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ON THE PERMEABILITY OF FROZEN SILT TO ORGANIC CONTAMINANTS

by

Kim Lianne Winnicky, B.Sc

**A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirement for the degree of
Master of Arts**

Department of Geography

**Carleton University
Ottawa, Ontario**

June 1995

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ON THE PERMEABILITY OF FROZEN SILT TO ORGANIC CONTAMINANTS

submitted by Kim L. Winnicky, B.Sc.
in partial fulfillment of the requirements for
the degree of Master of Arts

Thesis Supervisor

Chair, Department of Geography

Carleton University
June 13, 1995

ABSTRACT

In polar regions, permafrost has frequently been relied upon to contain a variety of wastes, as frozen soil is considered to be impermeable to contaminants. The assumption that frozen ground is impermeable to liquid contaminants is examined. The influence of soil moisture, soil temperature and contaminant miscibility on the infiltration of four organic contaminants into frozen soil was tested in macroscale and benchscale studies. The results of these experiments indicate that permafrost cannot be considered impermeable, as contaminants penetrate frozen soil under certain conditions.

The permeability of frozen silt to contaminants was dependent upon fluid and soil properties, particularly contaminant miscibility and soil saturation. Both miscible and immiscible fluids migrated through non-saturated silt at temperatures ranging from 4°C to -10°C. Saturated soils were impermeable to immiscible hydrocarbons at all temperatures studied, but were contaminated by water-soluble fluids.

Changes to soil structure associated with warming appeared to alter soil permeability. Observations during the macroscale study indicated that lubricating oil and arctic diesel fuel were contained by the frozen silt until soil temperatures approached -0.1°C. Once contaminated, hydrocarbon migration continued even when soil temperatures fell to approximately -0.4°C.

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Chapter One

INTRODUCTION

1.1 General

In discussions of waste disposal, frozen soil has been considered to be impermeable to contaminants (Kellems et al. 1991). Permafrost is often relied on in northern regions as a means of containment (Maunder et al. 1991), as no lining of waste disposal sites in regions of permafrost is required by law (E. Collins, pers. comm., 1995). Permafrost, however, has a measurable hydraulic conductivity at temperatures several degrees below 0°C, and unfrozen water present in frozen soil migrates along thermal, osmotic and pressure gradients (Burt and Williams 1976; Horiguchi and Miller 1983; Smith 1985). Solutes present within soil water are subjected to similar forces, and are transported through and with the water in continuous films (Murrmann 1973). As the redistribution of water and solutes through frozen soil has been documented by numerous researchers, the assumption that permafrost is impermeable must be qualified. Currently, no data exist on which to base such qualifications, as to date no experiments have tested this assumption. This thesis is an initial investigation into the permeability of frozen soil to a number of organic contaminants.

1.2 Organic Contaminants in Arctic Regions

Resource development and the operation of northern defence stations has introduced a variety of contaminants into the North. The operation of heavy machinery during the construction of drilling rigs, storage facilities, pipelines and the associated transportation and housing network in polar regions has required a wide range of compounds, including petroleum fuels, ethylene glycol (antifreeze) and polychlorinated biphenyls (PCBs). Many of these compounds have freezing points below that of water, with some, such as arctic diesel fuel (DF-A), remaining liquid at temperatures as low as -60°C (Diemand 1990).

Contamination, defined as the reduction in usability or prevention of use as a consequence of the addition of a substance (Bates and Jackson 1980), may result from the improper disposal or accidental spillage of wastes in polar regions. Petroleum hydrocarbon mixtures including crude oil, diesel, furnace oil, jet fuels and gasoline are the most common northern contaminants. Diesel fuel accounts for approximately 50% of spills in the Northwest Territories, and, together with gasoline and lubricating oil, comprises 80% of Territorial spills (K. Hall, pers. comm., 1994). Such spills are primarily associated with the use and distribution of petroleum fuels for heat and power generation. DF-A is also by far the most common fluid spilled at Department of National Defence sites (H. Poll, pers. comm., 1994). Large-scale crude oil spills, while infrequent, have occurred in the Arctic, including the recent pipeline spill in northern Russia.

The long-term operation of remote defense sites has resulted in the accumulation of substantial quantities of liquid waste. In a 1985 clean-up of 22 DEW line sites,

approximately 7,200 l of liquid PCBs and several hundred kilograms of contaminated soil and equipment were removed from the stations. Time restrictions limited cleanup to the removal of easily located PCBs and the burning of petroleum products. On average, 300 l of PCBs and 1000 kg of electrical equipment were removed from each of the sites. In total, approximately 225,000 l of lubricating oil, 8000 l of diesel fuel and 500 l of engine oil were burned at 13 stations (Ponton 1986)

Much of the waste generated at remote drilling sites and defense stations has been disposed of on-site as their location makes the costs of waste removal prohibitive. This is exemplified by the cost of the 4-week partial DEW line cleanup described above which has been estimated at between \$500,000 and \$2,000,000 (Ponton 1986). Waste disposal generally involves the stacking of fuel drums on the ground surface, and the disposal of waste in pits excavated into permafrost (Reimer et al. 1993, Kellems et al. 1991). This disposal method, referred to as below-grade freezeback, relies upon frozen soil to contain introduced substances and is currently employed by municipalities, industry and government in the arctic (Maunder et al. 1991; E. Collins pers. comm., 1995).

1.3 Permafrost

Permafrost is defined as ground (i.e. soil or rock) which remains at a temperature below 0°C for at least two years (Harris et al. 1988). Adsorptive, osmotic and capillary forces within frozen soil cause a portion of the soil moisture to remain unfrozen, with the proportion of water remaining unfrozen being dependent upon several variables including soil texture, soil temperature and the presence of solutes. This unfrozen moisture is

present i.e. continuous films around soil particles and in fine pores, and is subjected to thermal, osmotic, and pressure forces which can induce water migration (Miller 1970)

Although the coexistence of ice and liquid water in soils at temperatures below 0°C was described in the early 1950s (Institut Merzlotovedenia 1953), few studies have addressed the effects of unfrozen water in permafrost on contaminant containment (Mohamed et al. 1995) The vast majority of research addressing northern contaminants has focused on arctic marine spills and the transport of air-borne pollutants Several field studies have investigated the impacts of surficial petroleum spills on the biotic environment and on the flow of oil through the active layer, however reports of the rate and extent of contaminant spreading are generally descriptive and limited to short-term migration through the active layer (Freedman and Hutchinson 1975, Everett 1978, Collins 1983, Kershaw 1990) Laboratory experiments addressing contaminant behaviour in frozen soils are even more sparse, although two recent laboratory studies have investigated the behaviour of contaminants in freezing soils (Tumeo and Davidson 1993, Mohamed et al. 1995)

While the lack of basic research limits discussions of contaminant behaviour in frozen soil to theoretical considerations, several potential pathways for fluid transport through permafrost can be identified The unfrozen moisture films may act as conduits for the transport of water-soluble contaminants and the soluble fractions of immiscible fluids, as these compounds may dissolve into such water in the same manner as naturally occurring soil solutes Water-miscible substances may also interact with the ice phase, melting soil ice and creating an aqueous phase which is mobile

Permafrost is not a homogenous medium as it can be composed of soils of varying textures and moisture contents. The air-filled pores of non-saturated frozen soil may permit the transport of both water-miscible and immiscible liquids. Fissures and cracks present in permafrost may act as conduits to fluids, especially those with low freezing points and low viscosities at sub-zero temperatures. At a theoretical level, the potential for the transport of miscible and immiscible fluids through frozen ground exists, and research is therefore required to assess whether permafrost is, in fact, impermeable to contaminants.

1.4 Objectives

The objectives of this thesis are:

- 1) To determine if frozen silt is permeable to organic contaminants, and
- 2) To assess the influence of soil moisture, soil temperature and contaminant miscibility on the permeability of frozen soil to contaminants

1.5 Experimental Methods

The permeability of frozen silt to organic contaminants was investigated in macroscale studies conducted at the Centre de Geomorphologie, Université de Caen, France and in benchscale studies at Carleton University. Macroscale studies investigated the permeability of simulated permafrost to two common northern contaminants, lubricating oil and arctic diesel fuel. This phase of the project was restricted to immiscible contaminants due to concerns that water-miscible compounds would melt soil ice and contaminate groundwater. The selected contaminants were introduced to wells bored into

frozen silt in a controlled environment facility. Fluid levels in the wells and soil temperatures were recorded until the conclusion of the study period, when soil cores were taken, subsampled and analyzed by gas chromatography to determine levels of contamination in the soil adjacent to and underlying the contaminant source

Results from the experiments conducted in France prompted further research into the influence of soil temperature and moisture content on the permeability of frozen soil. The ubiquitous presence of water in soils dictates that the water miscibility of contaminants is a principal factor in controlling the extent and pattern of migration (Yong et al. 1992), and so the effect of contaminant miscibility on fluid behaviour was investigated in the benchscale trials. Ethylene glycol, a water-miscible fluid commonly used as antifreeze in northern regions, and kerosene, an immiscible petroleum hydrocarbon with similar chemical and physical properties to jet fuels and DF-A, were introduced to the surface of saturated and non-saturated silt columns at temperatures ranging from 4°C to -10°C. Following contamination, soil columns remained frozen for two weeks and were then sectioned, subsampled and analyzed by gas chromatography to determine contaminant distribution through the columns

1.6 Thesis Overview

To predict and analyze the fate of contaminants in arctic regions, an understanding of the hydraulic properties of frozen soil is required. Chapter two reviews these principles and discusses potential pathways and mechanisms of contaminant transport through frozen soil. Chapter three presents a description of the methods employed in the macroscale

studies and an analysis of the resulting data. The methods and results of the benchscale trials are described in chapter four. The final chapter summarizes the major finding of both the macroscale and benchscale studies, and concludes with a discussion of the practical implications of the project results and recommendations for further research.

Chapter Two

PERMAFROST AND TRANSPORT PROCESSES

2.1 Introduction

In discussions of contaminant containment and waste disposal, permafrost is often considered to be a barrier to fluid migration (Kellems et al 1991; Maunder et al 1991). Frozen soil, however, can be permeable to water and dissolved ions at temperatures several degrees below 0°C (Burt and Williams 1976, Horiguchi and Miller 1983, Smith 1985). An understanding of the unfrozen water present in frozen soil and the gradients controlling the migration of such water is required for predicting and analyzing the fate of contaminants in arctic regions. The first section of this chapter will review these principles. As any significant contaminant migration is likely confined to the fluid phases, the basic mechanisms of fluid transport will then be presented. These fundamental concepts will be used to define potential pathways for contaminant migration through frozen soil.

2.2 Permafrost

Permafrost, is defined as ground (soil or rock) which remains at or below 0°C for at least two years (Harris et al. 1988). At temperatures near to, but below 0°C, unfrozen water present in continuous films around soil particles migrates along thermal, osmotic

and pressure gradients through the ice, vapour and liquid water phases present in frozen soil. Soluble substances can be carried with and through the unfrozen films.

2.2.1 Unfrozen Water Content

The coexistence of ice and water in soils below 0°C was first documented in the 1950s, and has been the subject of much study since the late 1960s (Williams 1967; Williams and Smith 1989). The depressed freezing point of this water is generally attributed to adsorptive forces associated with the mineral surface, the presence of solutes in the soil solution and capillary effects produced by the confining nature of the soil pores.

Unfrozen water is found in capillary pores and in adsorbed films surrounding soil particles (Figure 2.1). Capillary effects are the dominant factor in depressing the freezing point within a few tenths of a degree below 0°C, while at colder temperatures adsorption is the principal control (Wood 1986). Under such cool conditions, only water within 10^{-9} m to 10^{-8} m of the mineral surface remains unfrozen, as water molecules within this layer are strongly bound to the mineral surface, and therefore not as free to reorient to form the crystal lattice structure characteristic of ice.

The presence of unfrozen water in soils at sub-zero temperatures has also been attributed to the supercooling of soil water. Supercooled water exists as a liquid at temperatures below 0°C where nucleation has not occurred and freezing has not

Figure 2.1

CONFIGURATION OF PORE ICE AND UNFROZEN WATER IN A FROZEN
NON-COLLOIDAL SOIL

Adapted from Miller et al. 1975.

commenced. While such systems are unstable (Williams and Smith 1989), it is possible that macropores isolated from adjacent ice crystals by micropores with radii too small to permit ice entry may remain unfrozen at temperatures below 0°C. When temperatures fall such that ice pressures are high enough to permit penetration through the surrounding micropores, water within the macropore will freeze as ice crystals are introduced.

Anderson and Morgenstern (1973) state that while supercooling is rarely observed in the field, it is a common phenomenon in laboratory studies.

The unfrozen moisture content of frozen soil decreases as temperatures fall below 0°C. At any temperature below 0°C, a difference in pressure exists between ice and water across the curved solid-liquid interface. This pressure difference increases as temperatures fall below 0°C, and can be expressed in one form of the Clausius-Clapeyron equation (Williams 1982):

$$T - T_o = \frac{(P_w V_w - P_i V_i) T}{L} \quad (1)$$

where T equals absolute temperature (K), T_o is the normal freezing point of water (273.15 K), P refers to the pressure (Pa), V equals the specific volume ($\text{m}^3 \text{kg}^{-1}$), and L is the latent heat of fusion (J kg^{-1}). The pressure difference is also defined by the Kelvin equation as a function of the surface tension and the radius of the interface at the point of ice entry (Burt 1974)

$$P_i - P_w = \frac{2S_{iw}}{r} \quad (2)$$

where P_i = ice pressure (Pa)

P_w = water pressure (Pa)

S_{iw} = surface tension at ice-water interface (Pa)

r = radius of interface (cm)

Equations 1 and 2 dictate that as soil temperature decreases ice penetrates into progressively smaller pores and liquid water is confined to thinner films and there is a corresponding decrease in the volume of unfrozen moisture (Burt 1974)

The relation between unfrozen water content and temperature has been demonstrated using a variety of methods, including time domain reflectometry and nuclear magnetic resonance (Smith and Tice 1988). The specific surface area of a given soil determines the proportion of unfrozen moisture present at any given temperature (Anderson and Tice 1973). As such, fine-grained soils with high specific surface areas will have far greater unfrozen moisture contents than coarse-grained soils although some unfrozen water will be present in all soils as adsorption occurs on particles of all sizes (Figure 2.2) The chemical composition of clay particles also contributes to the relatively high liquid water contents associated with clay soils (Horiguchi and Miller 1983)

Figure 2.2

INFLUENCE OF SOIL TEXTURE ON UNFROZEN MOISTURE CONTENT

From: Burt and Williams (1976; Figure 2).

2.2.2 Hydraulic Conductivity

Thermal, osmotic and pressure gradients within frozen soil induce water migration through the ice, water and vapour phases. Water transport through each of these phases results in frozen soils having a measurable hydraulic conductivity at temperatures several degrees below 0°C (Burt and Williams 1976; Horiguchi and Miller 1983; Smith 1985).

Burt and Williams (1976) demonstrated that flow through frozen soil conforms to Darcy's law

$$q = \frac{kA \Delta \psi}{\Delta Z} \quad (3)$$

where

q = flow ($\text{m}^3 \text{s}^{-1}$)

k = hydraulic conductivity (m s^{-1})

A = cross-sectional area of flow path (m^2)

$\frac{\Delta \psi}{\Delta Z}$ = gradient of potential (m m^{-1})

Hydraulic conductivity is dependent on soil temperature, but this relation is non-linear as there is a sharp decrease in conductivity within a few tenths of a degree below 0°C (Figure 2.3). This rapid decline corresponds to the sharp decrease in the thickness of unfrozen water films in this temperature range (Horiguchi and Miller 1983)

Figure 2.3

INFLUENCE OF SOIL TEXTURE ON HYDRAULIC CONDUCTIVITY

From: Burt and Williams (1976; Figure 3)

Soil texture also influences rates of water migration through its control over unfrozen moisture content (Williams and Smith 1989). Much of the water present in sandy soils freezes very close to 0°C as these soils have large capillaries and small specific surface areas. As such, very little water is free to migrate at temperatures below 0°C. Although the high specific surface areas of clay translate to high unfrozen moisture contents, the hydraulic conductivity of such fine soil is limited by the tortuous nature of the films.

Oliphant (1983) reports that the conductivity of silt ranges from $4 \times 10^{-13} \text{ m s}^{-1}$ at -2°C to $5 \times 10^{-12} \text{ m s}^{-1}$ at -0.3°C, while Loch and Kay (1978) report a hydraulic conductivity of approximately $10^{-12} \text{ m s}^{-1}$ for the frozen fringe of a heaving silt. The permeability of unfrozen silt is in the order of 10^{-9} to 10^{-8} ms^{-1} (Dallimore 1985).

Under isothermal conditions, osmotic gradients are a dominant factor controlling fluid migration rates. Such chemical flow is defined by Fick's Second Law (Mitchell 1976).

$$J_D = -D \frac{dc}{dx} A \quad (4)$$

where J_D = osmotic flow (moles s^{-1})

D = diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$)

c = concentration (moles cm^{-3})

x = depth (cm)

A = cross-sectional area (cm^2)

Osmotic gradients are present in frozen soil due to the selective exclusion of solutes from the soil water upon freezing, and localized accumulation of transported ions (Kay and Groenevelt 1983).

2.2.3 Regelation

While the majority of water movement takes place in the unfrozen interfacial films (Perfect and Williams 1980), pore ice may move through the soil in addition to liquid water (Miller et al. 1975). Such movement, referred to as regelation, involves pressure-induced freezing of water molecules at the warm side of an ice lens, and melting at the cold side (Williams and Smith 1989) with a subsequent slow displacement of the ice body towards the warmer face (Miller 1970). At -0.15°C , the permeability of ice lenses has been reported to be in the order of 10^{-10} ms^{-1} (Horiguchi and Miller 1980).

At temperatures near 0°C pore ice itself may be permeable on account of liquid-filled crystal boundaries in its structure, which act as microscopic channels for water flow (Osterkamp 1975). Such transport is associated only with very warm ice, and has been demonstrated to be negligible compared to regelation (Horiguchi and Miller 1980).

2.2.3 Vapour Transport

In non-saturated frozen soils, moisture can also be transported as vapour through air-filled pores though rates of diffusion may be several orders of magnitude less than

those for liquid flow (Smith and Burn 1987). Using vapour traps, several studies have monitored vapour flow out of the ground during winter months (Santeford 1978; Woo 1982; Smith and Burn 1987). Water vapour diffuses through frozen soil towards the surface where temperatures are lower in response to pressure gradients (Woo 1982)

The rate of soil vapour flux can be expressed as (Giddings and LaChapelle 1962).

$$Q = - \frac{D}{RT} \frac{de}{dZ} \quad (5)$$

where Q is the mass flux per unit area ($\text{kg m}^{-2} \text{s}^{-1}$), D is the diffusion coefficient for water vapour ($\text{m}^2 \text{s}^{-1}$), R is the gas constant for water vapour ($\text{J kg}^{-1} \text{K}^{-1}$), T is the temperature (K), e is the vapour pressure (J m^{-3}) and Z is the depth (m). In frozen soils, the vapour pressure of bulk ice is used, as liquid water is in equilibrium with the soil ice (Williams and Smith 1989)

Rates of vapour diffusion out of the ground have been consistently calculated to be in the order of $1 \text{ cm}^2 \text{s}^{-1}$. These values are much higher than those reported for vapour diffusion through unfrozen soils, and approximately five times as great as the diffusion coefficient for water vapour in air at 0°C (Smith and Burn 1987)

Rates of vapour outflow from frozen soil are greater than can be accounted for by vapour diffusion alone. It has been proposed that these high diffusion rates reflect the migration of liquid water to the soil surface through adsorbed water films (Smith and Burn 1987). The concurrent diffusion of water through the liquid and vapour phases has been observed in dry, unfrozen soils (Jackson 1965) as well as in frozen soils (Nakano et al.

1984). Laboratory experiments estimate vapour diffusion rates to be in the order of 10^{-6} $\text{cm}^2 \text{ s}^{-1}$ through soils at -1°C (Nakano et al. 1982).

2.2.4 Solute Exclusion and Transport

Water-soluble organic and inorganic compounds present in the soil system are transported with unfrozen moisture through the adsorbed films. Solutes present in the soil solution affect rates of freezing, and are redistributed upon freezing as water molecules reorient to form ice (Miller 1980).

The selective rejection of solutes during freezing is a property of most solutions, and has been well documented for NaCl and CaCO_3 and KOH solutions (Hallett 1978). The degree of solute exclusion is directly proportional to the temperature gradient, and inversely proportional to solute concentration (Qui et al. 1988), with the ratio between initial and excluded solute concentration ranging from 10^{-3} to almost unity (Hallett 1978).

The freezing of soil water is generally accompanied by some degree of solute exclusion. This is observed as an increase in the solute concentration of the adsorbed films (Miller 1980), and in the zone immediately ahead of an advancing freezing front or a region of ice lens development (Kay and Groenevelt 1983). Such localised accumulations create concentration gradients within the soil system which can induce osmotic diffusion (Ostroumov 1988).

The migration of solutes through frozen soil is controlled by thermal and concentration gradients (Cary and Mayland 1972; Cary et al. 1979; Ostroumov 1988; Qui et al. 1988). According to the Einstein-Brown Movement Equation, the square of the mean displacement of microparticles in a certain period of time is directly proportional to the absolute temperature (Qui et al. 1988). Ionic movement from warmer to colder regions under these forces will be greater than migration in the other direction, and concentrations will increase in the cooler regions. Solutes can also be transported with the aqueous phase as water migrates along thermal gradients. The exclusion of solutes upon freezing and the migration of solutes along these thermal gradients results in an increased solute concentration in the vicinity of the freezing front, and in regions of ice lens development (Osterkamp et al. 1970).

The redistribution of solutes has been studied in numerous experiments. Solute-spiked soil columns are partially frozen from one side, then sampled to determine the relative solute concentrations in the frozen and unfrozen zones. Several studies have observed that ions are more concentrated in the unfrozen zone (Osterkamp et al. 1970; Hallet 1978), while others have found higher concentrations in frozen regions (Kay and Groenvelt 1983; Taylor et al. 1990). These discrepancies are due to the relative strengths of osmotic diffusion (i.e. cold to warm) and thermal diffusion (i.e. warm to cold), and to the differences in soils used in each of the studies. High solute concentrations in the frozen region have been attributed to the redistribution of solutes resulting from convective transport, and inefficient solute exclusion in coarse grained soils (Kay and Groenvelt 1983). The higher hydraulic conductivities of fine soils relative to coarse soils at

temperatures below 0°C lead to solutes accumulating in the frozen zone as water migrates and ice lenses are formed. Generally, the higher freezing rates and low specific surface area of coarse soils contribute to inefficient solute exclusion upon freezing (Kay and Groenevelt 1983).

Within frozen soil, the rate of ion diffusion is dependent upon soil texture and temperature. Rates of diffusion through frozen clay and silt are both characterized by rapid decreases in ionic migration between 0°C and -3°C, and a much slower decrease to -15°C (Figure 2.4). Solute movement through clay at temperatures below -2°C occurs at higher rates than through silts at the same temperature. This is attributed to the relative amounts of unfrozen water present in these soils at temperatures below 0°C (Murrmann 1973).

Water-miscible liquids, or the soluble portion of immiscible fluids, introduced to frozen soil are likely subjected to forces similar to those outlined above. Tumeo and Davidson (1993) found that phenol, a water-miscible organic compound, was excluded by soil freezing and forced ahead of the advancing freezing front. A similar study investigating the effects of freezing on silts spiked with four organic compounds found no evidence of such exclusion (Taylor et al. 1990). Following partial freezing of the soil columns, organic compound concentrations were 30% - 50% higher in frozen zones than in the overlying unfrozen soils.

Figure 2.4

SODIUM ION DIFFUSION COEFFICIENT FOR FROZEN WYOMING BENTONITE,
FAIRBANKS SILT AND BARROW SILT AS INFLUENCED BY TEMPERATURE

From Muirmann (1973, Figure 1)

2.2.5 Field Hydraulic Conductivity

Laboratory experiments have determined that the hydraulic conductivity of frozen soil ranges from 10^{-8} m s^{-1} to $10^{-13} \text{ m s}^{-1}$ (Loch and Kay 1978; Perfect and Williams 1980; Horiguchi and Miller 1983; Kay and Groenvelt 1983; Oliphant et al 1983). Field observations of water migration generally suggest much more rapid rates of infiltration (Williams and Smith 1989). Discrepancies between predictions of fluid migration based on laboratory studies and rates observed in the field are partly due to the complexity and heterogeneity of natural soil systems.

While most laboratory work has addressed the permeability of saturated or supersaturated homogenous frozen soils (Cary and Mayland 1972; Burt and Williams 1976), soils in the field can be highly variable as they consist of a variety of textures with a variety of moisture contents. Cracks, fissures, relict ice wedges and root channels present in natural settings are fluid conduits which are generally not replicated in laboratory studies (Woo 1990; Calabrese and Kostecki 1992).

The hydraulic properties of soils also change over time. Variations in soil structure associated with wetting and drying, and/or freezing and thawing can greatly affect soil hydraulic conductivity (Yong 1992). Temperature-induced changes in the partitioning of water between the solid and liquid phases alter rates of water flow, and the thawing of ice lenses in ice-rich soils leads to increases in hydraulic conductivity (Dyke and Eggington 1990). Spaces initially filled with ice become saturated with water, increasing the bulk hydraulic conductivity by as much as three orders of magnitude over that of soil which was never subjected to freezing (Dyke and Eggington 1990).

2.3 Mechanisms of Fluid Transport

As outlined in Section 2.2 , frozen soils are permeable to both water and water-soluble ions. The potential therefore exists for contaminants to infiltrate and migrate through permafrost. Such migration would be controlled by the same factors influencing spill behaviour in non-frozen ground, mitigated by the presence of pore ice and ice lenses.

Contaminant migration through soil is generally limited to the fluid phases (Yong et al. 1992). Within the soil matrix, a fluid contaminant may exist as an aqueous solution, an immiscible contaminant phase, and/or as a vapour (Lyman et al. 1992). A single contaminant can be present in all three phases simultaneously, and partitioning between each phase can be highly dynamic, changing over time and space (Yong et al. 1992). Partitioning varies according to soil and contaminant properties, and with environmental conditions (Knox et al. 1993).

Transport through each of these fluid phases is the sum of advective flow and dispersion (Yong et al. 1992). Advection, as defined by Darcy's law, refers to flow induced by pressure gradients. The rate of advective flow is dependent on both soil and fluid properties. Soil texture controls flow as it determines pore size and the distribution of pores through the soil (Mitchell 1976). Clay loams, for example, are relatively resistant to flow because of their small diameter pores and highly tortuous flow paths. Such resistance can lead to greater vertical spreading, and slower rates of fluid penetration. The importance of texture to the fluid conductivity of frozen soils was reviewed in Section 2.2.2.

Advective flow is also dependent upon soil structure. Natural soils commonly contain macropores which are formed by a variety of processes including animal activity, root penetration, and the development of cracks and fissures (Brady 1990). Such macropores permit rapid fluid transmission, and thus conduct large volumes of fluid through the soil even if they comprise only a small fraction of the total soil volume (Lyman et al. 1992). Changes to soil structure with wetting and drying or freezing and thawing can result in significant changes to the permeability of a soil (Yong et al. 1992).

Advective flow rates are also dependent upon contaminant properties. Viscosity and density are of prime importance when considering liquid flow. Viscosity refers to a liquid's internal resistance to flow (Breck et al. 1981). Contaminants with high viscosities have slower flow rates, and do not penetrate into or move through porous media as readily as those with lower viscosities (Yong et al. 1992). Liquid densities also control flow rates and influence the direction of liquid flow, as contaminants with high densities have a greater vertical component to their flow paths than those which are less dense. High density liquids with low viscosities are the most mobile fluids in the subsurface (Mansour 1993).

The low temperatures associated with permafrost terrain affect contaminant flow rates as viscosity is temperature dependent. With decreasing temperatures, viscosities generally increase, and cause slower rates of flow through the soil matrix. Although fluid density is also dependent on temperature, the relation is generally not nearly as strong.

While advection refers to flow induced by pressure gradients, dispersion is defined as the process by which a substance spreads and dilutes in groundwater or soil gas (Lyman et al. 1992). At field scale, dispersion is caused by soil heterogeneity and anisotropy. On a microscopic scale, dispersion is due to the tortuosity of flow paths, variation in flow rates across individual pores and molecular diffusion (Figure 2.5). Molecular diffusion, as defined by Fick's Second Law, describes molecular migration along osmotic gradients. In unfrozen soils, diffusion is generally considered to be insignificant relative to mechanical dispersion and advective flow (Knox et al. 1993), however it can be the dominant transport mechanism in soils with low permeability, such as permafrost. Molecular diffusion across interfacial boundaries also acts as a means of partitioning contaminants between phases (Lyman et al. 1992).

2. 4 Contaminant Flow in Permafrost

Predicting the behaviour of terrestrial contaminants is highly complex as contaminants can be present in up to 13 interdependent loci within the soil environment (Figure 2.6). The fluid phases are the dominant transport loci, where dispersion and advection lead to contaminant redistribution through the soil (Yong et al. 1992). In permafrost terrain these processes are mitigated by the presence of ice and by low soil temperatures. This section will present possible mechanisms of contaminant transport through frozen ground for each of the fluid phases

Figure 2.5

PROCESSES OF DISPERSION ON A MICROSCOPIC SCALE

From: Freeze and Cherry (1979; Figure 2.30).

Figure 2.6

SCHEMATIC REPRESENTATION OF THE 13 LOCI IN SOIL

From Lyman et al (1992, Figure 1)

Table 2.1

BRIEF DESCRIPTIONS OF THE 13 PHYSICOCHEMICAL-PHASE LOCI

Locus Number	Description
1	Contaminant vapors as a component of soil gas in the unsaturated zone.
2	Liquid contaminants adhering to "water-dry" soil particles in the unsaturated zone.
3	Contaminants dissolved in the water film surrounding soil particles in the unsaturated zone.
4	Contaminants sorbed to "water-wet" soil particles or rock surface (after migrating through the water) in either the unsaturated or saturated zone.
5	Liquid contaminants in the pore spaces between soil particles in the saturated zone.
6	Liquid contaminants in the pore spaces between soil particles in the unsaturated zone.
7	Liquid contaminants floating on the groundwater table.
8	Contaminants dissolved in groundwater (i.e., water in the saturated zone).
9	Contaminants sorbed onto colloidal particles in water in either the unsaturated or saturated zone.
10	Contaminants that have diffused into mineral grains or rocks in either the unsaturated or saturated zone.
11	Contaminants sorbed onto or into soil microbiota in either the unsaturated or saturated zone.
12	Contaminants dissolved in the mobile pore water of the unsaturated zone.
13	Liquid contaminants in rock fractures in either the unsaturated or saturated zone.

From: Lyman et al. (1992; Table 1).

2.4.1 Aqueous Phase

In soils with temperatures above 0°C, contaminants which are soluble in water, and the water-soluble fractions of immiscible compounds, mix with soil water and become a single aqueous phase (Yong et al. 1992). As pore water moves under the force of gravity or under capillary tension, dissolved contaminants are redistributed through the soil (Calabrese and Kostecki 1993). In frozen soils, water-miscible compounds may dissolve into the unfrozen water and be transported along thermal, pressure and osmotic gradients in the same manner as dissolved ions (Section 2.2.4).

According to Raoult's Law, the addition of any soluble substance to a liquid decreases the freezing point of that liquid (Breck et al. 1981). The magnitude of freezing point depression depends upon the volume of solute added, and on the chemical nature of the solvent. The addition of substances such as ethylene glycol to frozen soil may initiate the melting of ice present in such soil, and produce a single aqueous phase (i.e. ethylene glycol + water). As soil ice is replaced with liquid, soil permeability increases. The magnitude of such increases depends upon the amount of fluid introduced, the chemical nature of the contaminant, the texture of the soil, and the distribution of ice lenses within the soil.

2.4.2 Immiscible Contaminants

Liquid contaminants which are not water-miscible are referred to as non-aqueous phase liquids (NAPLs). NAPLs introduced to a soil system generally exist as a separate

liquid phase (Lyman et al. 1993), although most compounds are at least partially soluble in water (Yong et al. 1992).

Theoretically, the permeability of saturated frozen soil to NAPLs would be extremely limited as only the miscible portions of such fluids could thaw soil ice or be incorporated into the unfrozen films. The permeability of non-saturated frozen soils to such fluids is likely far greater as the air phase could be displaced by an infiltrating liquid. The degree of penetration would be controlled by the distribution of air-filled pores within the soil, and influenced by the density and viscosity of the fluid.

2.4.3 Vapour Transport

In non-saturated soil, air may become contaminated if exposed to volatile compounds. Rates of vaporization are dependent upon contaminant vapour pressure, concentration of the contaminated solution, soil temperature and the volume of air present (Lyman et al. 1992). Substances with high vapour pressures such as gasoline are volatile and evaporate quickly (Yong et al. 1992), however volatilization rates are generally highly temperature dependent (Lyman et al. 1992). Stiver and Mackay (1987) report that evaporation rates of Norman Wells crude oil are 70% less at 0°C than at 22°C. The volume of air present in the system is also important, as vaporization will only proceed until saturation is reached (Lyman et al. 1992).

Volatilization of subsurface contaminants induces concentration gradients which lead to vapour diffusion. Volatilization rates will generally be lower at greater depths as soil bulk density increases with distance from the soil surface (Yong et al. 1992).

2.5 Conclusion

The permeability of frozen soil to water and solutes suggests that other fluids, including contaminants, may not be contained by permafrost. While rates of water migration are relatively slow, such rates may become significant when considering the long-term behaviour and impacts of contaminants spilled, stored or disposed in permafrost terrain.

Theoretically, contaminant behavior in frozen soil will depend on the saturation, structure, texture and temperature of the soil, as well as on the physical and chemical properties of the contaminant. The research defined in this thesis focuses on the influence of contaminant miscibility, soil temperature and soil saturation on fluid migration through frozen silt. This study is an initial step in defining the potential for contaminant migration and the main factors controlling fluid behavior

Chapter Three

MACROSCALE STUDIES

3.1 Introduction

The permeability of frozen silt to contaminants was investigated in macroscale studies conducted at the CNRS Centre de Geomorphologie, Caen, France, and in benchscale experiments at Carleton University. Macroscale studies investigated the fate of two petroleum hydrocarbons (arctic diesel fuel and a synthetic motor oil) injected into frozen ground. Fluid levels were recorded until the conclusion of the study period, when soil cores were taken, subsampled and analyzed by gas chromatography to determine levels of contamination in the soil adjacent to and underlying the contaminant source. Soil temperatures were monitored to ascertain the influence of soil temperature on contaminant behaviour.

3.2 Experimental Facility

The Station de Gel is a controlled environment facility located at the Centre de Geomorphologie. The facility is a refrigerated hall 18 m long x 8 m wide x 5 m high, with two adjacent rooms which accommodate instrumentation and mechanical equipment. The hall is a basin approximately 1.8 m deep with a bedrock base (Burgess et al. 1982). Basin walls are insulated with 10 cm of Styrofoam and the trough perimeter is lined with a

geotextile layer (BIDIM) and PVC membrane (Figure 3.1). For the current experiment, modifications allowed soil to be piled 63 cm above the top of the basin by extending an impermeable membrane to this height and by installing cribbing around the entrances to the cold room.

The test basin was filled with Caen silt to a depth of 240 cm. Soil was placed progressively in the trough in lifts of approximately 40 cm. Each lift was compacted to 30 cm with a vibrating plate and a small compressor roller, resulting in an average dry bulk density of 1.56 g cm^{-3} . In earlier experiments at Caen, the behaviour of a gas pipeline buried in frost-susceptible soil was investigated. The 27.3 cm-diameter pipeline remained in place at a depth of 33 cm during this experiment.

A network of sensors distributed symmetrically through the facility monitored soil and air temperatures (Figure 3.2). Twenty-five YSI-44033 interchangeable thermistors and 160 copper-constantan thermocouples measured soil temperatures to depths of 185 cm at intervals ranging from 15 - 20 cm (Table 3.1). Air temperatures were monitored by thermocouples 100 cm above the soil surface. Temperature data were collected every 12 hours over the course of the study.

Experiments investigating contaminant behaviour in the active layer and the frozen soil studies outlined herein ran concurrently in the test facility. To accommodate the objectives of the active layer studies, air temperatures within the hall were manipulated to induce two freeze-thaw cycles over the 73-day study period, with an average active-layer depth of 50 cm. This thesis concentrates on the behaviour of contaminants in frozen soil only.

Figure 3.1

LONGITUDINAL CROSS-SECTION OF THE STATION DE GEL

From: Dallimore and Crawford (1984; Figure 2.1).

Figure 3.2

PLAN OF EXPERIMENT DEPICTING BOREHOLE AND SENSOR LOCATIONS

Table 3.1

SPACING OF SENSORS ON THERMISTOR CABLES

	Depth (cm)											
T10	0.1	0.3	0.50	0.65	0.8	0.95	1.1	1.25	1.4	1.55	1.7	1.85
T11	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9		
T12	0.1	0.35	0.6	0.85	1.1	1.3	1.6	1.85				
T13	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9		
T14	0.1	0.3	0.5	0.65	0.8	0.95	1.1	1.25	1.4	1.55	1.7	1.85
T15	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9		
T16	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9		
T17	0.1	0.3	0.50	0.65	0.8	0.95	1.1	1.25	1.4	1.55	1.7	1.85
T18	0.1	0.3	0.5	0.7	0.9	1.1	1.3	1.5	1.7	1.9		

3.3 Silt Properties

Caen silt is an eolian, frost-susceptible soil composed of 3 -10 % sand, 75-85 % silt and 10-20% clay. It has a hydraulic conductivity of between 1×10^{-9} to $1.5 \times 10^{-8} \text{ ms}^{-1}$ when unfrozen, and a particle density of 2.665 g cm^{-3} (White 1992). A freezing characteristic curve of Caen silt has been determined by time-domain reflectometry (Figure 3.3).

In-situ structure of Caen silt has been described in detail by Smith and Williams (1992), and White (1992). Ice lenses in the silt dip slightly in the upper 20 - 30 cm of the ground, but are generally horizontal at greater depths (Figure 3.4). Ice lenses observed in the cores extracted at the end of the contaminant study, and those described in White (1992) and Smith and Williams (1992) were several millimetres in length and consistently horizontal below a depth of 55 cm. This is to be expected as ice lenses form with their long axes perpendicular to the direction of heat flow (Carlson and Nixon 1988).

Moisture contents near the soil surface ranged from 12% (ground surface) to 32% (15 cm depth). At greater depths, lower soil moisture was observed (Figure 3.5).

3.4 Installation

A caterpillar-mounted "Sedi-Tech" Geotechnical drill was used to bore two 5 cm diameter holes into the frozen silt to 80 cm depth. Drilling was performed when the ground was frozen to minimize soil backfilling. Forty-eight hours following drilling, 300 ml of contaminant (arctic diesel fuel or motor oil) equilibrated to air

Figure 3.3

FREEZING CHARACTERISTIC CURVE OF CAEN SILT

From: Dallimore and Crawford (1984; Figure 2.3).

Figure 3.4

ICE LENS ORIENTATION WITHIN STATION DE GEL

From White 1992

Figure 3.5

GRAVIMETRIC SOIL MOISTURE CONTENTS OF CAEN SILT

temperature (-8°C) were poured into each of the holes. Contaminants were poured slowly through funnels to prevent splashing against the borehole walls. Casing was not required as only minimal sloughing of the borehole wall was observed during the first three days of the experiment

3.5 Contaminant Properties

3.5.1 Arctic Diesel Fuel

Arctic grade diesel fuel (DF-A) is a heterogenous petroleum mixture with a pour point of -57°C and a vapour pressure of 0.6 kPa at 38°C . Like the majority of the low temperature fuels, including JP-5, JP-8, Jet A, and Jet A1, DF-A is a kerosene, composed chiefly of paraffins and naphthenes. The viscosity of DF-A increases from 1.1 cp at 40°C to 4.3 cp at -20°C .

3.5.2 Motor Oil

Dynastar S VEEDOL, a 5W-30 synthetic motor oil was used in this series of experiments. It is a high performance oil with a viscosity ranging from 70 cp at 40°C to 11.3 cp at 100°C . This lubricant has a density of 0.87 g cm^{-3} , and a pour point of -45°C .

3.6 Monitoring and Sample Extraction

Contaminant levels in the boreholes (hereafter referred to as borehole levels) were monitored daily over the entire course of the experiment. After 73 days (the end of the

second freezeback period) residual contaminants were cleared from the hole using a manual coring device designed for soft sediments. The holes were then refilled with saturated sand. Sand was initially mixed with water and frozen. Additional water was then added until the mixture was malleable, ensuring that the temperature of the introduced sand was close to 0°C, minimizing the risk of thawing soil pore ice.

One week later, a single core was extracted at each of the permafrost hole sites. A 12 cm diameter coring auger attached to the Sedi-Tech drill was used in this procedure. The drill was placed such that the original hole, apparent in the core as a sandplug, was on the core perimeter. Each core was 90 cm in length, sampling soil to 10 cm below the bottom of the original hole.

To ensure that samples were not accidentally contaminated during the coring procedure, the surface of each core was scraped to remove thawed material and any hydrocarbons which may have smeared during extraction. Slices which spanned the entire width of the core were extracted at the desired depths with a chisel. From these slices eight subsamples from each core were taken at the desired distance from the sandplug, then mixed thoroughly. Approximately 40 g was sampled from each of the mixed sections, and transferred to pre-weighed 40 ml EPA water specimen bottles. Ali samples were then transported to Ottawa for further analysis. All sampling trays and hand tools were cleaned after use with each specimen to prevent accidental contamination of subsequent specimens.

3.7 Chemical Analysis

Chemical analysis was conducted at the Centre for Analytical and Environmental Chemistry at Carleton University. Gas chromatographic (GC) analysis was performed on all DF-A specimens. Due to difficulties resulting from the synthetic composition of the motor oil, a number of techniques (GC, Ultraviolet spectrophotometry, U.S. Environmental Protection Agency oil and grease gravimetric standard technique) were used to analyze samples from the oil-contaminated core.

3.7.1 Moisture Content

Prior to the initiation of chemical analysis, the gravimetric moisture content of a portion of each soil sample was determined.

3.7.2 DF-A Analysis

A Varian 3400 Gas Chromatographer (GC) was used to determine the contaminant concentration of all DF-A samples. The mass of each soil-filled vial was recorded. Approximately 40 ml of HPLC grade acetone (a volume sufficient to cover the sample to a depth of 0.5 - 1 cm) was then added to each vial. Samples were left overnight to maximize dissolution of the DF-A into the solvent.

A 500 ppm standard (500 parts DF-A per million parts acetone) was used to calibrate the chromatographer. Approximately 1.6 µl of this standard was injected by syringe into the GC. The complex molecular composition of this petroleum mixture produced a complicated chromatograph with dozens of peaks (Figure 3.6). Twelve of

Figure 3.6

DE-A CHROMATOGRAPH

Each peak in this chromatograph represents one compound. Twelve of the peaks (labelled Peak 1 - 12 on the bottom of the chromatograph) were selected as characteristic peaks on the basis of their magnitude and degree of separation. The sum of the integrated areas of these peaks was compared to a standard solution to quantify the amount of contaminant present in each sample. The numbers at the top of the peaks indicate the time elapsed from the onset of the GC run to the occurrence of each peak (eg. Peak 11= 16.382 minutes).

these peaks were designated characteristic peaks based on their integrated area and resolution. The integrated area of these peaks, which is directly related to contaminant concentration, was then used as a reference to which all DF-A runs were compared

A small volume (approximately 1.6 μ l) of the solvent-contaminant solution was extracted from each of the vials and injected into the GC. By comparing the integrated areas of the characteristic peaks from the soil specimens (contaminant concentration unknown) to those of the 500 ppm standard, the DF-A concentrations of all samples were determined.

For all runs, the GC injector and detector temperatures were set to 250°C. The initial column temperature was 80°C, increasing to 250°C at a rate of 15°C min⁻¹. Helium was used as the carrier gas at a pressure of 15 psi.

3.7.3 Motor Oil Analysis

The complex chemical make up of the synthetic motor oil impeded chemical analysis. Gas chromatography was first attempted using hexane as a solvent, and the same GC parameters as those used on the DF-A samples (Section 3.7.2). These initial attempts were unsuccessful due to the presence of compounds with high molecular weights which could not be forced through the column. Ultraviolet spectrophotometry was then attempted. This method was also unsuccessful as the solid mineral phase preferentially absorbed UV wavelengths and interfered with the absorption peaks characteristic of the lubricating oil as identified with a standard oil-in-hexane solution.

Figure 3.12

OIL CONCENTRATIONS (g g^{-1}) IN SOIL ADJACENT TO BOREHOLE

well defined, as highly refined oils are composed of large organic molecules which are not easily vaporized (Figure 3.7). The total integrated area of these "humps" were therefore used for analysis. As with the DF-A samples, the integrated area of the chromatographs were compared to those of a standard oil in hexane solution.

3.8 Thermal Regime

Over the course of the 73-day study two freeze-thaw cycles were induced through the manipulation of air temperatures within the hall (Figure 3.8). At the start of the study, soil was frozen to depths ranging from 125 cm at the hall perimeter to at least 190 cm near the centre of the facility (Figure 3.9). Degradation of the simulated permafrost was observed over time, with the greatest thaw occurring near the perimeter of the Station de Gel. Temperature data from cables T10, T11 and T12 were selected for this thermal transect as these monitoring stations were the most proximal to the experimental boreholes (Figure 3.2).

Soil temperatures during the first freeze-thaw cycle were consistently lower than those of the second cycle at all thermal monitoring points (Figure 3.10). Thermal analysis was limited to those cables nearest to the boreholes (T10-18), with the exception of T16 which did not function properly during the study. Maximum thaw depths in this half of the Station de Gel ranged from 45 cm (T12) to 72.5 cm (T17), with an average active layer of 67 cm. Active-layer depth increased dramatically within 1 m of the central axis, and then was consistent at a depth of approximately 70 cm from this point to the facility perimeter

Figure 3.7

LUBRICATING OIL CHROMATOGRAPH

Figure 3.8

AMBIENT AIR TEMPERATURES WITHIN STATION DE GEL

Figure 3.9

DEPTH OF SOIL FREEZING ACROSS STATION DE GEL

Figure 3.10

SOIL TEMPERATURES AT CABLES T10-T18

Boreholes were not located in the immediate vicinity of the thermal cables as a second series of studies was running concurrently with the borehole experiments which extended over the majority of the sensed half of the facility. Temperatures are assumed to be symmetrical about the central axis, therefore data recorded at site T11 are assumed to be representative of the soil in the immediate vicinity of the boreholes. While thaw at T11 progressed to 70 cm, the soil forming the borehole walls was likely cooler as this soil was directly exposed to -8°C air for 48 hours prior to the introduction of contaminants which would have led to more rapid freezing. Cooler temperatures were likely maintained throughout the experiment as the higher density of cool air may have led to its ponding within the boreholes. A 0.4°C decrease in soil temperature would raise the base of the active-layer at this point to 66 cm (Figure 3.11).

3.9 Fate of Contaminants

Lubricating oil and arctic diesel fuel migrated laterally and vertically through the simulated permafrost. Little or no migration occurred until day 18 of the study. Infiltration of both contaminants began as soil temperatures warmed to -0.1°C and continued even when soil temperatures fell to -0.4°C .

Figure 3.11

EFFECT OF 0.4°C COOLING OF BOREHOLE WALLS ON ACTIVE LAYER DEPTH

3.9.1 Fate of Lubricating Oil

In total, eight samples were extracted from the lubricating oil core. Maximum contamination ($1.44 \times 10^{-2} \text{ g g}^{-1}$) was detected 8-10 cm below the borehole, while minimum oil levels ($1.74 \times 10^{-3} \text{ g g}^{-1}$) were detected in the soil adjacent to the borehole 60-66 cm below the ground surface (Figure 3.12). Contaminant levels in soil adjacent to the borehole at 70-75 cm depth demonstrate that lateral migration had progressed a minimum of 8 cm over the 73 day study period. Contaminant levels in this lateral transect ranged from $4.39 \times 10^{-3} \text{ g g}^{-1}$ at the most distal sample point to $1.00 \times 10^{-2} \text{ g g}^{-1}$ between 4 and 6 cm from the borehole wall. Lubricating oil penetrated a minimum of 14 cm into the silt underlying the borehole, with a sharp increase in oil concentration observed 8 cm below the borehole. This sharp increase may be due to the higher moisture contents observed in this region.

A plot of borehole levels against soil temperature provides insight into the conditions conducive to oil transport (Figure 3.13). Oil borehole levels remained constant for the first 17 days of the experiment but began to decline when soil temperatures reached -0.1°C . Borehole levels continued to drop over the entire study period, even as soil temperatures cooled to -0.4°C .

3.9.2 Fate of Arctic Diesel Fuel

The behaviour of diesel fuel is similar to that of lubricating oil. Diesel was detected in all extracted samples, including one from the region above the original contaminant level (Figure 3.14). A concentration of $1.12 \times 10^{-2} \text{ g g}^{-1}$ was detected

Figure 3.12

OIL CONCENTRATIONS (g g^{-1}) IN SOIL ADJACENT TO BOREHOLE

Figure 3.13

**CONTAMINANT LEVELS AND SOIL TEMPERATURE OVER
STUDY PERIOD**

Figure 3.14

DE-A CONCENTRATIONS (g g^{-1}) IN SOIL ADJACENT TO BOREHOLE

10-20 cm above the contaminant source. Such contamination may have resulted from accidental splashing as the DF-A was poured into the borehole, though precautions were taken to prevent such accidental contamination. It is also possible that diesel fuel migrated towards the surface through non-saturated pores in response to capillary and osmotic forces as either a liquid or vapour.

Contamination levels above the source were an order of magnitude greater than that detected in soil immediately adjacent to or below the boreholes. Diesel penetrated a significant distance into the soil adjacent to and underlying the contaminant borehole. Contamination was detected 8 cm horizontally away from the borehole wall, with contamination levels ranging from $8.7 \times 10^{-3} \text{ g g}^{-1}$ immediately adjacent to the borehole to $2.27 \times 10^{-4} \text{ g g}^{-1}$ at the most distal point. Diesel penetrated vertically a minimum of 5 cm into the silt beneath the borehole. Contamination in the vertical plane ranged from $4.21 \times 10^{-4} \text{ g g}^{-1}$ within 2 cm of the bottom of the contaminant source to $8.9 \times 10^{-5} \text{ g g}^{-1}$, 5 cm below the borehole.

Frozen silt initially contained the diesel fuel. As soil temperatures approached -0.1°C , diesel borehole levels declined, and continued to fall until Day 55 when the borehole was completely evacuated (Figure 3 13)

3.9.3 Methods of Transport

In both cores the extent and magnitude of contaminant migration was higher than anticipated given the immiscible nature of arctic diesel fuel and the synthetic lubricating oil. The two most probable mechanisms of transport were the melting of ice by water-

soluble contaminant fractions and subsequent aqueous transport, and/or movement through small fissures and along pore pressure gradients induced by soil warming.

In general, petroleum hydrocarbons are immiscible with water (Yong et al. 1992). These fluids, however, are complex mixtures of a myriad of individual compounds, some of which may be miscible in water. The water-soluble portions of such compounds may interact with the soil water phases, melting soil ice and mixing with unfrozen moisture. This hypothesis was tested in the benchscale studies described in Chapter 4. Those studies demonstrated that frozen saturated silt was impermeable to petroleum hydrocarbon infiltration, and therefore migration under suction and through fissures induced by soil warming is considered to be the main method of contaminant transport

The abrupt drop in borehole levels observed as soil temperatures rose to -0.1°C suggests that thermally-induced soil structural changes and not the melting of pore ice were responsible for increasing soil permeability. Soil structure is altered in response to mineral and pore volume changes generated by soil warming and cooling, and by the migration of unfrozen moisture along pressure, osmotic and thermal gradients

During freezing, the conversion of water to ice results in a 9% volumetric increase (Williams and Smith 1989). As a soil cools, its pore volume increases by an amount depending on the amount of water converted to ice, which in turn is dependent upon the soil freezing characteristic curve. Soil cooling also leads to a contraction of the mineral particles. The magnitude of mineral volumetric decrease is dependent upon the coefficient of thermal expansion which is approximately $10^{-5}^{\circ}\text{C}^{-1}$ for frozen soil.

As soil temperatures increase, the above processes are reversed. The mineral particles expand as dictated by the coefficient of thermal expansion, while the volume of pore phases decreases as a fraction of the soil ice is converted to liquid water. While there is an overall decrease in pore volume, soil particles remain in place as they are supported and separated by the ice matrix. The decrease in pore phase volume leads to a fall in pore pressure, which induces fluid infiltration and transport through the soil.

The relative magnitude of matrix and pore volumetric changes can be demonstrated through a simple calculation. First, the in-situ porosity of Caen silt is calculated to be 42% as:

$$\% \text{pore space} = 100 - \left(\frac{D_b}{D_p} \times 100 \right)$$

where D_b is the dry bulk density (1.56 g cm^{-3}) and D_p is the particle density (2.665 g cm^{-3}). A 100 cm^3 block of soil is comprised of 59 cm^3 mineral particles, and 41 cm^3 pore space. If saturated, the mass of ice plus unfrozen water within the soil is 41 g

At -3°C , approximately 5% of this 41 g of water remains unfrozen (2.1 g), while 95% (39.9 g) exists as ice. As a 9% volumetric expansion accompanies the freezing of water, the total volume of water present increases to 45.391 cm^3 ($39.9 \text{ g} + 0.09 \times 39.9 \text{ g} + 2.1 \text{ g}$).

As soil temperatures warm to -0.1°C , the unfrozen moisture content approaches 20%, which translates to a volumetric decrease in pore water (ice + liquid). At this

temperature, 33.6 g of soil moisture is present as ice, 8.4 g is water and the total volume of pore fluid falls 2.17 cm³ to 43.22 cm³.

The warming of soil from -3°C to -0.1°C also induces a change in volume of the soil particles. Given a temperature increase of 2.9°C and the coefficient of thermal expansion for mineral particles ($10^{-5} \text{ }^{\circ}\text{C}^{-1}$), the volumetric increase of the mineral phase is calculated to be $1.67 \times 10^{-3} \text{ cm}^3$. The expansion of the soil matrix is therefore two orders of magnitude less than volumetric decrease of the pore fluids. The decrease in pore fluid volumes induces a decrease in pore pressure. In the Caen boreholes, such pressure gradients likely induced the infiltration of hydrocarbons into the proximate soil

Following contamination, the frozen silt remained permeable to both contaminants even as temperatures fell to -0.4°C. As a fluid infiltrates a porous matrix it establishes continuous flow paths. The petroleum flow paths established near -0.1°C would remain liquid and mobile due to their low pour points. The presence of such conduits would account for the continued drop in contaminants in the borehole even as soil temperatures decreased

3.10 Summary

Frozen silt was permeable to lubricating oil and diesel fuel. While frozen soil initially contained the petroleum mixtures, contaminant migration was initiated as soil temperatures at depth approached -0.1°C and continued even as temperatures approached -0.4°C. Given the immiscible nature of the fluids employed, the main transport mechanism is considered to be transport under thermal-induced negative pore pressures. Once

established, continuous contaminant flow paths appear to have remained liquid and mobile even as the soil cooled.

Chapter Four

BENCHSCALE STUDIES

4.1 Introduction

The results described in Chapter Three demonstrate that frozen soil is permeable to diesel and lubricating oil. These results raise several questions that can only be addressed by controlled experiments with intensive sampling regimes, particularly the influence of soil temperature and saturation on fluid behaviour. Small-scale experiments were therefore designed to investigate the influence of these factors on contaminant behaviour.

Benchscale studies investigated the permeability of saturated and non-saturated silt to a miscible fluid, ethylene glycol, and an immiscible liquid, kerosene. Miscible contaminants were not used in the Caen experiments for fear that they would not be contained by the simulated permafrost and would contaminate the groundwater. In the benchscale studies, contaminants were introduced to columns of frozen silt and left for a two-week period. At the conclusion of the experiment columns were subsampled and GC analysis was used to determine the extent of lateral and vertical migration.

A description of the methods employed in the benchscale studies and an analysis of the ensuing results are presented in this chapter. The benchscale study findings confirm that frozen silt is permeable to petroleum hydrocarbons at temperatures as low as -10°C , although kerosene infiltration is limited to non-saturated soil. Ethylene glycol infiltrates

both saturated and non-saturated soil, contaminating the entire sample under all temperature regimes.

4.2 Contaminant Properties

4.2.1 Ethylene Glycol

Ethylene glycol, commonly used as anti-freeze, is a water-miscible fluid.

Reochem's Turbo Power All Season Antifreeze/Coolant was used in all benchscale trials. This fluorescent green coolant is comprised of ethylene glycol (94%), soluble corrosion inhibitors (2.5%) and water (maximum 4%). At 16°C, it has a density gravity of 1.12-1.14 g cm⁻³. The freezing point of this product changes as it is diluted with water. Listed freezing points of ethylene glycol - water solutions range from -24 4°C at 40% ethylene glycol to -52.5°C at 60%.

4.2.2 Kerosene

As no arctic diesel fuel was available for purchase at the time of project initiation, a representative of Esso Products and Chemicals Division recommended that kerosene be used as a substitute due to its similar physical and chemical properties (K. Richardson, pers. comm., 1994). Kero 1-K, an Imperial Oil product, was therefore used in all trials. This product has a pour point of -64°C, and a density of 0.7935 g cm⁻³ at 15°C.

4.3 Soil Properties

Caen silt (transported from France to Ottawa) was used in all of the bench scale studies. Soil aggregates were mechanically broken down, and particles larger than 2 mm were removed by sieving. The properties of Caen silt are defined in Section 3.3.

4.4 Preparation of Silt Columns

For each saturated (S) column, 900 g of distilled water was mixed with 3.0 kg of air-dried silt. Three kilograms of moist soil was then transferred to a 24 cm long x 14 cm (i.d.) aluminum mould. To remove air pockets, moulds were tapped 30 times on the counter surface. Following compaction, moulds were transferred to a freezer at -10°C for a period of 24 hours. Height of the soil surface was measured before and after freezing to determine if heave had occurred during the freezing process. No heave was observed in any of the trials, implying that the freezing rate was sufficient to prevent the development of ice lenses.

Non-saturated (NS) columns were created by mixing 600 g of distilled water and 3.0 kg of silt. 2.75 kg of this mixture was then transferred to the same moulds used in the creation of the saturated columns. This soil was compacted under a constant load of 20 kg for 8 hours. The soil columns were frozen at -10°C for 24 hours, with no heaving observed in any of the trials.

A total of six columns were prepared for each experimental run (3 S; 3 NS). During column preparation, thermistors were inserted into 1 NS and 1 S column. These

columns acted as temperature controls during the freezing runs. Following the freezing period, moulds were removed from the freezer, inverted, and gently tapped to extract the soil column. Columns were immediately wrapped in cellophane, set into an insulated cooler, and transferred into a cold room set to the desired temperature (-10°C , -2.5°C , -1°C , 4°C). Two 25 ml aliquots of each contaminant were also placed into the cold room. Soil columns and contaminants were left for a period of 24 hours to attain the desired temperature.

Moulds were designed such that a 1.5 cm deep x 5 cm diameter depression was formed at the surface of the soil column (Figure 4.1). After the equilibration period, 25 ml of ethylene glycol or kerosene was "spilled" into the reservoir of the four experimental columns. Columns were then resealed with cellophane, the insulative cooler closed, and left for a 2 week period. Once set into the cold room, columns were not removed until sampling was completed.

Control runs were conducted to determine the permeability of non-frozen soils to each contaminant. Non-saturated unfrozen columns were prepared in the same manner as outlined above. These columns were removed from the moulds and were left free standing in the cold room for the study period. Unfrozen saturated columns did not maintain their moulded form. Contaminants were therefore applied to the centre of the soil column (no reservoir could be established) and soil columns remained in the mould for the duration of the study. Soil columns and contaminants were brought to 4°C in a cold room. Contaminants were then applied to the column surface, and left for two weeks.

Figure 4.1

SOIL COLUMN DIMENSIONS

4.5 Sampling of Contaminated Silt Columns

4.5.1 Experimental (Frozen) Columns

Following the two week experimental run, frozen soil columns were sectioned and sampled to determine the lateral and vertical extent of contaminant migration. Columns were taken from the cooler and cellophane removed. Within the cold room, a chisel was used to extract a 5 cm wide section from the centre of the soil sample. This slab ran the entire length and height of the sample. Neither melting nor smearing was observed at the point of chisel contact (the bottom centre of the sample), and therefore this method was chosen over sawing which likely would have resulted in cross-sample contamination.

From the central slab, two 2 cm wide cores were extracted. Core 1 consisted of that portion of the soil column lying immediately below the contaminant reservoir, while Core 2 sampled soil lying between 4 cm and 6 cm from the centre of the column (Figure 4.2). Each core was then divided into three vertical sections (A: 0-2 cm from surface, B: 2-5 cm from surface, C: 5-8 cm from surface). Each of these subsections were broken apart and thoroughly mixed. A 10 g sample was then taken and transferred to a pre-weighed beaker. Remaining soil was force dried to determine gravimetric moisture content.

4.5.2 Control (Non-Frozen) Columns

Non-saturated control columns were sampled using the same procedure outlined in Section 4.5.1. The fluid nature of the non-frozen saturated columns required alternate sampling technique. A 3 cm diameter iron corer was placed such that one edge rested on

Figure 4.2

SOIL COLUMN SAMPLE POINTS

the centre of the column. A core was extracted from this point, following which the walls of the resulting hole were scraped to remove contaminants which may have smeared during insertion of the coring device. A spatula was used to extract samples from this inner wall. Samples were collected 0-2 cm, 2-5 cm and 5-8 cm from the soil surface, and transferred to pre-weighed beakers. This procedure was repeated at the periphery of the column such that a face was exposed 6 cm from the column centre

4.6 Chemical Analysis

Contaminant concentrations of all samples were determined with gas chromatographic analysis performed at the Centre for Analytical and Environmental Chemistry at Carleton University. A Varian 3300 FID Gas Chromatograph was used to determine the contaminant concentration of both the ethylene glycol and kerosene samples. The procedure employed in the analysis of the benchscale samples was identical to that for the macroscale DFA analysis (Section 3.7.2)

In preparation for analysis, approximately 25 ml of the appropriate solvent (methanol for ethylene glycol samples, acetone for kerosene) was added to each of the samples. Beakers were covered with tin-foil and left overnight to maximize dissolution of contaminants into the solvent

In the analysis of ethylene glycol runs, initial GC column temperature was set to 60° C increasing to 250°C at a rate of 30°C min⁻¹. Injector and detector temperatures were set to 250°C, using helium as the carrier gas and methanol as the solvent. During the

analysis of kerosene, the column ramp was decreased to $10^{\circ}\text{C min}^{-1}$ to increase peak separation.

A standard 500 ppm contaminant-solvent solution was prepared for each of the contaminants. Chromatographs of the ethylene glycol standard consisted of one peak as ethylene glycol is a homogenous fluid (Figure 4.3). Kerosene, like DFA, is a highly complex petroleum mixture resulting in a complicated chromatograph. Six peaks were designated characteristic peaks (Figure 4.4). Each standard was subjected to three GC runs to determine variations in the standard integrated area. The average of the integrated peak areas of these three runs was used as the reference area in the analysis of all soil samples. The ratio of sample trace area to standard trace area was used to calculate the degree of contamination (g contaminant per g dry soil) for each sample.

Accuracy of the GC procedure for each contaminant was determined using the integrated areas of the 500 ppm standard triplicates. Maximum deviation from the mean of these three runs was calculated then divided by the average standard integrated area. GC determinations of ethylene glycol concentrations were within $\pm 2.1\%$, while kerosene concentrations were within $\pm 1.7\%$.

4.7 Contaminant Behaviour in Frozen Silt

The permeability of frozen silt was dependent on soil saturation and contaminant miscibility. At all temperatures, non-saturated silt was permeable to both kerosene and ethylene glycol. The permeability of frozen saturated silt was dependent upon the miscibility of the contaminant. Saturated silt was impermeable to kerosene at all

Figure 4.3

ETHYLENE GLYCOL CHROMATOGRAPH

This trace is much simpler than the petroleum chromatographs as ethylene glycol is a relatively pure substance. The ethylene glycol peak occurs approximately 5.4 minutes after the onset of the run. The large solvent peak which occurs in the first minutes of the trial is not used in the analysis.

Figure 4.4

KEROSENE CHROMATOGRAPH

temperatures, while water-miscible ethylene glycol was detected throughout the saturated columns at all temperatures.

4.7.1 Kerosene

Soil saturation is the dominant factor controlling the permeability of frozen silt to kerosene. The pattern of kerosene distribution was consistent for all saturated trials as kerosene was completely restricted to the upper two centimetres of the soil column. Saturated soils were impermeable to kerosene relative to non-saturated columns which were contaminated at all temperatures.

4.7.1.1 Saturated Silt

Kerosene was restricted to the upper two centimetres of both experimental and control saturated silt columns (Table 4.1). Contaminants were detected at the surface of the peripheral cores, indicating some degree of lateral kerosene transport. Surface kerosene concentrations ranged from a low of 0.0014 g g^{-1} at the periphery of the -10°C sample to 0.006 g g^{-1} at the centre of the -2.5°C column. While these figures represent the concentration in the upper two centimetres of the soil column, it is proposed that only the upper two to three millimetres of the sample were contaminated as kerosene spread over the surface of the columns in response to edge effects.

Immediately following the introduction of kerosene to the column reservoir, a staining of the column surface was observed. As the volume of the contaminant did not exceed that of the reservoir, this staining is attributed to the spreading of kerosene over

Table 4.1

KEROSENE CONCENTRATIONS (g g^{-1}) THROUGH SILT COLUMNS

CONTROL (4°C)					
SATURATED			NON-SATURATED		
DEPTH (cm)	CENTRE CONC. (g g^{-1})	EDGE CONC. (g g^{-1})	DEPTH (cm)	CENTRE CONC (g g^{-1})	EDGE CONC. (g g^{-1})
0-2	0.0028	0.0027	0-2	0.0032	0.0026
2-5	0	0	2-5	0.0038	0.0005
5-8	0	0	5-8	0.0016	0.0019
-1°C					
0-2	0.0029	0.0030	0-2	0.0707	0.0160
2-5	0	0	2-5	0.0763	0.0186
5-8	0	0	5-8	0.0021	0.0257
-2.5°C					
0-2	0.0023	0.0014	0-2	0.0162	0.0049
2-5	0	0	2-5	0.0204	0.0231
5-8	0	0	5-8	0.0500	0.0324
-10°C					
0-2	0.006	0.0026	0-2	0.0153	0.0175
2-5	0	0	2-5	0.0085	0.0032
5-8	0	0	5-8	0.0088	0.1347

the column surface in response to capillary forces. Kerosene staining progressed in all directions from the soil surrounding the reservoir to the column periphery, and was accompanied by a drop in contaminant levels within the reservoir. Within 12 hours of the onset of each trial, no kerosene remained in any of the saturated sample reservoirs. Kerosene immediately spread over the surface of the control column as no reservoir could be maintained in the saturated unfrozen soil.

During the sectioning process, significant variations in soil cohesion were observed. Regions contaminated by kerosene or ethylene glycol were malleable and considerably easier to break apart than those which were not contaminated. When sectioning saturated kerosene columns, the soil was consistently rigid with the exception of the uppermost two to three millimetres. This was taken as further evidence that kerosene migration in saturated silt was largely limited to lateral spreading over the frozen soil surface.

4.7.1.2 Non-Saturated Silt

Kerosene was detected in all samples extracted from non-saturated columns. Contaminant levels ranged from 0.0005 g g^{-1} at the middle edge of the control sample to 0.1347 g g^{-1} at the bottom edge of the -10°C column (Table 4.1). This maximum concentration is an order of magnitude greater than the kerosene concentrations observed at all other periphery sample points, and is twice as large as the maximum concentration detected in samples taken from the column centre (Figure 4.5). The kerosene

Figure 4.5

KEROSENE CONCENTRATIONS THROUGH NON-SATURATED COLUMN
TEMPERATURE = -10°C

accumulation observed at this point may be due to preferential flow paths associated with the pore geometry of this column, though no channels were apparent upon sectioning.

Kerosene concentrations in the unfrozen non-saturated column were lower than those of the experimental columns. The lower contamination levels of the unfrozen column may have been in part due to the higher rates of volatilization associated with higher temperatures.

Kerosene contaminated non-saturated columns at all sub-zero temperatures. Levels of contamination were higher and more variable within each experimental column than in the control trial. While kerosene levels ranged from 0.0005 g g^{-1} to 0.0038 g g^{-1} within the control, concentrations within the -10°C column ranged from 0.0032 g g^{-1} to 0.1347 g g^{-1} .

4.7.1.3 Overview of Kerosene Behaviour in Frozen Silt

Clearly, soil saturation is a dominant control over kerosene migration through frozen soil. Under saturated conditions, kerosene was completely restricted to the soil surface, and not even the water-soluble fractions of this immiscible fluid penetrated into the column. This may be partially due to the low volumes of contaminants introduced to the soil, as solubility is directly related to the volume of contaminant present.

In non-saturated silt, kerosene permeated the entire soil column. The behaviour of kerosene in saturated silt indicates that interaction with the solid and liquid water phases is limited. As the wetting fluid in non-saturated soil, water occupies the smallest pores and channels. Kerosene is immiscible with water, and therefore is restricted to the pores which

are not occupied by water or ice, i.e. the largest pores within the system. It can therefore be assumed that kerosene migrates as a bulk liquid, and is limited to large, interconnected soil pores.

Kerosene infiltration into non-saturated silt is rapid. Upon introduction to the contaminant reservoirs, kerosene immediately began to penetrate the silt. Under all temperature regimes, kerosene had completely migrated out of the reservoir within five minutes of trial initiation. Rates of infiltration were far greater through the non-saturated silt relative to the saturated samples.

4.7.2 Ethylene Glycol

Ethylene glycol permeated the silt column in all experimental and control trials. In both saturated and non-saturated frozen columns, concentrations were higher near the column surface than at depth, with lower levels of contamination at depth observed in non-saturated samples

4.7.2.1 Saturated Silt

Unlike kerosene which is immiscible with water, water-soluble ethylene glycol migrated through the entire column in all saturated trials (Table 4.2). In the control column, ethylene glycol concentrations ranged from 0.0149 g g^{-1} at the centre to 0.006 g g^{-1} at the periphery. In all experimental trials, contaminant levels in the centre of the column decreased by at least one order of magnitude from the surface to the lower two subsamples

Table 4.2

ETHYLENE GLYCOL CONCENTRATIONS THROUGH SILT COLUMNS

CONTROL (4°C)					
SATURATED			NON-SATURATED		
DEPTH (cm)	CENTRE CONC. (g g ⁻¹)	EDGE CONC. (g g ⁻¹)	DEPTH (cm)	CENTRE CONC. (g g ⁻¹)	EDGE CONC. (g g ⁻¹)
0-2	0.0147	0.0025	0-2	0.0120	0.0074
2-5	0.0104	0.0006	2-5	0.0007	0.0004
5-8	0.0149	0.0063	5-8	0.0034	0.0022
-1 °C					
0-2	0.0292	0.0912	0-2	0.0745	0.0496
2-5	0.0113	0.0007	2-5	0.0008	0.0005
5-8	0.0011	0.0045	5-8	0.0004	0.0001
-2.5 °C					
0-2	0.0419	0.0444	0-2	0.0529	0.0264
2-5	0.0261	0.0078	2-5	0.0028	0.0009
5-8	0.0029	0.0005	5-8	0.0034	0.0002
-10 °C					
0-2	0.0503	0.0130	0-2	0.0312	0.0149
2-5	0.0015	0.0002	2-5	0.0006	0.0006
5-8	0.0002	0.0001	5-8	0.0001	7.5 x 10 ⁻⁵

4.7.2.2 Non-Saturated Silt

Once again, ethylene glycol contaminated all unfrozen non-saturated samples. Levels of contamination were lower in all samples extracted from the non-saturated control column when compared with those from the saturated column (Table 4.2). The pattern of glycol distribution through the columns is similar for all frozen trials. At the centre of the -1°C column, glycol concentration falls two orders of magnitude from the surface (0.074 g g^{-1}) to the mid-section (0.0008 g g^{-1}). Concentrations less than 0.001 g g^{-1} are observed throughout the lower portions of this column. Similar patterns are observed in the -2.5°C and -10°C columns.

Lateral migration through frozen non-saturated silt was limited as contamination levels were lower at the periphery than at the centre of the columns at all depths.

4.7.3.3 Overview of Ethylene Glycol Behaviour in Frozen Silt

Ethylene glycol contaminated both saturated and non-saturated columns at all temperatures. As a water-soluble fluid, ethylene glycol melted pore ice and dissolved into the resulting water. The continuous aqueous channels may have permitted glycol to migrate through the entire sample as an aqueous solution. While some glycol may have dissolved into the adsorbed water film, rates of diffusion through this phase would have been significantly lower than through the aqueous phase. The highly polar nature of ethylene glycol results in a strong tendency to adsorb onto mineral surfaces, as the electrostatic attraction is sufficient to displace adsorbed water from the mineral surface.

Ethylene glycol immediately adjacent to the soil particles is virtually immobilized as it is adsorbed to soil particles.

In frozen saturated silt, ethylene glycol again permeates the entire column though levels of contamination are significantly higher at the surface. The higher surficial concentrations may be attributed to edge effects and/or to the lower permeability of ice-rich soil. In all frozen saturated samples, a concentration of small ice lenses (2-3 mm long) was observed at the column surface, including the region underlying the contaminant reservoir. When ethylene glycol was introduced to the soil column, it immediately encountered an ice-rich layer which may have initially offered more resistance to glycol penetration.

Thawing of surficial ice lenses was confirmed upon column sectioning as samples were malleable and no lenses were visible. Samples appeared moist, and a large number of cracks dissected the column surface. Fissures in the saturated glycol columns were several centimetres long and penetrated several centimetres into the column. The dissolution of ice and subsequent liquid transport away from the soil surface created these fissures. Once established, these cracks would greatly increase soil permeability to any introduced fluid.

As observed in the kerosene trials, ethylene glycol began to infiltrate the non-saturated columns immediately following its introduction to the contaminant reservoir though the higher viscosity of ethylene glycol resulted in slower rates of infiltration. Ethylene glycol had completely evacuated the reservoir within 15 minutes of the initiation of all trials.

In non-saturated samples, ethylene glycol contamination is more pronounced near the column surface. Ethylene glycol displaces air which occupies the largest pores and channels in the silt, and exists as a bulk fluid in these voids where it appears to be held under capillary tension near the surface of non-saturated columns. Ethylene glycol may also be adsorbed to particle surfaces, rendering it immobile. A small proportion of contaminants migrates through the silt to the column bottom. Such migration may occur through the bulk phase, or as a result of glycol-induced thawing and transport through the newly-created aqueous phase.

Surficial cracks were again apparent following the trial period, though they were considerably smaller and penetrated to a shallower depth than those observed in the saturated columns.

4.8 Summary

These studies confirm that frozen silt cannot be termed impermeable as contaminants migrate through soils at temperatures as low as -10°C . The permeability of frozen silt to contaminants is dependent upon contaminant miscibility and soil saturation. While kerosene was restricted to the surface of saturated columns it contaminated non-saturated silt at all temperatures. Water-miscible ethylene glycol contaminated all soil columns at all temperatures. Differences in the ability of the two contaminants to penetrate saturated frozen soil are due to the ability of water-soluble substances to depress the freezing point of ice and mix with the resulting water. The melted portions of the ice phase

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PM-1 3½"x4" PHOTOGRAPHIC MICROCOPY TARGET
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acted as conduits for ethylene glycol transport, and as such the ice-filled pores did not act as barriers to migration. Kerosene, in contrast, did not interact with the ice or water phases and was restricted to the column surface of saturated soils, and to air-filled pores in non-saturated soils.

Chapter Five

SUMMARY AND CONCLUSIONS

5.1 General

The assumption that permafrost is impermeable to contaminants has been a key component of policies addressing arctic waste disposal. In regions of permafrost, no legislation requires that waste disposal sites be lined, as frozen ground has been considered impermeable to contaminant infiltration. The results presented indicate that permafrost cannot be considered impermeable, as contaminants penetrate frozen soil under certain conditions. The permeability of frozen soil is dependent upon fluid and soil properties, particularly contaminant miscibility and soil saturation.

5.2 Summary of Results

The major findings of this thesis are summarized as follows

1. Frozen soil is permeable to contaminant infiltration under certain conditions
Saturated silts were selectively permeable to water-soluble contaminants at temperatures as low as -10°C while non-saturated silts were permeable to both miscible and immiscible fluids at temperatures ranging from 4°C to -10°C

2. Contaminant miscibility is a critical factor controlling fluid behaviour. Miscible contaminants depressed the freezing point of soil ice and dissolved into water which resulted from the melting. All pores, whether ice-, water- or air-filled were potential pathways for the transport of water-soluble fluids. Immiscible contaminants were restricted to water-free pores.

3. Saturation influences soil permeability, particularly to immiscible fluids. Saturated silt was impermeable to kerosene while kerosene infiltrated and contaminated non-saturated silt at temperatures ranging from 4°C to -10°C. Ethylene glycol distribution was influenced by saturation though this water-soluble fluid permeated both saturated and non-saturated silt columns.

4. Changes to soil structure associated with warming alter soil permeability. Observations during the macroscale study indicated that lubricating oil and arctic diesel fuel were contained by the frozen silt until soil temperatures approached -0.1°C. As demonstrated by the benchscale studies, transport of immiscible contaminants is limited to air-filled pores. This suggests that diesel and lubricating oil migration occurred through small fissures which developed as the silt warmed, or under suction in response to pore volume changes as ice was converted to water. Once contaminated, transport continued even when soil temperatures fell to -0.4°C.

5. Contamination alters soil structure and cohesion. The melting of soil ice by ethylene glycol replaced a solid phase with a liquid. The creation of such a liquid phase would likely increase soil permeability to subsequent water-miscible compounds. If this phase is mobile, and the volume of soil liquid falls below saturation, an increase in soil permeability to both miscible and immiscible compounds would result.

5.3 Conclusion

This study has demonstrated that contaminants infiltrate frozen soil under certain conditions. Guidelines addressing waste disposal are needed to clarify under what circumstances permafrost may be used as a means of contaminant containment. Further research is required to develop specific guidelines.

Results reported here have established that both miscible and immiscible fluids migrate through non-saturated frozen soils, and that saturated frozen silt is permeable to water-soluble substances at temperatures as low as -10°C . Further research is needed to quantify the rate at which the contaminant wetting front progresses, the rate of contaminant flow through contaminated soil, and the factors which influence such flow.

It can be assumed that the permeability of frozen soil, like that of non-frozen soil, is dependent on soil texture, as texture influences the volume and mobility of unfrozen moisture present, the distribution of pore spaces, and pore size. Research is required to determine the relative permeability of soils of varying textures to a wide range of contaminants. Permeameters could be employed to determine rates of progression of the

contaminant wetting front through non-contaminated soils.

It appears that the permeability of frozen soil is altered with contaminant infiltration. As water-soluble compounds melt soil ice, water and solutes are free to migrate through the aqueous phase along pressure and osmotic gradients. The melting of ice and redistribution of water alters the soil structure, decreasing cohesion and creating fissures which form potential conduits for subsequent fluids, whether miscible or immiscible. The establishment of continuous flow paths as air, ice and/or water are displaced by contaminants decreases flow resistance, and increases rates of flow. Changes to the permeability of frozen material must be studied and considered when developing waste management policies in permafrost regions.

Generally, laboratory determinations of unfrozen soil permeability are far lower than those observed in the field. Discrepancies between laboratory-based predictions and field determinations can be in excess of three orders-of-magnitude. Similar discrepancies can be expected when considering frozen soil. Field tests are therefore required to quantify the ability of various frozen materials to contain contaminants. The numerous fuel dumps and disposal sites in permafrost regions could be tested to determine their containment performance.

The results of these proposed studies could be used to develop guidelines for waste disposal and the clean-up of contaminated sites as permafrost cannot be relied upon to contain all contaminants under all conditions.

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