is capable to some extent of obtaining results for specific compounds; however, this capability is severely limited by the types of bonds which are indicated by the spectra and interferences from the matrix. Overall, if a viable calibration set for diesel contaminated soils were available, NIRS could be a valuable analytical tool for quantification of diesel fuel contaminants in soil.

### 4.3.5 Spiked Sample Results

Spiked soil samples were sent to the two commercial laboratories in this study for the purpose of evaluating potential loss of volatile analyte in each of the commercial Methods (Methods 1 and 2). These results might not necessarily be extrapolated to the extraction efficiency of a method for real-world, aged and weathered samples, but they can be used to indicate general biases of a method since the extraction of the freshly

spiked diesel from a sandy soil should be relatively easy. The data is presented in Table 4.16, and graphically depicted in Figure 4.39. It is evident that the only reported result higher than the spike concentration was by Method 2, at the highest concentration. All other results were reported to be lower than the spiked concentration. This indicates that Method 1 is consistently biased low, and Method 2 is biased low at the spiked concentrations of 1,000 and 75 ppm. The low bias of the methods might indicate a loss of volatile analyte at some stage of the analysis.

Table 4.16 Spiked sand results from commercial methods.

| Spike Concentration (ppm) | SD | Method 1 Result (ppm) | % of spike | Method 2 Result (ppm) | % of spike |
|---|---|---|---|---|---|
| 10,000 | 1.0-1.5 | 7300 | 73% | 10018 | 100% |
| 10,000 | 1.5-1.9 | 7900 | 79% | 11161 | 112% |
| 1,000 | 2.0-2.5 | 780 | 78% | 895 | 90% |
| 1,000 | 2.5-2.9 | 750 | 75% | 944 | 94% |
| 75 | 3.0-3.5 | 73 | 97% | 56 | 75% |
| 75 | 3.5-3.9 | 58 | 77% | 42 | 56% |
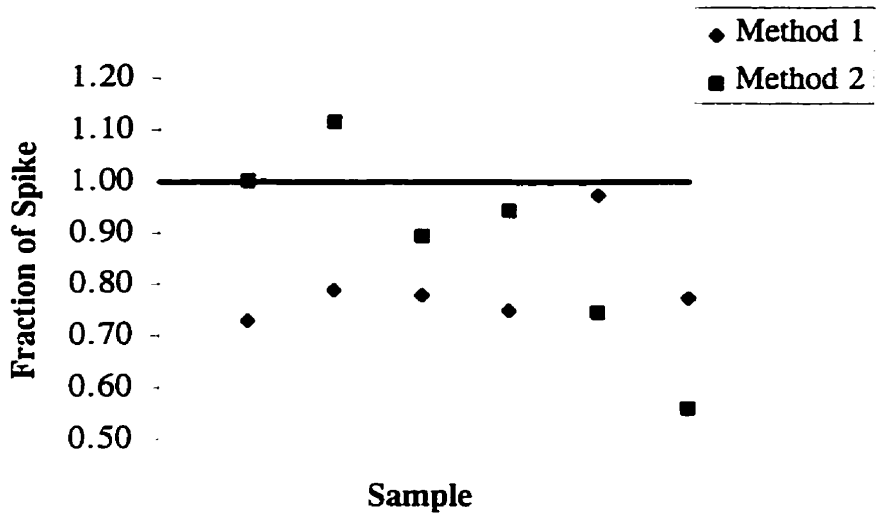
Figure 4.39   Spiked sand results from commercial methods as a fraction of spiked concentration.

### 4.3.6 Comprehensive Phase III Comparison

Table 4.17 Comprehensive phase III comparison of methods.

| | Hazardous Materials | Extraction & Work-up Time | Instrumentation | Easily Performed in Field Lab | Specificity |
|---|---|---|---|---|---|
| 1) SON | $10^+$ mL | 1.25 h | sonicator, glassware, wrist action shaker, GC | No | Depends on choice of solvent |
| 2) SHAKE | $20^+$ mL | 1.45 h | glassware, wrist action shaker, GC | No | Depends on choice of solvent |
| 3) PROBE | $300^+$ mL | 1 h | sonicator, glassware, GC | No | Depends on choice of solvent |
| 4) H-SPME | 0 mL | 0.25 h | SPME device, GC | Yes | Depends on choice of fibre coating & extraction temperature |
| 5) HH-SPME | 0 mL | 0.25 h | SPME device, GC | Yes | Depends on choice of fibre coating & extraction temperature |
| 6) D-SPME | 0 mL | 0.25 h | SPME device, wrist action shaker, GC | Yes | Depends on choice of fibre coating & extraction temperature |
| 7) SFE | 8 mL | 0.75 h | supercritical fluid extractor, GC | No | Pressure & temperature adjustments increase specificity |
| 8) Soxhlet | $150^+$ mL | 16.5 h | glassware, concentration apparatus, GC | No | Depends on choice of solvent |
| 9) Magnetic Stirring | $40^+$ mL | 1.75 h | glassware, concentration apparatus, GC | No | Depends on choice of solvent |
| 10) NIRS | 0 mL | 0.16 h | NIRS system | Yes | Only if compounds of interest reflect in NIR spectra |

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# 5. SUMMARY AND CONCLUSIONS

The goal of this study was to evaluate selected analytical methodologies for diesel fuel contaminants in soil. This goal was fulfilled through the following objectives:

i) to observe a typical soil sampling procedure,

ii) to research standard analytical methods,

iii) to compare the results obtained by different methods in commercial laboratories,

iv) to perform analyses by "new" methods (which are not currently being used in commercial laboratories in Manitoba),

v) to compare all results obtained,

vi) to pinpoint sources of variability and

vii) to make recommendations on methods to be used for the analysis of diesel contaminated soils. Using these objectives, the following hypothesis was tested:

*That new analytical methods[a] for diesel fuel related contaminants in soil perform as well as standard analytical methods[b], while possessing a variety of other benefits.*

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New analytical methods are defined as those which are not widely used in commercial laboratories for such analysis, and are generally not recommended for use by regulatory agencies. These include solid phase micro-extraction (SPME) methods, super-critical fluid extraction (SFE), and near infra-red spectroscopy (NIRS).

[b] Standard analytical methods are those which are currently being used in commercial laboratories in Manitoba for the analysis of diesel fuel related contaminants in soil, and are usually recommended for use by regulatory agencies. These include sonication methods (SON & PROBE), shaker solvent extraction (SHAKE), soxhlet extraction (SOX), and a magnetic stirring solvent extraction (STIR).


Through the fulfillment of each objective over the course of the study, it is evident that the goal was achieved, and that the hypothesis has been tested and proven. For each stage of soil analysis (sampling, subsampling, analytical methods and data analysis), conclusions may be drawn and recommendations made.


## 5.1 Sampling


Obtaining soil samples from a contaminated site, often in remote areas, and under adverse environmental conditions can be a difficult and arduous task. Appropriate preparation and well trained personnel can make the job less daunting, and smooth running, as was demonstrated in this study. The sampling operation was run flawlessly by the skilled team of professionals assembled by Manitoba Hydro. Overall

the task was efficiently and properly carried out. A number of recommendations should however be considered for their potential to improve current operations.

The potential for the matrix to interfere with laboratory analysis for hydrocarbons in soil is an important consideration which is often not dealt with by the analytical laboratory. To help to understand these potential matrix interferences, it would be beneficial to obtain matrix blanks. These would be similar soils which are not contaminated that are submitted for the same analyses as the contaminated soils. The results of these analyses can provide baseline data on the soil type which may be interfering with the analysis of the contaminant. The baseline can then be taken into consideration when evaluating the data from a contaminated sample of the same soil type.

Choosing the number of samples for laboratory analysis is a difficult task. Looking at the situation in conference with the laboratory manager from a data quality objective standpoint may be useful. The number of samples taken would then be determined by the number of analyses that are necessary to reach the confidence levels required of the data. Obtaining data quality objectives is the joint responsibility of the client and the analytical laboratory. Communication on the issue is essential if targets are to be met.

A technical consideration during sample gathering is the physical disruption of the sample while the soil is being loaded into the sample jar. Increased disruption will

inevitably increase the loss of volatile components. If the volatile components are of interest, special attention may be paid to obtaining a sample that is relatively intact. This may be achieved through careful loading of the conventional sample jars, or by using a volatile containment drill core. The loss of volatile analytes which occurs at this stage will vary depending on ambient conditions such as temperature and wind speed, as well as on the practices of the sample handler. For this reason, continuity of procedures is very important, and the use of standard operating procedures would benefit the process.

Another factor to consider at the sampling stage is the occurrence of phase separation of the contaminant in the subsurface environment. Diesel is a complex mixture and its components will disperse in the environment according to their individual physiochemical properties. The solubility, volatility and sorption characteristics of the diesel component will help to determine where the contaminant will tend to accumulate. The result of this scenario is that different fractions of the contaminant may be present in different soil environments, including pore water, pore atmosphere, inorganic and organic matricies, and so on. This separation of contaminant in the environment must be considered when obtaining a sample, and when deciding on the most appropriate analytical method. The data should also be considered in light of the tendency for such differential partitioning to occur.

Last, but certainly not least, is the need to be aware of the harmful effects that exposure to diesel fuel can have on humans. Although diesel fuel is a very commonly used substance, it should not be assumed that exposure to the fumes or contaminated soil and water does not have deleterious effects on human health and safety. Indeed, one of the primary reasons for investigating contaminated soils is that diesel can have negative impacts on human health. However, the people that perform these investigations, both in the field an in the laboratory, must not be forgotten when discussing health and safety. More stringent monitoring of worker exposure to the volatile contaminants should be performed, and proper safety equipment should be provided and used. The absence of such safety equipment and use guidelines is associated with lax management of employees and sub-contractors, and may also become a liability issue in the future. It is strongly recommended that a health and safety training program be undertaken by all those working with and managing contaminated sites and materials. Proper education and communication is the key to the successful implementation of such guidelines.

## 5.2 Subsampling

Subsampling generally is conducted in the laboratory by trained laboratory personnel, following the in-house method. It is recommended that the data user become familiar with the various subsampling methods and discuss with the laboratory personnel which method is to be used for the analyses being undertaken. It has been shown that the

modified syringe method has many benefits over the traditional scoopula method. Thus it is important for the data users to inquire about the subsampling method employed at the laboratory, and to communicate their analytical expectations to the laboratory personnel. The laboratories might also consider providing this information to the client with the data and methodological information, as details such as these can strongly influence the quality and bias of the data.

## 5.3  Analytical Methods

Analytical methods are subject to many possible interferences. The analyst and the data user must be aware of these possible interferences to be able to minimize them and to be cognizant of their potential effects. Interferences such as the spill characteristics, the soil type, drying agents used, and method of quantification are all important for consideration. For proper use and interpretation of analytical results, it would be best for all parties involved to interact and exchange information regularly. This interaction would allow the analyst to be aware of the project objectives and the required quality of the analytical data. The interaction would also assist the data user in planning the sampling regime required to achieve the set goals. The data user would also then have an intimate understanding of the strengths and weaknesses of the data. Anomalies in the data could be quickly dealt with if the analyst and the data user were in close communication. A simple outcome such as a shift in the chromatogram towards higher molecular weight compounds might be of significance to the data user. A change in

the contaminant mixture might be indicated, different regulations might apply, and different actions might be warranted.

To assist in greater understanding of the strengths and weaknesses of the data set by the end users it would be helpful to see more emphasis placed on the QA/QC procedures of the laboratory, and the accuracy and precision determination methods employed. Simply reporting high accuracy and precision values, without stating how those numbers were derived can be deceptive to the data user. This strategy does not actually give better data, but rather gives a false sense of confidence in the data, leading to misuse of the results. Greater openness regarding precision and accuracy of the data set, and of actual integration of the data would greatly assist in better understanding of the analytical process and limitations by the data users.

Properties of contamination such as bioavailability and variable toxicity are of significance to the interaction of the contaminant with the biosphere, yet are rarely actually dealt with in a routine analytical situation. As regulators move increasingly towards risk-based criteria as endpoints for remediation of contaminated sites, issues such as these will become more relevant to the assessment of a contaminated site. Considerations beyond what is solvent extractable from the soil will become more important. Answering questions of what is biologically available, and what effects will these contaminants have on the biosphere over time will become more significant. For these reasons it is important to begin looking towards new and better analytical

methods which may be able to answer these questions. One method which was investigated in this study may be promising in this area. The direct SPME method evaluates the water soluble fraction of the contaminant, which can be associated with the bioavailable portion. If future soil analyses are aimed towards quantifying this aspect of the contamination, direct SPME may become an important analytical tool.

After an extensive and detailed comparison of the ten different analytical methods in this study, a few generalizations can be made. It was noticed that results from sandier soils tended to be more variable than the results from high clay content soils. It is thought that this effect may be due to the high potential for loss of volatile analytes from the more permeable sandy soils than from the clayey soils. This finding implies that to obtain more accurate analytical results for sandy soils, it may be necessary to take measures in both the field and the laboratory to minimize volatile analyte losses.

When comparing the results obtained by the new analytical methods to those obtained by the standard analytical methods, it is possible to state that many of the new methods perform at least as well as the standard methods, yet have a number of other beneficial attributes. This supports the original hypothesis, and suggests the need to further investigate these new analytical methods.

Parameters which affect the applicability of a method were looked at in the Phase III evaluation. Issues of hazardous material generation, time required to perform the

analysis, instrumentation needed, and portability and specificity of the method were evaluated. When performing complex multivariate analyses on the data, each parameter must be weighted appropriately. The importance of a particular parameter will determine the relative weight of that parameter for a given situation or data user. For this reason it is impossible to recommend one particular method for all situations and purposes. It is intended however, that the parameters of major importance to data users and analysts have been examined in this study, and the comparison will provide useful information for those selecting an analytical method for diesel fuel contaminants in soil.

# 6. FUTURE WORK

The comparisons of new and established analytical methods for diesel fuel contaminants in soil from actual aged samples made in this study provide information which had previously not been available. While this study was as comprehensive as possible under the conditions provided, there are areas which this study touched on that should be expanded in order to implement changes to regulatory analytical procedures. In particular, the SPME technique is a method which has many benefits and should be sought for implementation as a method accepted by Manitoba Environment. This method should also be adapted for use by Manitoba Hydro and other organizations, particularly for field applications. Future research related to this study should include:

1. The development of headspace SPME as a portable method for field use. Research to date has brought this method very close to being applicable in a field method. Trials of spikes and real samples should be attempted under a variety of field conditions. When satisfactory reproducibility and detection limits can be documented, the method should be written up for approval by the regulatory agencies. Automation of the system if possible should be considered as this may be relevant for high use scenarios. Two parameters now affecting the implementation of automated SPME for diesel in soil analysis are the vial sizes available, and the number of vials which may be loaded onto the instrument at any one time. The 5 g

sample size used in this study proved comparable to other methods and thus the 20 mL vial size used in the automated Varian system might be applied to this method either in field or laboratory settings.

2. Once developed, the field SPME method could be integrated into the field investigation procedures of Manitoba Hydro. The use of SPME as an on-site testing method could result in quicker analytical result turn around time and this could modify the speed with which field investigation decisions are made. The rapid feedback possible with this method could be used in sampling decisions which could result in fewer samples needing to be taken. An unexpected result could be revisited immediately rather than days or weeks later saving unnecessary travel and backtracking. Informed sampling plans would help to minimize unnecessary soil analysis, saving time and money. The on-site testing method proposed could have important benefits to the investigation procedure, and could thus reform the means by which samples are taken, analyzed and decisions are made.

3. Diesel fuel should be characterized based on a set of quantifiable, environmentally relevant compounds within the mixture. It is thought that this type of characterization of complex fuels such as diesel would provide more reliable and informative representation of the contaminant. For example, problems associated with loss of volatile compounds could be eliminated if they are not target analytes. Also, it would then be possible to focus analytical assessments on certain

compounds of toxicological or environmental significance. When only compounds of interest are evaluated, the error involved in the quantification of all the other peaks is eliminated, and a more reliable and relevant evaluation can be made. Furthermore, the use of a highly specific detector such a mass spectrometer (MS) coupled to a conventional GC would allow for confirmation of specific analytes at time of analysis based on spectral analysis rather than just retention time. Confirmation of the analyte is particularly useful when interested in the toxicity of specific analytes.

The evaluation of specific analytes of environmental importance will assist in predicting the actual toxicity of a particular spill, which has undergone various degrees of contaminant weathering and degradation. In this way a site specific contaminant and toxicity fingerprint may be developed. Toxicity based analyses are appropriately used in risk based site assessments and remediation decision making. As shown by Parkerton and Stone (1998), SPME methods can be used to link toxicity ratings to hydrocarbon content. Therefore, SPME techniques may be instrumental in moving towards risk based analyses and decision making.

4. The expansion of field SPME methods to be applied to analysis of water for BTEX, TPH and toxicologically relevant diesel related compounds. When this method is applied to water analysis in a field setting, it may be useful for well and groundwater monitoring, providing near real time results. This feature may be

useful for monitoring plume movement and / or degradation. As shown by Motlagh and Pawliszyn (1993), it is possible to apply automated SPME to the analysis of flowing streams. This technique may be adapted to situations of stream or industrial outflow monitoring.

5. The development of alternative methods for possible use as regulatory methods for hydrocarbon analysis of soils. The novel analytical methods investigated in this study such as SPME, SFE and NIRS have many advantages over conventional analytical techniques, for example, reduced solvent use and decreased analytical time and cost. For this reason these methods should be considered for their applicability as regulatory methods for the analysis of diesel fuel in soil. To realize any changes in the regulatory guidelines, method validation studies may be necessary. For effective implementation of any regulatory changes undertaken it would be prudent to implement an education program for dissemination of information on the new methods.

# 7. CONTRIBUTION TO KNOWLEDGE

This study has made significant contributions to the existing body of knowledge in the field of soil analytical methods by comparing a wide range of analytical methods. Although some methods such as SFE and soxhlet have been compared to one another before, a large study encompassing these ten different analytical methods for diesel fuel in soil has never before been undertaken to the knowledge of the author. This study has compared established and emerging analytical methods, and has used existing analytical methods in new applications (NIRS). Of particular interest is the fact that this study did not limit comparisons to laboratory-contrived samples for excessive experimental control, but rather tested the methods on real world, aged samples which had been collected and handled in a normal commercial fashion. Although such a comparative study involves many uncontrollable factors and potential sources of error, the value of the results may be greater because the study was performed under actual operating conditions in the real world. This implies that extrapolation of these results to other real world situations will not be difficult, and may be more valuable than extrapolation of results from highly controlled laboratory studies. While this study did not have the mandate to develop new analytical techniques, in broadening applications and demonstrating feasibility of novel analytical methods it is expected that interest in further developing and applying such methods will be fostered.

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# APPENDIX

## Soil Characterisation Data and Microtip PID Readings

# MANITOBA HYDRO
Engineering
OVERBURDEN LOG

GEOTECHNICAL

CHURCHILL
TANK FARM

CH-209
1 OF 1
Prj.# 46672-158

**Sampler Types**

- ☒ Split Spoon
- ▨ Auger
- ▧ Sonic
- ☐ Shelby
- ☐ Auger Barrel
- ☒ Core Barrel
- ☒ Special Samplers
- ▽ Tricone
- ☐ Bulk Sample
- ☐ Grab Sample
- ▷ Air Hammer

| DEPTH (m) | SAMPLER | SAMPLE # | USCS | SOIL DESCRIPTION | Total Extractable Hydrocarbons (ppm) ⊕ | Microtip PID Reading ○ | Moisture | Vane Shear |
|---|---|---|---|---|---|---|---|---|

Moisture: PL | M.C. | LL — 20% 40% 60% 80%
Vane Shear (kPa): 25 50 75 100
Total Extractable Hydrocarbons (ppm): 100 200 300 400
Microtip PID Reading: 100 200 300 400

| Depth | Sampler/Sample | USCS | Soil Description | TEH | PID |
|---|---|---|---|---|---|
| 0 | 1 ES/EG | SM | (0.00-0.51) Sand, with silt, trace gravel/ cobbles, trace rootlets, wet, moderate odor. | ● 120 | |
| | 2 ES/EG | | Pushing stone, no recovery. Moved drill 1.0m North and 0.5m East. (0.51-1.02) Sand as above, moderate odor. | ● | ○17.4 |
| 1 | | | (1.02-1.52) Pushing cobble; <5cm recovery. Blocked bit. Peat layer somewhere in the run, estimate at 1.50m. | | |
| | 3 ES/EG | CL | (1.52-1.77) Clay, grey brown, and silt, mottled brown, some sand, trace gravel, wet, above PL, slight odor. | ⊢ | |
| 2 | 4 ES/EG | | (1.77-3.05) Clay as above, no odor. | ● | ○18.2  □50 |
| | 5 ES/EG | | | ● | ○21.4 |
| | 6 ES/EG | | | ● | ○13.8 |
| | 7 ES/EG | | | ● | ○7.5  □200 |
| 3 | 8 ES/EG | | | ● | ○9.8  □215 |

(3.05) End of Hole.
No odor at EOH.

MANITOBA HYDRO          <u>ATTERBERG LIMITS</u>
ENGINEERING
GEOTECHNICAL DEPT.
MATERIALS LAB

<u>PROJECT –</u>         CHURCHILL TANK FARM
<u>SAMPLE NO. –</u>    ES – 3
<u>HOLE NO. –</u>        CH – 209          <u>DIRECTORY –</u>     CH95A
<u>DEPTH –</u>          1.52 – 1.77 m
<u>DATE –</u>           95 11 17          <u>FILE NO. –</u>      3CH209A
<u>TESTED BY –</u>      JL

## ATTERBERG CALCULATIONS

### LIQUID LIMIT

| NO. OF BLOWS | 17 | 17 | 17 |
|---|---|---|---|
| WT. WET SAMPLE AND TARE | 37.60 | 37.60 | 37.00 |
| WT. DRY SAMPLE AND TARE | 34.90 | 35.00 | 34.50 |
| WT. OF TARE | 21.90 | 22.50 | 22.20 |
| WT. OF MOISTURE | 2.70 | 2.60 | 2.50 |
| WT. OF SOLIDS | 13.00 | 12.50 | 12.30 |
| PERCENT MOISTURE | 20.77 | 20.80 | 20.33 |
| LIQUID LIMIT | 19.82 | 19.85 | 19.40 |

### PLASTIC LIMIT

| WT. WET SAMPLE AND TARE | 35.50 | 33.40 |
|---|---|---|
| WT. DRY SAMPLE AND TARE | 33.90 | 32.10 |
| WT. OF TARE | 21.30 | 22.10 |
| WT. OF MOISTURE | 1.60 | 1.30 |
| WT. OF SOLIDS | 12.60 | 10.00 |
| PERCENT MOISTURE | 12.70 | 13.00 |

| LL | 19.69 |
|---|---|
| PL | 12.85 |
| PI | 6.84 |

<u>CLASS. –</u>    CL–ML

| DEPTH (m) | SAMPLER | SAMPLE # | USCS | SOIL DESCRIPTION | Total Extractable Hydrocarbons (ppm) ⊕ | Microtip PID Reading O | DEPTH (m) |
|---|---|---|---|---|---|---|---|

**Sampler Types:** ⊠ Split Spoon | ⊞ Core Barrel | ▤ Bulk Sample | ■ Auger | ⟩⟩ Sonic | ▣ Special Samplers | ▤ Grab Sample | ■ Shelby | ‖ Auger Barrel | ▽ Tricone | ⊿ Air Hammer

**Moisture:** PL — M.C. — LL   20% 40% 60% 80%

**Vane Shear (kPa):** 25 50 75 100

Total Extractable Hydrocarbons (ppm): 100 200 300 400

Microtip PID Reading: 100 200 300 400

| Depth interval | Description | TEH / PID readings |
|---|---|---|
| (0.00-1.02) SM | Sand, brown, some silt, with gravel to 2cm size, rootlets, wet, loose insitu, weak odor. | ●140 (TEH); O24.6, O15.3 (PID) |
| (1.02-1.19) PT CL | Peat, brown, fibrous, humic, thin black mesic layers. | O17.4 |
| (1.19-2.55) | Clay, grey brown, and silt, with sand, trace gravel, wet, above PL, very slight odor. | O13.1, O12.3, O11.8 |
| (2.55-2.60) | Clay as above, and black cobble. | O10.7 |
| (2.60-3.05) | Clay, grey, with silt, some sand, trace gravel to 2cm, hard insitu. | O11.5 |

Sample column: 1 ES/EG, 2 ES, 3 ES, 4 ES/EG B, 6 ES/EG, 7 ES, 8 ES/EG

(3.05) End of Hole.
No odor at EOH.

| WATER TABLE | | | |
|---|---|---|---|
| Water level not obtained. | NORTH: 997.287 | EQUIPMENT: RM 30 Ranger | COMPLETION: 95/8/24 |
| | EAST: 1042.560 | METHOD: 3-1/4" Hollow Stem Auger | INSPECTOR: W. Reynolds |
| | TREND: —— | DRILLER: Paddock Drilling Ltd | DEPTH: 3.05 (m) |
| | PLUNGE: -90.0 (deg) | STATUS: FINAL: D/W 97/03/20 O/S | Printed: 97/3/20 11:22 CH95D GEOTE |
| | ELEV G/S: 97.94 (m) | Overlays: HCX500 HCPID ATT10 VAN10 LINE USCS TITLE | |

| Sampler Types | | |
|---|---|---|
| ⊠ Split Spoon | ▨ Sonic | ⊠ Core Barrel |
| ▮ Shelby | ▯ Auger Barrel | ⊻ Tricone |

Auger, Special Samplers, Bulk Sample, Grab Sample, Air Hammer

**Moisture**  
PL — M.C. — LL  
20%  40%  60%  80%

**Vane Shear** (kPa)  
25  50  75  100

**Total Extractable Hydrocarbons (ppm)** ⊕  
100  200  300  400

**Microtip PID Reading** ○  
100  200  300  400

## SOIL DESCRIPTION

**USCS**

| DEPTH (m) | USCS | SOIL DESCRIPTION |
|---|---|---|
| | SM | (0.00-0.75) Sand, grey, and silt, some clay, trace gravel, wet, loose insitu, slight odor. |
| | PT | (0.76-1.10) Peat, brown, fibrous. |
| | CL | (1.10-2.00) Clay, medium grey, some sand, and silt, trace gravel, frozen, crystals 1-2mm, few fine stratifications, weak odor. |
| | | (2.00-3.00) Clay as above, stratified, slight odor. |
| | | (3.00-3.56) Clay as above, non-frozen, stiff to hard insitu, no odor. |

(3.56) End of Hole.  
No odor at EOH.  
CH-213A: Moved and redrilled. Plug-in to  
1.52m, samples 1A and 2A off auger flygts.

PID readings: 36.0, 388.0, 27.4, 164.0, 33.6, 37.5, 49.0, 40.3, 24.4

Vane shear values: 400, 350

| WATER TABLE | NORTH: 995.287 | EQUIPMENT: RM 30 Ranger | COMPLETION: 95/8/24 |
|---|---|---|---|
| Water level not obtained. | EAST: 1019.795 | METHOD: 3-1/4" Hollow Stem Auger | INSPECTOR: W. Reynolds |
| | TREND: — | DRILLER: Paddock Drilling Ltd | DEPTH: 3.56 (m) |
| | PLUNGE: -90.0 (deg) | | |
| | ELEV G/S: 97.95 (m) | STATUS: FINAL: D/W 97/03/20 O/B | Printed: 97/3/20 11:23 CH950 GEOTE |

GEOTECHNICAL

| DEPTH (m) | SAMPLER | SAMPLE # | USCS | SOIL DESCRIPTION |
|---|---|---|---|---|

**Sampler Types:** Split Spoon, Shelby, Auger, Sonic, Auger Barrel, Core Barrel, Special Samplers, Tricone, Bulk Sample, Grab Sample, Air Hammer

**Moisture:** PL — M.C. — LL (20% 40% 60% 80%)

**Vane Shear (kPa):** 25 50 75 100

**Total Extractable Hydrocarbons (ppm):** ⊕ 100 200 300 400

**Microtip PID Reading:** ○ 100 200 300 400

| USCS | SOIL DESCRIPTION |
|---|---|
| SM | (0.00-1.50) Sand, grey brown, some gravel, some silt, very wet, strong diesel odor. |
| PT | (1.50-1.54) Peat, black, mesic, with dark grey sand, strong odor. |
| CL | (1.54-2.27) Clay, grey, mottled brown, with silt, some sand, trace gravel, soft insitu, near PL, moderate odor. |
| | (2.27-2.74) Clay as above, medium stiff insitu, below PL, weak to slight odor. |
| | (2.74-3.39) Clay, grey, some silt, some sand, trace gravel, stiff to hard insitu, below PL, very slight odor. |

(3.39) End of Hole due to auger refusal on boulder.

Note: This log is an amalgamation of CH-219 and CH-219A.

PID Readings: 30000, 303.0, 517.0, 285.0, 157.0, 98.5, 132.0, 68.2, 15.8, 17.9, 9.7

| WATER TABLE | NORTH: | 1063.792 | EQUIPMENT: | RM 30 Ranger | COMPLETION: | 95/8/25 |
|---|---|---|---|---|---|---|
| Water level not obtained. | EAST: | 1017.991 | METHOD: | 3-1/4" Hollow Stem Auger | INSPECTOR: | W. Reynolds |
| | TREND: | — | DRILLER: | Paddock Drilling Ltd | DEPTH: | 3.39 (m) |
| | PLUNGE: | -90.0 (deg) | STATUS: | FINAL: DIW 97/03/20 O/B | | 97/3/20 11:28 CH950 GEOTE |
| | ELEV G/S: | 98.32 (m) | | Overlay: HCX500 HCPID ATT10 VAN10 LINE USCS TITLE | | |

MANITOBA HYDRO
ENGINEERING
GEOTECHNICAL DEPT.
MATERIALS LAB

PROJECT –       CHURCHILL TANK FARM
SAMPLE NO. –    ES – 3
HOLE NO. –      CH – 219        DIRECTORY –    CH95A
DEPTH –         1.54 – 1.77 m
DATE –          95 11 17        FILE NO. –     3CH219A
TESTED BY –     JL

ATTERBERG CALCULATIONS
LIQUID LIMIT

| NO. OF BLOWS | 14 | 14 | 14 |
|---|---|---|---|
| WT. WET SAMPLE AND TARE | 42.10 | 34.10 | 34.50 |
| WT. DRY SAMPLE AND TARE | 38.83 | 32.08 | 32.52 |
| WT. OF TARE | 22.47 | 21.91 | 22.56 |
| WT. OF MOISTURE | 3.27 | 2.02 | 1.98 |
| WT. OF SOLIDS | 16.36 | 10.17 | 9.96 |
| PERCENT MOISTURE | 19.99 | 19.86 | 19.88 |
| LIQUID LIMIT | 18.63 | 18.52 | 18.53 |

PLASTIC LIMIT

| WT. WET SAMPLE AND TARE | 37.10 | 35.80 |
|---|---|---|
| WT. DRY SAMPLE AND TARE | 35.55 | 34.34 |
| WT. OF TARE | 23.04 | 22.26 |
| WT. OF MOISTURE | 1.55 | 1.46 |
| WT. OF SOLIDS | 12.51 | 12.08 |
| PERCENT MOISTURE | 12.39 | 12.09 |

| LL | 18.56 |
|---|---|
| PL | 12.24 |
| PI | 6.32 |

CLASS. –    CL-ML

MANITOBA HYDRO
ENGINEERING
GEOTECHNICAL DEPT.
MATERIALS LAB

## ATTERBERG LIMITS

PROJECT –          CHURCHILL  TANK  FARM

SAMPLE NO. –      ES – 7

HOLE NO. –        CH – 219         DIRECTORY –       CH95A

DEPTH –           2.54 – 2.74 m

DATE –            95 11 17         FILE NO. –        7CH219A

TESTED BY –       JL

## ATTERBERG CALCULATIONS

### LIQUID LIMIT

| NO. OF BLOWS | 19 | 19 | 19 |
|---|---|---|---|
| WT. WET SAMPLE AND TARE | 40.90 | 40.40 | 39.00 |
| WT. DRY SAMPLE AND TARE | 37.77 | 37.46 | 36.23 |
| WT. OF TARE | 22.10 | 22.49 | 22.38 |
| WT. OF MOISTURE | 3.13 | 2.94 | 2.77 |
| WT. OF SOLIDS | 15.67 | 14.97 | 13.85 |
| PERCENT MOISTURE | 19.97 | 19.64 | 20.00 |
| LIQUID LIMIT | 19.32 | 19.00 | 19.35 |

### PLASTIC LIMIT

| WT. WET SAMPLE AND TARE | 31.69 | 29.20 |
|---|---|---|
| WT. DRY SAMPLE AND TARE | 30.68 | 28.34 |
| WT. OF TARE | 22.30 | 21.18 |
| WT. OF MOISTURE | 1.01 | 0.86 |
| WT. OF SOLIDS | 8.38 | 7.16 |
| PERCENT MOISTURE | 12.05 | 12.01 |

| LL | 19.22 |
|---|---|
| PL | 12.03 |
| PI | 7.19 |

CLASS. –      CL

**Sampler Types:**
- ⊠ Split Spoon
- ▨ Sonic
- ▮ Shelby
- ▰ Auger
- ▱ Auger Barrel
- ⊠ Core Barrel
- ⊠ Special Samplers
- ▽ Tricone
- ▮ Bulk Sample
- ▮ Grab Sample
- ▷ Air Hammer

| DEPTH (m) | SAMPLER | SAMPLE # | USCS | SOIL DESCRIPTION | Moisture (PL · M.C. · LL) 20% 40% 60% 80% / Total Extractable Hydrocarbons (ppm) ⊕ 100 200 300 400 | Vane Shear (kPa) 25 50 75 100 / Microtip PID Reading ○ 100 200 300 400 | DEPTH |
|---|---|---|---|---|---|---|---|
| | | 1 ES/EG | SM | (0.00-1.16) Sand, grey brown, some gravel, some silt, very wet, strong diesel odor. | >>●6500 | >>○517. | |
| 1 | | 2 ES/EG | | | | ○295.0 | 1 |
| | | | PT | (1.16-1.32) Peat, brownish black, fibrous. | | | |
| | | | CL | (1.32-1.52) Clay, grey. | | | |
| | | | | (1.52) End of Hole. | | | |

| WATER TABLE | NORTH: 1065.592 | EQUIPMENT: RM 30 Ranger | COMPLETION: 95/8/25 |
|---|---|---|---|
| Water level not obtained. | EAST: 1017.591 | METHOD: 3-1/4" Hollow Stem Auger | INSPECTOR: W. Reynolds |
| | TREND: — | DRILLER: Paddock Drilling Ltd | DEPTH: 1.52 (m) |
| | PLUNGE: -90.0 (deg) | | |
| | ELEV G/S: 98.32 (m) | STATUS: FINAL: DRW 97/03/20 O/B Overlays: HCX500 HCPID ATT10 VAN10 LINE USCS TITLE Printed: 97/3/20 11:28 CH950 GEOTE | |

| Sampler Types | | | |
|---|---|---|---|
| ⊠ Split Spoon | ◪ Auger | ⊠ Core Barrel | Bulk Sample |
| | ⧄ Sonic | ☒ Special Samplers | Grab Sample |
| ▦ Shelby | ⊓ Auger Barrel | ▽ Tricone | ⧖ Air Hammer |

**SOIL DESCRIPTION**

| DEPTH (m) | SAMPLER | SAMPLE # | USCS | SOIL DESCRIPTION |
|---|---|---|---|---|
| | | | SM | (0.00-0.70) Sand, green brown, and silt, with gravel, loose insitu, wet, very strong odor. |
| | | 1 GS/GG | | |
| | | | PT | (0.70-0.90) Peat, brown, fibrous, mesic. |
| 1 | | ES/EG GS/GG | CL | (0.90-1.74) Clay green grey, moist, soft insitu, above PL, very strong odor. Moved drill 0.70m South to core same run; reamed to 1.02m. |
| | | 5 ES/EG ES/EG | | |
| 2 | | 7 ES/EG | | (1.74-2.03) Clay as above, medium insitu, moderate odor. |
| | | 8 ES/EG | | (2.03-2.28) Clay as above, stiff insitu, weak odor. |
| | | ES/EG | | (2.28-3.05) Clay as above, no odor. |
| 3 | | 10 ES/EG | | |

(3.05) End of Hole.
No odor at EOH.

**Moisture** M.C.  PL 20% 40% 60% 80% LL

**Total Extractable Hydrocarbons (ppm)** ⊕ 100 200 300 400

**Vane Shear** (kPa) 25 50 75 100

**Microtip PID Reading** ○ 100 200 300 400

PID / TEH readings:
>>11000  ○175.0
>>9800  ○96.7  ○199.0
○41.1
>>4200  ○48.3
○22.9
○19.2
○13.4
○9.8
○16.5

| WATER TABLE | | | |
|---|---|---|---|
| Water level not obtained. | NORTH: 1064.808 | EQUIPMENT: RM 30 Ranger | COMPLETION: 95/8/25 |
| | EAST: 1007.792 | METHOD: 3-1/4" Hollow Stem Auger | INSPECTOR: W. Reynolds |
| | TREND: — | DRILLER: Paddock Drilling Ltd | DEPTH: 3.05 (m) |
| | PLUNGE: -90.0 (deg) | STATUS: FINAL: DW 97/03/20 O/B | Printed: 97/3/20 11:31 CH950 GEOTE |
| | ELEV G/S: 98.11 (m) | Overlays: HCXS00 HCPID ATT10 VAN10 LINE USCS TITLE | |

| DEPTH (m) | SAMPLER | SAMPLE # | USCS | SOIL DESCRIPTION |
|---|---|---|---|---|
| | | | PT | (0.00-0.08) Peat, brown, dry. |
| | | 1 CS/CG | CH | (0.08-0.50) Clay, dark grey brown, some fine rootlets, trace silt, very hard insitu, below PL. |
| | | 2 CS/CG | | Field pen at 0.25m = +450 kPa. |
| | | 3 CS/CG | | (0.50-1.00) Clay, dark grey brown, trace silt, laminated, stiff insitu, above PL. |
| | | 4 CS/CG | | Field pen at 0.70m = 200 kPa. |
| 1 | | 5 CS/CG | | (1.00-1.50) Clay, dark grey brown, trace silt, trace sand, stiff insitu, above PL. |
| | | 6 CS/CG | | Field pen at 1.25m = 225 kPa. |
| | | 7 CS/CG | CI | (1.50-2.50) Clay, olive grey, varved, with silt, trace sand, varved, crumbling texture, medium insitu, above PL. |
| | | 8 CS/CG | | Field pen at 1.75m = 100 kPa. |
| 2 | | 9 CS/CG | | Field pen at 2.00m = 225 kPa. |
| | | 10 CS/CG | | |
| | | 11 CS/CG | CI | (2.50-2.65) Clay, grey brown, with silt, trace fine |
| | | 12 CS | | grained sand, medium insitu, above PL. |
| | | | | (2.65) End of Hole due to auger refusal on bedrock. |

**Sampler Types:** ⬛ Auger   ▨ Core Barrel   Bulk Sample   ⊠ Split Spoon   ⧄ Sonic   ⊠ Special Samplers   Grab Sample   ⬛ Shelby   ⬜ Auger Barrel   ▽ Tricone   Air Hammer

**Moisture** — PL · M.C. · LL — 20% 40% 60% 80%

**Total Extractable Hydrocarbons (ppm)** ⊕ — 500 1000 1500 2000

**Vane Shear (kPa)** ☐ — 25 50 75 100

**Microtip PID Reading** ○ — 100 200 300 400

Total Extractable Hydrocarbons (ppm) values: 300, 310, 750, 120

Microtip PID Reading values: O102.0, O321.0, O223.0, O218.0, O119.0, O193.0, O35.6, O49.2, O35.2, O22.7, O10.8, O140.0

| WATER TABLE | NORTH: 40.000 | EQUIPMENT: Ranger | COMPLETION: 96/8/24 |
|---|---|---|---|
| Dry hole. | EAST: 20.000 | METHOD: Hollow Stem Auger | INSPECTOR: F. Demchenko |
| | TREND: —— | DRILLER: Paddock Drilling Ltd | DEPTH: 2.65 (m) |
| | PLUNGE: -90.0 (deg) | STATUS: FINAL: WTR 96/11/21 O/B   Overlay: HCX2K HCPID ATT10 VAN10 LINE USCS TITLE | Printed: 96/11/21 10:48 GV96A GEOTE |
| | ELEV G/S: 269.96 (m) | | |

## Chart Headers

| DEPTH (m) | SAMPLER | SAMPLE # | Sampler Types | USCS | SOIL DESCRIPTION | Moisture (PL – M.C. – LL) 20% 40% 60% 80% | Vane Shear (kPa) 25 50 75 100 | DEPTH (m) |
|---|---|---|---|---|---|---|---|---|

Sampler Types legend:
- Auger
- Core Barrel
- Bulk Sample
- Split Spoon
- Sonic
- Special Samplers
- Grab Sample
- Shelby
- Auger Barrel
- Tricone
- Air Hammer

Total Extractable Hydrocarbons (ppm) ⊕  500 1000 1500 2000
Microtip PID Reading ○  100 200 300 400

## Soil Description

(0.00–0.05) Peat, black. — PT

(0.05–0.25) Clay, dark grey brown, trace silt, trace sand, medium insitu, above PL. — CH

(0.25–1.25) Clay, grey brown, trace silt, trace fine grained sand, medium insitu, above PL. — CH

Field pen at 0.90m = 200 kPa.

(1.25–2.00) Clay, grey brown, faintly varved, some silt, trace sand, medium insitu, above PL. — CH
Field pen at 1.40m = 125 kPa.

(2.00–2.40) Clay, grey brown, some silt, trace sand, varved, medium insitu, above PL.

(2.40) End of Hole due to auger refusal on bedrock.

Sample column entries (Sampler CS/CG):
1 CS/CG, 2 CS/CG, 3 CS/CG, 4 CS/CG, 5 CS/CG, 6 CS/CG, 7 CS/CG, 8 CS/CG, 9 CS/CG, 10 CS/CG

Microtip PID Readings: ○45.7, ○73.4, ○60.1, ○70.5, ○64.8, ○73.7, ○77.0, ○67.2, ○67.1, ○67.4

Total Extractable Hydrocarbons values: >>87500, 1800, >>3410, 470, 480

WATER TABLE — Dry hole.

NORTH: 37.000
EAST: 9.400
TREND: —
PLUNGE: -90.0 (deg)
ELEV G/S: 269.76 (m)

EQUIPMENT: Ranger
METHOD: Hollow Stem Auger
DRILLER: Paddock Drilling Ltd
STATUS:   FINAL: WTR 96/11/21 O/B   Overley: HCX2X HCPID ATT10 VAN10 LINE USCS TITLE

COMPLETION: 96/8/25
INSPECTOR: F. Demchenko
DEPTH: 2.40 (m)
Printed: 96/11/21 10:56 GV96A GEOTE

# MANITOBA HYDRO
### Engineering
## OVERBURDEN LOG
GEOTECHNICAL

# GRANVILLE LAKE
## DECOMMISSIONED DIESEL GENERATING STATION

## GV-017
### 1 OF 1
Prj.# 46664

**Sampler Types**

- Split Spoon
- Shelby
- Auger
- Sonic
- Auger Barrel
- Core Barrel
- Special Samplers
- Tricone
- Bulk Sample
- Grab Sample
- Air Hammer

| DEPTH (m) | SAMPLER | SAMPLE # | USCS | SOIL DESCRIPTION | Moisture M.C. (PL 20% 40% 60% LL 80%) / Total Extractable Hydrocarbons (ppm) 500 1000 1500 2000 | Vane Shear (kPa) 25 50 75 100 / Microtip PID Reading 100 200 300 400 | DEPTH (m) |
|---|---|---|---|---|---|---|---|
| | CS | 1 | PT | (0.00-0.10) Peat. | | ○65.0 | |
| | | | CH | (0.10-0.75) Clay, dark grey brown, some rootlets, very hard insitu, at PL. Field pen at 0.25m = +450 kPa. | | ○28.5 | |
| | CS/CG | 2 | | | | | |
| | CS/CG | 3 | | | | ○26.8 | |
| | CS/CG | 4 | | (0.75-1.00) Clay, dark grey brown, trace silt, very stiff insitu, at PL. Field pen at 0.90m = 350 kPa. | | ○26.2 | |
| 1 | CS/CG | 5 | CI | (1.00-2.39) Clay, grey brown, trace silt, trace sand, above PL, faintly varved. | | ○34.4 | 1 |
| | CS/CG | 6 | | | | ○15.7 | |
| | CS/CG | 7 | | | | ○37.4 | |
| | CS/CG | 8 | | | | ○28.2 | |
| 2 | CS/CG | 9 | | | | ○26.3 | 2 |
| | CS/CG | 10 | | | | ○18.9 | |
| | CS/CG | 11 | ML | (2.39-2.49) Silt, greenish grey, some sand, damp, diesel odor. | >>2800 | ●  ○381.0 | |

(2.49) End of Hole due to auger refusal on bedrock.

| WATER TABLE Dry hole. | NORTH: 60.000 EAST: 10.000 TREND: — PLUNGE: -90.0 (deg) ELEV G/S: 268.12 (m) | EQUIPMENT: Ranger METHOD: Hollow Stem Auger DRILLER: Paddock Drilling Ltd STATUS: | COMPLETION: 96/8/26 INSPECTOR: F. Demchenko DEPTH: 2.49 (m) |
|---|---|---|---|

| Sampler Types | | |
|---|---|---|
| ▨ Auger | ▧ Core Barrel | ▮ Bulk Sample |
| ⊠ Split Spoon | ⟋ Sonic | ⊠ Special Samplers | ▤ Grab Sample |
| ▮ Shelby | ▯ Auger Barrel | ▽ Tricone | ⊐ Air Hammer |

| DEPTH (m) | SAMPLER | SAMPLE # | USCS | SOIL DESCRIPTION | Moisture PL — M.C. — LL (20% 40% 60% 80%) / Total Extractable Hydrocarbons (ppm) ⊕ (500 1000 1500 2000) | Vane Shear (kPa) (25 50 75 100) / Microtip PID Reading ○ (100 200 300 400) |
|---|---|---|---|---|---|---|
| | | | PT | (0.00-0.10) Peat. | | |
| | | 1 CS/CG | CH | (0.10-0.25) Clay, dark grey brown, trace silt, trace rootlets, crumbling texture, below PL. | | ○108.0 |
| | | 2 CS/CG | | (0.25-0.50) Clay, dark grey brown, trace silt, stiff insitu, above PL. | | ○56.1 |
| | | 3 CS/CG | CH | (0.50-1.25) Clay, grey brown, trace silt, trace sand, trace gravel, stiff insitu, above PL. | ● | ○52.8 |
| | | 4 CS/CG | | | | ○37.2 |
| 1 | | 5 CS/CG | | | | ○237.0 |
| | | 6 CS/CG | CI | (1.25-2.10) Clay, olive grey, some silt, trace sand, blocky, diesel odor, above PL. | ●● | ○456.0 |
| | | 7 CS/CG | | | >>● 4200 | ○474. |
| | | 8 CS/CG | | | ● >>● 3200 | ○477. |
| 2 | | 9 CS/CG | | | ● >>● 3500 | ○439 |

(2.10) End of Hole due to auger refusal on bedrock.

# MANITOBA HYDRO
### Engineering
### GEOTECHNICAL FIELD OVERBURDEN LOG

## CRANBERRY PORTAGE
### DECOMMISSIONED DIESEL GENERATING STATION

**CB-004**
**1 OF 1**
Prj.# 46466-1580

**Sampler Types:** Auger | Core Barrel | Bulk Sample | Split Spoon | Sonic | Special Samplers | Grab Sample | Shelby | Auger Barrel | Tricone | Air Hammer

| DEPTH (m) | RUN DEPTH | SAMPLER | USCS | FIELD DESCRIPTION | SAMPLE # | TYPE | SIZE | DEPTH | RECOVERED LENGTH | FIELD POCKET PENETROMETER | FIELD HAND VANE SHEAR | BLOW COUNT | SPT COUNTS | PERMEABILITY (cm/sec) | TEST INTERVAL | DEPTH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.00 | | | FILL SP | (0.00-0.05) Gravel; "fill". (0.05-0.75) Sand, dark brown, with silt, trace gravel, damp. | 1 | CS/CG | | 0.00 | 0.37 | | | | | | | |
| | | | | | 2 | CS/CG | | 0.37 | 0.38 | | | | | | | |
| | | | | (0.75-1.50) Sand, medium tan brown, trace silt, damp. | 3 | CS/CG | | 0.75 | 0.37 | | | | | | | 1 |
| 1 | | | | | 4 | CS/CG | | 1.12 | 0.38 | | | | | | | |
| | | | | (1.50-2.28) Sand, light brown, medium to fine grained, damp. | 5 | CS/CG | | 1.50 | 0.37 | | | | | | | |
| 2 | | | | | 6 | CS/CG | | 1.87 | 0.38 | | | | | | | 2 |
| | | | ML | (2.28-2.85) Silt, medium brown grey, with sand, damp. | 7 | CS/CG | | 2.28 | 0.57 | | | | | | | |
| 3 | | | SP | (2.85-3.05) Sand, light brown, medium to fine grained, damp. | 8 | CS/CG | | 2.85 | 0.20 | | | | | | | 3 |
| | | | | (3.05-4.27) Sand, light brown, medium grain, damp. | 9 | CS/CG | | 3.05 | 0.37 | | | | | | | |
| | | | | | 10 | CS/CG | | 3.42 | 0.38 | | | | | | | |
| | | | | | 11 | CS/CG | | 3.80 | 0.47 | | | | | | | |
| 4 | | | | (4.27-4.55) Sand, light brown, fine to medium grained, trace silt, damp. | 12 | CS/CG | | 4.27 | 0.28 | | | | | | | 4 |
| | | | ML | (4.55-5.30) Silt, light brown, and sand, damp. | 13 | CS/CG | | 4.55 | 0.37 | | | | | | | |
| 5 | | | | | 14 | CS/CG | | 4.92 | 0.38 | | | | | | | 5 |
| | | | SM | (5.30-6.10) Sand, medium brown, fine grained, with silt, damp. | 15 | CS/CG | | 5.30 | 0.37 | | | | | | | |
| | | | | | 16 | CS/CG | | 5.67 | 0.43 | | | | | | | |
| 6 | | | SP | (6.10-7.10) Sand, light brown, trace silt, medium to fine grained, damp. | 17 | CS/CG | | 6.10 | 0.37 | | | | | | | 6 |
| | | | | | 18 | CS/CG | | 6.47 | 0.38 | | | | | | | |
| 7 | | | | | 19 | CS/CG | | 6.85 | 0.40 | | | | | | | 7 |
| | | | ML SP | (7.10-7.25) Silt, light brown, with sand. (7.25-7.55) Sand, light brown, fine grained, trace silt. | 20 | CS/CG | | 7.25 | 0.30 | | | | | | | |
| | | | | (7.55-9.15) Sand as above, with silt. | 21 | CS/CG | | 7.55 | 0.37 | | | | | | | |
| 8 | | | | | 22 | CS/CG | | 7.92 | 0.38 | | | | | | | 8 |
| | | | | | 23 | CS/CG | | 8.30 | 0.37 | | | | | | | |
| | | | | | 24 | CS/CG | | 8.67 | 0.48 | | | | | | | |
| 9 | | | | | | | | | | | | | | | | 9 |

PRELIMINARY

(9.15) End of Hole.

No bedrock encountered.
No water table.

| WATER TABLE | | | |
|---|---|---|---|
| No water level recorded. | NORTH: EAST: TREND: — PLUNGE: -90.0 (deg) ELEV G/S: (m) | EQUIPMENT: Canterra METHOD: Hollow Stem Auger DRILLER: Paddock Drilling Ltd | COMPLETION: 96/09/20 INSPECTOR: F. Demchenko DEPTH: 9.15 (m) |
| | | STATUS: PRELIM: SLM 96/10/02 O/BFIELD Overlays: SPT UNC1 ATT10 VAN10 LINE USCS TITLE | Printed: 97/04/24 10:32 CB96A GEOTE |

# MANITOBA HYDRO

**Engineering**
GEOTECHNICAL **FIELD OVERBURDEN LOG**

## CRANBERRY PORTAGE
### DECOMMISSIONED DIESEL GENERATING STATION

**CB-005**
**1 OF 1**
Prj.# 46466-1580

**Sampler Types:**
- Auger
- Core Barrel
- Bulk Sample
- Split Spoon
- Sonic
- Special Samplers
- Grab Sample
- Shelby
- Auger Barrel
- Tricone
- Air Hammer

| DEPTH (m) | RUN DEPTH | SAMPLER | USCS | FIELD DESCRIPTION | SAMPLE # | TYPE | SIZE | DEPTH | RECOVERED LENGTH | FIELD POCKET PENETROMETER | FIELD HAND VANE SHEAR | BLOW COUNT | SPT COUNTS | PERMEABILITY (cm/sec) | TEST INTERVAL | DEPTH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.00 | | SM | | (0.00-0.30) Sand, medium brown, with silt, trace gravel, damp. | 1 | CS/CG | | 0.00 | 0.30 | | | | | | | |
| | | | | (0.30-0.75) Sand, medium brown, some silt, trace oxidation, damp. | 2 | CS/CG | | 0.30 | 0.45 | | | | | | | |
| | | ML | | (0.75-1.20) Silt, medium brown, with fine grained sand, damp. | 3 | CS/CG | | 0.75 | 0.45 | | | | | | | 1 |
| | | SP | | (1.20-1.65) Sand, light brown, medium grained, damp. | 4 | CS/CG | | 1.20 | 0.30 | | | | | | | |
| | | | | | 5 | CS/CG | | 1.50 | 0.45 | | | | | | | |
| | | SM | | (1.65-2.25) Sand, light brown, fine grained, and silt, damp. | 6 | CS/CG | | 1.95 | 0.30 | | | | | | | 2 |
| | | SP | | (2.25-3.05) Sand, medium brown, medium grained, damp. | 7 | CS/CG | | 2.25 | 0.40 | | | | | | | |
| | | | | | 8 | CS/CG | | 2.65 | 0.40 | | | | | | | |
| | | | | (3.05-4.40) Sand, medium brown, medium grained, damp. | 9 | CS/CG | | 3.05 | 0.37 | | | | | | | 3 |
| | | | | | 10 | CS/CG | | 3.43 | 0.38 | | | | | | | |
| | | | | | 11 | CS/CG | | 3.80 | 0.60 | | | | | | | 4 |
| | | ML | | (4.40-4.55) Silt, light brown, some sand, damp. | 12 | CS/CG | | 4.40 | 0.15 | | | | | | | |
| | | SP | | (4.55-4.80) Sand, light brown, some silt, damp. | 13 | CS/CG | | 4.55 | 0.25 | | | | | | | |
| | | ML | | (4.80-5.00) Silt, light brown, some sand, damp. | 14 | CS | | 4.80 | 0.20 | | | | | | | 5 |
| | | | | (5.00-6.10) Silt, light brown, and fine sand. | 15 | CS/CG | | 5.00 | 0.30 | | | | | | | |
| | | | | | 16 | CS/CG | | 5.30 | 0.37 | | | | | | | |
| | | | | | 17 | CS/CG | | 5.67 | 0.43 | | | | | | | 6 |
| | | SP | | (6.10-6.85) Sand, light brown, fine grained, damp. | 18 | CS/CG | | 6.10 | 0.37 | | | | | | | |
| | | | | | 19 | CS/CG | | 6.47 | 0.38 | | | | | | | |
| | | ML | | (6.85-7.22) Silt, light brown, trace sand, damp. | 20 | CS/CG | | 6.85 | 0.37 | | | | | | | 7 |
| | | | | (7.22-7.70) Silt as above, with sand. | 21 | CS/CG | | 7.22 | 0.33 | | | | | | | |
| | | | | | 22 | CS/CG | | 7.55 | 0.15 | | | | | | | |
| | | SP | | (7.70-7.80) Sand seam, medium brown, medium grained, damp. | 23 | CS/CG | | 7.70 | 0.10 | | | | | | | |
| | | ML | | (7.80-8.30) Silt, light brown, and fine grained sand, damp. | 24 | CS/CG | | 7.80 | 0.50 | | | | | | | 8 |
| | | | | (8.30-9.15) Silt as above, some fine grained sand. | 25 | CS/CG | | 8.30 | 0.37 | | | | | | | |
| | | | | | 26 | CS/CG | | 8.67 | 0.38 | | | | | | | 9 |
| | | | | (9.15) End of Hole. | | | | | | | | | | | | |

PRELIMINARY

| WATER TABLE | | | |
|---|---|---|---|
| No water level recorded. | | | |

| NORTH: | |
|---|---|
| EAST: | |
| TREND: | — |
| PLUNGE: | -90.0 (deg) |
| ELEV G/S: | (m) |

| EQUIPMENT: | Canterra |
|---|---|
| METHOD: | Hollow Stem Auger |
| DRILLER: | Paddock Drilling Ltd |
| STATUS: | PRELIM: SLM 96/10/02 O/8FIELD Printed: 97/04/24 10:34 CB96A GEOTE Overlays: SPT UNC1 ATT10 VAN10 LINE USCS TITLE |

| COMPLETION: | 96/09/20 |
|---|---|
| INSPECTOR: | F. Demchenko |
| DEPTH: | 9.15 (m) |

# MANITOBA HYDRO

GEOTECHNICAL

Engineering
FIELD OVERBURDEN LOG

## CRANBERRY PORTAGE

DECOMMISSIONED DIESEL GENERATING STATION

**CB-006**

**1 OF 1**

Prj.# 46466-1580

**Sampler Types:**
Split Spoon, Shelby, Auger, Sonic, Auger Barrel, Core Barrel, Special Samplers, Tricone, Bulk Sample, Grab Sample, Air Hammer

| SAMPLE # | TYPE | SIZE | DEPTH | RECOVERED LENGTH | FIELD POCKET PENETROMETER | FIELD HAND VANE SHEAR | BLOW COUNT | SPT COUNTS | PERMEABILITY (cm/sec) | TEST INTERVAL |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | CS/CG | | 0.10 | 0.50 | | | | | | |
| 2 | CS/CG | | 0.60 | 0.15 | | | | | | |
| 3 | CS/CG | | 0.75 | 0.37 | | | | | | |
| 4 | CS/CG | | 1.12 | 0.38 | | | | | | |
| 5 | CS/CG | | 1.50 | 0.37 | | | | | | |
| 6 | CS/CG | | 1.87 | 0.38 | | | | | | |
| 7 | CS/CG | | 2.25 | 0.30 | | | | | | |
| 8 | CS/CG | | 2.55 | 0.35 | | | | | | |
| 9 | CS | | 2.90 | 0.15 | | | | | | |
| 10 | CS/CG | | 3.05 | 0.37 | | | | | | |
| 11 | CS/CG | | 3.42 | 0.38 | | | | | | |
| 12 | CS/CG | | 3.80 | 0.37 | | | | | | |
| 13 | CS/CG | | 4.17 | 0.38 | | | | | | |
| 14 | CS/CG | | 4.55 | 0.35 | | | | | | |
| 15 | CS/CG | | 4.90 | 0.40 | | | | | | |
| 16 | CS/CG | | 5.30 | 0.37 | | | | | | |
| 17 | CS/CG | | 5.67 | 0.43 | | | | | | |
| 18 | CS/CG | | 6.10 | 0.50 | | | | | | |
| 19 | CS/CG | | 6.60 | 0.25 | | | | | | |

**FIELD DESCRIPTION (USCS)**

- PT (0.00-0.10) Peat.
- ML (0.10-0.60) Silt, light brown, trace sand, trace gravel, damp.
- SP (0.60-2.55) Sand, light brown, medium grained, damp.
- ML (2.55-2.90) Silt, medium brown, trace sand, damp.
- SP (2.90-4.55) Sand, light brown, medium grained, damp.
- ML (4.55-4.75) Silt, medium brown, trace sand, damp.
- SP (4.75-4.82) Sand seam.
- ML (4.82-4.90) Silt, medium brown, trace sand, damp.
- SP (4.90-6.60) Sand, light brown, medium grained, damp.
- ML (6.60-6.85) Silt, medium brown, some fine sand, damp.
- (6.85) End of Hole.

PRELIMINARY

| WATER TABLE | NORTH: | EQUIPMENT: Canterra | COMPLETION: 96/09/20 |
|---|---|---|---|
| No water level recorded. | EAST: | METHOD: Hollow Stem Auger | INSPECTOR: F. Demchenko |
| | TREND: — | DRILLER: Paddock Drilling Ltd | DEPTH: 6.85 (m) |
| | PLUNGE: -90.0 (deg) | | |
| | ELEV G/S: (m) | STATUS: PRELIM: SLM 96/10/02 O/6FIELD  Printed: 97/04/24 10:35 CB96A GEOTE  Overlays: SPT UNC1 ATT10 VAN10 LINE USCS TITLE | |

**Sampler Types**

- ⊠ Split Spoon
- ■ Shelby
- ◼ Auger
- ⧄ Sonic
- ⊞ Auger Barrel
- ⊠ Core Barrel
- ☒ Special Samplers
- ▽ Tricone
- Bulk Sample
- Grab Sample
- ▷ Air Hammer

| DEPTH (m) | RUN DEPTH | SAMPLER | USCS | FIELD DESCRIPTION | SAMPLE # | TYPE | SIZE | DEPTH | RECOVERED LENGTH | FIELD POCKET PENETROMETER | FIELD HAND VANE SHEAR | BLOW COUNT | SPT COUNTS | PERMEABILITY (cm/sec) | TEST INTERVAL | DEPTH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0.00 | | PT | (0.00-0.05) Peat, with topsoil. | | | | | | | | | | | | |
| | | | SP | (0.05-0.30) Sand, brown, trace silt, damp. | | | | | | | | | | | | |
| | | | CI | (0.30-1.50) Clay, brown, trace silt, trace sand, blocky, hard insitu, above PL. | 1 | CS/CG | | 0.30 | 0.45 | | | | | | | |
| | | | | | 2 | CS/CG | | 0.75 | 0.37 | | | | | | | |
| 1 | | | | | 3 | CS/CG | | 1.12 | 0.38 | | | | | | | 1 |
| | | | ML | (1.50-1.85) Silt, light brown, some fine grained sand, damp. | 4 | CS/CG | | 1.50 | 0.35 | | | | | | | |
| 2 | | | SP | (1.85-3.05) Sand, brown, coarse to fine grained, trace gravel, damp. | 5 | CS/CG | | 1.85 | 0.40 | | | | | | | 2 |
| | | | | | 6 | CS/CG | | 2.25 | 0.37 | | | | | | | |
| | | | | | 7 | CS/CG | | 2.62 | 0.43 | | | | | | | |
| 3 | | | | (3.05-4.82) Sand, brown, medium grained, damp. | 8 | CS/CG | | 3.05 | 0.30 | | | | | | | 3 |
| | | | | | 9 | CS/CG | | 3.35 | 0.45 | | | | | | | |
| 4 | | | | | 10 | CS | | 3.80 | 0.37 | | | | | | | 4 |
| | | | | | 11 | CS | | 4.17 | 0.38 | | | | | | | |
| | | | | | 12 | CS/CG | | 4.55 | 0.27 | | | | | | | |
| 5 | | | | (4.82-5.30) Sand, brown, medium to fine grained, trace silt, damp. | 13 | CS/CG | | 4.82 | 0.46 | | | | | | | 5 |
| | | | | (5.30-6.10) Sand, brown, fine grained, with silt, damp. | 14 | CS | | 5.30 | 0.37 | | | | | | | |
| | | | | | 15 | CS | | 5.67 | 0.43 | | | | | | | |
| 6 | | | ML | (6.10-6.35) Silt, medium brown, trace sand, damp. | 16 | CS | | 6.10 | 0.25 | | | | | | | 6 |
| | | | SP | (6.35-6.85) Sand, light brown, fine grained, damp. | 17 | CS/CG | | 6.35 | 0.50 | | | | | | | |
| 7 | | | ML | (6.85-6.90) Silt seam, light grey brown. | 18 | CS | | 6.85 | 0.05 | | | | | | | 7 |
| | | | SP | (6.90-7.60) Sand, light brown, fine grained, some silt, damp. | 19 | CS | | 6.90 | 0.30 | | | | | | | |
| | | | | | 20 | CS/CG | | 7.20 | 0.40 | | | | | | | |
| | | | | (7.60-8.55) Sand as above, trace silt. | 21 | CS | | 7.60 | 0.37 | | | | | | | |
| 8 | | | | | 22 | CS/CG | | 7.97 | 0.38 | | | | | | | 8 |
| | | | | | 23 | CS | | 8.35 | 0.20 | | | | | | | |
| | | | | (8.55-9.15) Sand as above, no silt. | 24 | CS/CG | | 8.55 | 0.60 | | | | | | | |
| 9 | | | | | | | | | | | | | | | | 9 |
| | | | ML | (9.15-9.25) Silt, light brown, some sand, trace gravel, damp. | 25 | CS | | 9.15 | 0.10 | | | | | | | |
| | | | SM | | 26 | CS | | 9.25 | 0.30 | | | | | | | |
| | | | | (9.25-10.65) Sand, light brown, fine gravel, with silt, damp. | 27 | CS | | 9.55 | 0.35 | | | | | | | |

*PRELIMINARY* (watermark)

| WATER TABLE | NORTH: | EQUIPMENT: Canterra | COMPLETION: 96/09/21 |
|---|---|---|---|
| No water level recorded. | EAST: | METHOD: Hollow Stem Auger | INSPECTOR: F. Demchenko |
| | TREND: ---- | DRILLER: Paddock Drilling Ltd | DEPTH: 10.65 (m) |
| | PLUNGE: -90.0 (deg) | | |
| | ELEV G/S: (m) | STATUS: PRELIM | Continued... |

**MANITOBA HYDRO**

GEOTECHNICAL · Engineering · **FIELD OVERBURDEN LOG**

**CRANBERRY PORTAGE**

**DECOMMISSIONED DIESEL GENERATING STATION**

**CB-008**

**2 OF 2**

Prj.# 46466-1580

| Sampler Types | | | | |
|---|---|---|---|---|
| | Auger | Core Barrel | Bulk Sample | |
| Split Spoon | Sonic | Special Samplers | Grab Sample | |
| Shelby | Auger Barrel | Tricone | Air Hammer | |

| DEPTH (m) | RUN DEPTH | SAMPLER | USCS | FIELD DESCRIPTION | SAMPLE # | TYPE | SIZE | DEPTH | RECOVERED LENGTH | FIELD POCKET PENETROMETER | FIELD HAND VANE SHEAR | BLOW COUNT | SPT COUNTS | PERMEABILITY (cm/sec) | TEST INTERVAL | DEPTH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | 28 | CS | | 9.90 | 0.38 | | | | | | | |
| | | | | | 29 | CS/CG | | 10.28 | 0.37 | | | | | | | |
| | | | SP SM | (10.50-10.52) SP sand seam, more granular. (10.65) End of Hole. | | | | | | | | | | | | |

No bedrock encountered.
Installed well. Location: 7.0m East of the east
door from of the helicopter hangar. 45 in a line
through the storm sewer manhole cover.
Well is screened to 7.60m with fiber sock. Caved
and backfilled to ground surface.

PRELIMINARY

| WATER TABLE | | | | |
|---|---|---|---|---|
| No water level recorded. | NORTH: | | EQUIPMENT: Canterra | COMPLETION: 96/09/21 |
| | EAST: | | METHOD: Hollow Stem Auger | INSPECTOR: F. Demchenko |
| | TREND: | —— | DRILLER: Paddock Drilling Ltd | DEPTH: 10.65 (m) |
| | PLUNGE: -90.0 (deg) | | | |
| | ELEV G/S: (m) | | STATUS: PRELIM: SLM 96/10/02 O/8FIELD Printed: 97/04/24 10:37 C896A GEOTE Overlays: SPT UNC1 ATT10 VAN10 LINE USCS TITLE | |

# MANITOBA HYDRO

Engineering
FIELD OVERBURDEN LOG

GEOTECHNICAL

## CRANBERRY PORTAGE

DECOMMISSIONED DIESEL GENERATING STATION

**CB-015**
**1 OF 1**
Prj.# 46466-1580

**Sampler Types:** Split Spoon, Shelby, Auger, Sonic, Auger Barrel, Core Barrel, Special Samplers, Tricone, Bulk Sample, Grab Sample, Air Hammer

| DEPTH (m) | RUN DEPTH | SAMPLER | USCS | FIELD DESCRIPTION | SAMPLE # | TYPE | SIZE | DEPTH | RECOVERED LENGTH | FIELD POCKET PENETROMETER | FIELD HAND VANE SHEAR | BLOW COUNT | SPT COUNTS | PERMEABILITY (cm/sec) | TEST INTERVAL | DEPTH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.00 | | | FILL | (0.00-0.30) Fill. | | | | | | | | | | | | |
| | | | SP | (0.30-1.20) Sand, tan brown, coarse to fine grained, damp. | 1 | CS | | 0.30 | 0.45 | | | | | | | |
| | | | | | 2 | CS | | 0.75 | 0.45 | | | | | | | |
| 1 | | | | (1.20-2.00) Sand, brown, medium to fine grained, damp. | 3 | CS | | 1.20 | 0.30 | | | | | | | 1 |
| | | | | | 4 | CS | | 1.50 | 0.50 | | | | | | | |
| 2 | | | | (2.00-3.55) Sand, brown, coarse to fine grained, trace gravel, damp. | 5 | CS | | 2.00 | 0.25 | | | | | | | 2 |
| | | | | | 6 | CS | | 2.25 | 0.37 | | | | | | | |
| | | | | | 7 | CS | | 2.62 | 0.43 | | | | | | | |
| 3 | | | | | 8 | CS | | 3.05 | 0.50 | | | | | | | 3 |
| | | | | (3.55-4.00) Sand, brown, fine to medium grained, damp. | 9 | CS | | 3.55 | 0.25 | | | | | | | |
| 4 | | | | | 10 | CS | | 3.80 | 0.20 | | | | | | | 4 |
| | | | | (4.00-4.25) Sand, brown, medium grained, damp. | 11 | CS | | 4.00 | 0.25 | | | | | | | |
| | | | ML | (4.25-4.80) Silt, light grey brown, some sand, damp. | 12 | CS | | 4.25 | 0.30 | | | | | | | |
| | | | | | 13 | CS | | 4.55 | 0.25 | | | | | | | |
| | | | SP | (4.70-4.72) Sand seam. | 14 | CS | | 4.80 | 0.50 | | | | | | | |
| 5 | | | ML SP | (4.80-5.50) Sand, brown, medium to fine grained, damp. | | | | | | | | | | | | 5 |
| | | | | | 15 | CS | | 5.30 | 0.20 | | | | | | | |
| | | | ML | (5.50-5.70) Silt, light grey brown, trace sand, damp. | 16 | CS | | 5.50 | 0.20 | | | | | | | |
| | | | | (5.70-6.50) Silt, light brown, with sand, damp. | 17 | CS | | 5.70 | 0.40 | | | | | | | |
| 6 | | | | | 18 | CS | | 6.10 | 0.40 | | | | | | | 6 |
| | | | SP | (6.50-6.65) Sand, brown, some gravel, damp. | 19 | CS | | 6.50 | 0.15 | | | | | | | |
| | | | ML | (6.65-7.10) Silt, medium brown, some sand, damp. | 20 | CS | | 6.65 | 0.20 | | | | | | | |
| 7 | | | | | 21 | CS | | 6.85 | 0.25 | | | | | | | 7 |
| | | | | (7.10-7.92) Silt as above, light brown. | 22 | CS | | 7.10 | 0.45 | | | | | | | |
| | | | | | 23 | CS | | 7.55 | 0.37 | | | | | | | |
| 8 | | | | (7.92-8.30) Silt as above, trace gravel. | 24 | CS | | 7.92 | 0.38 | | | | | | | 8 |
| | | | | (8.30-8.75) Silt, medium brown, with sand, damp. | 25 | CS | | 8.30 | 0.15 | | | | | | | |
| 9 | | | SP | (8.75-9.15) Sand, brown, some silt, some gravel, damp. | 26 | CS | | 8.75 | 0.40 | | | | | | | 9 |

(9.15) End of Hole.

No bedrock encountered.
No water level recorded.

| WATER TABLE | NORTH: | EQUIPMENT: Canterra | COMPLETION: 96/09/22 |
|---|---|---|---|
| No water level recorded. | EAST: | METHOD: Hollow Stem Auger | INSPECTOR: F. Demchenko |
| | TREND: —— | DRILLER: Paddock Drilling Ltd | DEPTH: 9.15 (m) |
| | PLUNGE: -90.0 (deg) | STATUS: PRELIM: SLM 96/10/04 O/BFIELD Printed: 97/04/24 10:43 CB96A GEOTE | |
| | ELEV G/S: (m) | Overlays: SPT UNC1 ATT10 VAN10 LINE USCS TITLE | |

# MANITOBA HYDRO
Engineering
**FIELD OVERBURDEN LOG**
GEOTECHNICAL

## CRANBERRY PORTAGE
DECOMMISSIONED DIESEL GENERATING STATION

**CB-016**
1 OF 1
Prj.# 46466-1580

**Sampler Types:** Split Spoon, Shelby, Auger, Sonic, Auger Barrel, Core Barrel, Special Samplers, Tricone, Bulk Sample, Grab Sample, Air Hammer

| DEPTH (m) | RUN DEPTH | SAMPLER | USCS | FIELD DESCRIPTION | SAMPLE # | TYPE | SIZE | DEPTH | RECOVERED LENGTH | FIELD POCKET PENETROMETER | FIELD HAND VANE SHEAR | BLOW COUNT | SPT COUNTS | PERMEABILITY (cm/sec) | TEST INTERVAL | DEPTH |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0.00 | | FILL | (0.00-0.20) Gravel; "fill". | | | | | | | | | | | | |
| | | | SM | (0.20-0.75) Sand, light brown, fine grained, with silt. | 1 | CS/CG | | 0.20 | 0.55 | | | | | | | |
| 1 | | | SP | (0.75-2.62) Sand, light brown, fine grained, trace silt, damp. | 2 | CS/CG | | 0.75 | 0.75 | | | | | | | 1 |
| | | | | | 3 | CS/CG | | 1.50 | 0.37 | | | | | | | |
| 2 | | | | | 4 | CS/CG | | 1.87 | 0.38 | | | | | | | 2 |
| | | | | | 5 | CS/CG | | 2.25 | 0.37 | | | | | | | |
| | | | | (2.62-3.80) Sand, light brown, very fine grained, damp. | 6 | CS/CG | | 2.62 | 0.43 | | | | | | | |
| 3 | | | | | 7 | CS/CG | | 3.05 | 0.37 | | | | | | | 3 |
| | | | | | 8 | CS | | 3.42 | 0.38 | | | | | | | |
| 4 | | | ML | (3.80-4.17) Silt, light grey brown, with sand, damp. | 9 | CS | | 3.80 | 0.37 | | | | | | | 4 |
| | | | SP | (4.17-4.85) Sand, brown, very fine grained, trace silt, damp. | 10 | CS | | 4.17 | 0.38 | | | | | | | |
| | | | | | 11 | CS | | 4.55 | 0.30 | | | | | | | |
| 5 | | | ML | (4.85-4.90) Silt, light grey brown, some sand, damp. | 12 | CS | | 4.90 | 0.40 | | | | | | | 5 |
| | | | SP | (4.90-5.30) Sand, brown, very fine grained, trace silt, damp. | 13 | CS | | 5.30 | 0.37 | | | | | | | |
| | | | ML | (5.30-6.10) Silt, light grey brown, some sand, damp. | | | | | | | | | | | | |
| 6 | | | | | | | | | | | | | | | | 6 |
| | | | | (6.10-6.60) Silt, light brown, some sand, dry. | 14 | CS | | 6.10 | 0.50 | | | | | | | |
| | | | | (6.60-6.80) Silt, light grey brown, trace sand, damp. | 15 | CS | | 6.60 | 0.25 | | | | | | | |
| 7 | | | | (6.80-7.97) Silt, light brown, trace sand, damp. | 16 | CS | | 6.85 | 0.37 | | | | | | | 7 |
| | | | | | 17 | CS | | 7.22 | 0.38 | | | | | | | |
| | | | | | 18 | CS | | 7.60 | 0.37 | | | | | | | |
| 8 | | | | (7.97-8.30) Silt, light brown, some fine grained sand, dry. | 19 | CS | | 7.97 | 0.33 | | | | | | | 8 |
| | | | | (8.30-8.50) Silt as above, damp. | 20 | CS | | 8.30 | 0.20 | | | | | | | |
| | | | | (8.50-8.85) Silt as above, trace gravel. | 21 | CS | | 8.50 | 0.35 | | | | | | | |

(8.85) End of Hole due to auger refusal on cobbles.

PRELIMINARY

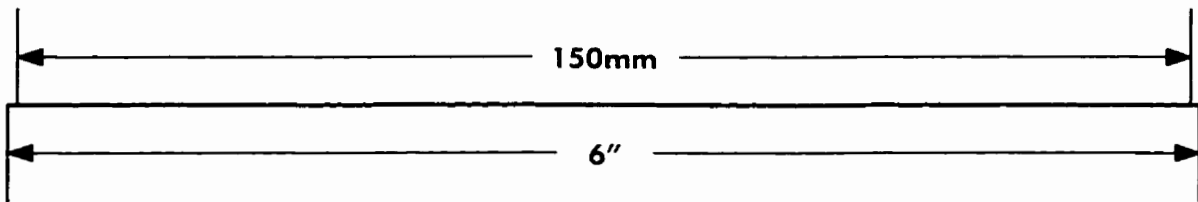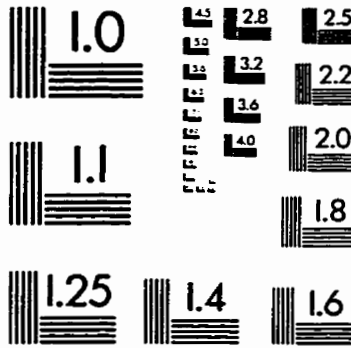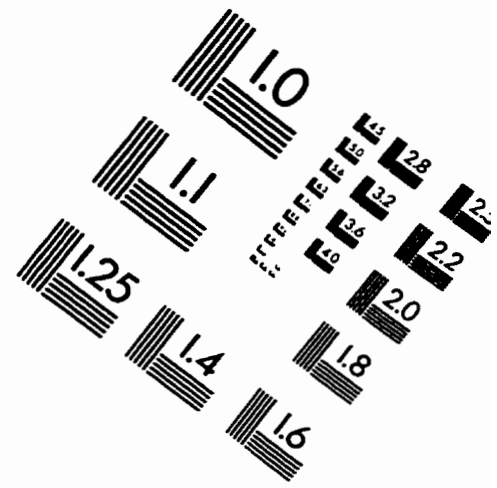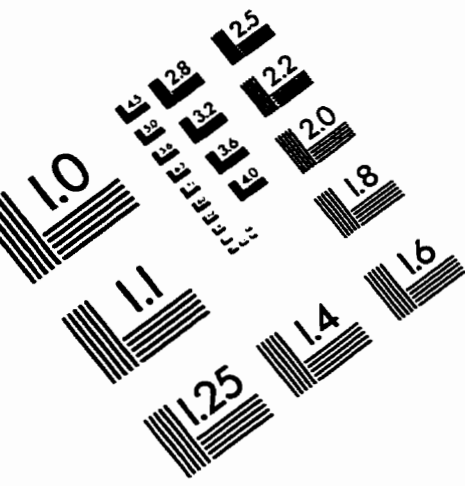| WATER TABLE | | | |
|---|---|---|---|
| No water level recorded. | NORTH:<br>EAST:<br>TREND: ——<br>PLUNGE: -90.0 (deg)<br>ELEV G/S: (m) | EQUIPMENT: Canterra<br>METHOD: Hollow Stem Auger<br>DRILLER: Paddock Drilling Ltd | COMPLETION: 96/09/22<br>INSPECTOR: F. Demchenko<br>DEPTH: 8.85 (m) |

STATUS: PRELIM: SLM 96/10/07 O/SFIELD  Printed: 97/04/24 10:44 CB86A GEOTE
Overlays: SPT UNC1 ATT10 VAN10 LINE USCS TITLE

# IMAGE EVALUATION
## TEST TARGET (QA—3)

1.0   1.1   1.25   1.4   1.6

1.0   1.1   1.25

4.5  2.8  2.5
3.0
3.2  2.2
3.6
1.0  2.0
1.8

150mm

6"
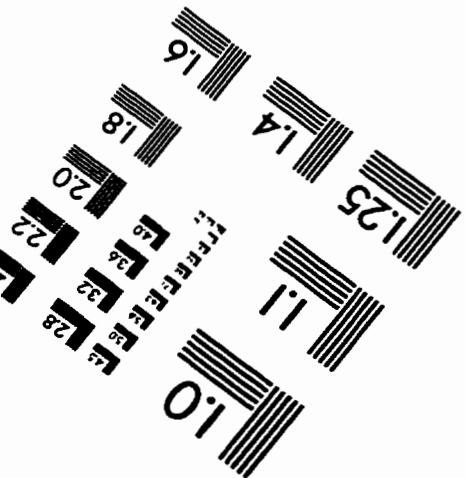
APPLIED IMAGE . Inc

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