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Characterization of Crude Oil Associated Hydrophobic Soil Sites in Alberta

by

Heather A. Lowen ©

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Master of Science

in

Soil Science

Department of Renewable Resources

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled *Characterization of Crude Oil Associated Hydrophobic Soil Sites in Alberta* submitted by *Heather Ann Lowen* in partial fulfillment of the requirements for the degree of *Masters of Science in Soil Science*.

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For my father

William K. Lowen

Abstract

Decades after a crude oil contamination event, soils may become hydrophobic. We characterized landscape and soil conditions at 27 hydrophobic soil sites in Alberta, Canada. Unlike natural hydrophobicity, the generation of crude oil-associated hydrophobicity is not restricted to any particular soil textural class or topographical position. We found that residual oil contamination, powdery surface structure, and absence of vegetation can indicate the presence of hydrophobic soil, however, these conditions are not present at all sites. We conducted a detailed soil profile examination at 12 sites and determined a positive correlation between hydrophobicity and dichloromethane extractable organic concentration. This relationship may be modified by soil conditions related to pH as the addition of sodium sulfate to samples reduced hydrophobicity. However, the removal of carbonates or salts from hydrophobic soil samples and the addition of calcium carbonate did not alter hydrophobicity.

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Table of Contents

Chapter 1: A General Introduction

Chapter 2: Landscape and Soil Characterization of Hydrophobic Soil Sites

Chapter 3: Characterization of Twelve Hydrophobic and Wettable Soil Pedons in Alberta

Chapter 4: The Expression of Soil Hydrophobicity in the Presence of Carbonates and Salts

Chapter 5: Synthesis

List of Tables

List of Figures

Glossary[1]

Aggregate	A group of soil particles cohering in such a way that they behave mechanically as a unit.
Amphiphilic	A molecule with two portions; one which is strongly attracted to water molecules (hydrophilic), and one that is strongly attracted to oils (oleophilic, lipophilic or hydrophobic)
Discharge area	An area in the landscape that receives net discharge of water from the ground water.
Field-wettable soil	Moist soils that sorb droplets of water within 10 s, if oven-dried they may express hydrophobicity.
Hardpan	A layer of soil usually below the surface in which resistance to penetration is markedly greater than in the layer above or below. These layers may be brittle of flexible. Hardpans at hydrophobic sites were composed of a mixture of viscous oil and soil and were approximately 10 cm thick.
Hydrophilic	The property of a molecule, substance or material that imparts a high affinity for water molecules.
Hydrophilic soils	Hydrophilic soils sorb water in 10 s or less. Hydrophilic is a synonym for water-wettable soil.
Hydrophobic	The property of a molecule, substance or material that causes it to repel water molecules. Hydrophobic substances have a greater affinity for other hydrophobic substances than for water.
Hydrophobic soil	Soils that do not sorb water droplets within 10 s. Hydrophobic is a synonym for water-repellent.
Macro-aggregate	An aggregate that is > 250 μm.
Micro-aggregate	An aggregate that is < 250 μm.
Mottles	Localized zones of enhanced pigmentation formed by oxidation/reduction of Fe or Mn or the physical accumulation of Fe-Mn minerals.
Powdery surface soil	Hydrophobic surface soil that appears to be disaggregated and structureless.
Pristine soil	Soil that has not received crude oil contamination.

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[1] Largely derived from Roy et al. 2000

Recharge area	An area in the landscape that experiences net water entry through soil to the saturated zone below.
Saline soil	A non alkali soil that contains enough soluble salts to interfere with the growth of most crop plants. The pH is usually less than 8.5, the electrical conductivity is greater than 4 ds/m and the exchangeable- sodium percentage is less than 15.
Sodic soil	Soils that have an electrical conductivity greater than 4 ds/m and an exchangeable-sodium percentage greater than 15.
Surface tension	Is the tendency of a liquid surface to assume a form of minimal surface exposure relative to volume, hence the shape of a sphere, droplet or ball.
Tar ball	Soil aggregates containing viscous oil in the form of tar.

List of Abbreviations and Acronyms

θ	Contact angle in the liquid phase at the line of three-phase contact.
γ_{LV}	Interfacial tension at the interface of liquid and vapour phases.
γ_{SL}	Interfacial tension at the interface of the solid and liquid phase.
γ_{SV}	Interfacial tension at the interface of the solid and vapour phase.
C/N	The ratio of total organic carbon to total nitrogen
$CaCl_2$	Calcium chloride
$CaCO_3$	Calcium carbonate
DEO	Dichloromethane extractable organics
EC	Electrical conductivity
IPA/NH_2OH	*Iso*propanol ammonia
MED	Molarity of ethanol droplet test
Na_2SO_4	Sodium sulphate
PGM	Parent geologic material
SEM	Scanning electron microscope
TC	Total carbon
TIC	Total inorganic carbon
TN	Total nitrogen
TOC	Total organic carbon
WDPT	Water drop penetration test

Chapter 1: A General Introduction

1.1 Introduction

1.1.1 Soil and Water Interactions at the Molecular Level

To understand soil hydrophobicity and the entities that prevent water-wetting, it is necessary to understand soil-water interactions and how wettable soils absorb water at a molecular level. Wetting may be described as the process of achieving molecular contact. Thus, the extent of water-wetting could be defined as the number of molecular contacts between water and soil solids and the displacement of a third phase, air. Two types of molecular contact may occur between the three phases: drops of liquid placed on a solid surface will either spread out indefinitely, displacing air and thereby wetting the solid; or the liquid may spread to a limited area and halt so that the film at the edge of the drop meets the surface at a definite angle. In the latter case the solid surface repels the liquid (Burdon 1949).

Molecules in a droplet of water on the soil surface frequently collide, and through kinetic energy, molecules at the surface of the droplet may escape from the liquid phase into the atmosphere. Conversely, water molecules in the gas phase may strike the liquid surface and be absorbed in it or they may strike the soil surface and may be adsorbed by it. The molecules that become adsorbed to the soil surface may trigger the spreading of the water droplet as predicited by the vapour-pressure theory of spreading (also called the distillation theory of spreading) (Burdon 1949). This theory states that the process of wetting is initiated by the formation of a film on a solid by condensation from the vapour phase or by surface diffusion of molecules from the edge of the drop (Burdon 1949). The formation of this initial film is dependant on the volatility of the liquid (Bascom et al. 1964), and may result in the wetting of the solid by either reducing the surface tension sufficiently to enable the spreading of a droplet of liquid (Burdon 1949); or, by forces of cohesion, pulling molecules of the liquid from a droplet (Hardy 1936).

Water displaces air over the surface of a solid, such as soil when the adhesion of water and soil exceeds the cohesion of water. If cohesive forces are greater than adhesive forces, a solid will repel water. Therefore, the balance of adhesive forces between the liquid and solid and cohesive forces in the liquid determine wettability.

A drop of liquid placed on a dry surface will usually spread over the surface, displacing gas as it spreads. Where spreading ceases the edge of the drop forms an angle with the surface of the solid, termed the contact angle. Young's equation treats the contact angle (θ) of a liquid as a function of the equilibrium between three interfacial tensions that can act on a drop resting on a horizontal, solid surface (Figure 1-1): (1) γ_{LV} at the interface of the liquid and vapour phases; (2) γ_{SL} at the interface of the solid and liquid and; (3) γ_{SV} at the interface of the solid and the vapour phase. Hence, Young's equation (Zisman 1964):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$$

Theoretically, a 90 ° contact angle ($\cos \theta = 0$) marks the division between infiltration and non-infiltration of water into porous soil (Fink 1976). According to this equation, water will spontaneously enter the soil if cos θ is greater than zero ($\theta < 90$ °). Contact angles (θ) < 90 ° occur when the adhesive forces between the solid and liquid exceed cohesive forces within the liquid (Hillel 1998). At contact angle equal to zero water will wet soil completely and spread freely at a rate depending on its viscosity and soil surface roughness. In contrast, water will not spontaneously enter the soil if cos θ is a negative number ($\theta \geq 90$ °). A contact angle of 180 ° implies complete rejection of the liquid by the solid surface; in this case the droplet would retain its spherical shape modified only by forces of gravity. However, there is always some adhesion of any liquid to every solid, therefore the contact angle never equals 180 ° (Zisman 1964). Surfaces on which the contact angle (θ) is > 90 ° are considered hydrophobic.

Differences between readily wettable and hydrophobic soil may relate to the density of hydrophilic surface groups (Miyamoto et al. 1972). The formation of a continuous film of adsorbed water may take longer on surfaces that have a low surface density of hydrophilic groups; this could result in complete evaporation of the water before a continuous film has had time to form.

1.1.2 Measurement of Soil Hydrophobicity

The contact angle of water on soil is the basis for conceptualizing hydrophobicity. As the contact angle ranges from 90 ° to 180 ° the soil will display increasing degrees of hydrophobicity. However, measurements of the contact angle of water on soil are difficult to obtain, often unreliable, and applicable only to extremely hydrophobic soils;

consequently they are rarely used (Wallis and Horne 1992). Despite these difficulties, contact angles are used to interpret the water droplet penetration time (WDPT) test and the molarity of ethanol droplet (MED) test.

WDPT involves placing a droplet of water on the soil and measuring the time it takes to penetrate (Letey et al. 2000). This procedure divides soils into two broad categories: hydrophobic soils, those with apparent contact angles greater than 90 ° (WDPT > 10 s); and water-wettable soils, those with apparent contact angles below 90 ° (WDPT < 10 s). The distinction between hydrophobic and wettable soils based on the WDPT is arbitrary (Wallis and Horne 1992). It is a better index of repellency persistence than an actual estimate of the initial contact angle (Watson and Letey 1970; Letey et al. 2000). However, WDPT is sensitive to only a narrow range of hydrophobicity and cannot be used to quantify low degrees of hydrophobicity (King 1981; Savage et al. 1972).

Watson and Letey (1970) proposed the Ninety Degrees Surface Tension procedure as an index for soil hydrophobicity. This method is based on the ability of a liquid to completely infiltrate the soil if its contact angle is less than 90 °. This procedure measures the surface tension of a droplet of aqueous ethanol solution applied to the soil. Ethanol lowers the air-liquid interfacial tension and the solid-liquid interfacial tension, eventually yielding a positive $\cos\theta$ ($\theta < 90°$) to allow infiltration into hydrophobic soil. The surface tension of a solution, which penetrates the soil in 5 s is considered the solution that wets the soil at 90 ° (Letey et al. 2000).

King (1981) developed the MED test as an adaptation of the Ninety-Degree Surface Tension Test, but recommended measuring the molarity (M) (rather than surface tension) of the aqueous ethanol solution that allows complete droplet absorption within 10 s. King (1981) proposed a classification where soils with MED ≤ 1 M are not significantly hydrophobic and soils with a MED ≥ 2.2 M are severely hydrophobic.

According to Roy (1999), soil moisture potential is the most important source of variability in soil hydrophobicity assessments. To reduce variability, she recommended that the soil be oven-dried prior to the assessment of hydrophobicity to diminish soil water and test liquid interactions. Sieving (1-2 mm) of soil samples prior to hydrophobicity assessments is also recommended to reduce the variability of undisturbed soils because surface roughness and the uneven distribution of organic matter may alter the results of the MED test.

1.1.3 Soil Hydrophobicity

Operationally, soil hydrophobicity is diagnosed as the inability of dry soil to absorb water droplets within 10 s or less. It varies greatly in its degree of severity, persistence and the circumstances leading to its occurrence. Hydrophobic soils have been reported as being able to absorb water at reduced infiltration rates compared to wettable soils (Wallis et al. 1991; Dekker and Ristema 2000), while other reports discuss soil that remain dry even after heavy rainfalls (Roy et al. 1999). Hydrophobicity may be a seasonal condition, which influences soils only during dry months; or it may persist unabated for decades (Roy et al. 1999).

Three principle forms of soil hydrophobicity have been reported: (1) naturally-occurring, (2) fire-induced and (3) petroleum-associated. Most of the literature on soil hydrophobicity is concerned with naturally occurring hydrophobicity. The sources of organic material implicated in causing hydrophobicity include plant material, fungal hyphae and the metabolic products of soil microorganisms. Natural hydrophobicity has been reported in Southern Australian pasture sands (Ma'shum and Farmer 1985); citrus groves in the United States (Jamison 1942; Wander 1949); coastal sands dunes in the Netherlands and New Zealand (Dekker and Jungerius 1990; Bisdom et al. 1993; Dekker et al. 1998; Wallis et al. 1990); forested soils in Japan and Canada (Nakaya et al. 1977; Barret and Slaymaker 1989); golf greens (Miller and Wilkinson 1977; Hudson et al. 1994) and cultivated soils (Chan 1992).

As with natural hydrophobicity, fire-induced hydrophobicity is related to the presence of organic materials in the soil. The generally accepted hypothesis is that the heat associated with forest-fires vaporises organic substances, which move downward into the soil and condense in cooler regions of the subsoil. When the organic substances condense they coat soil particles, imparting soil hydrophobicity (DeBano et al. 1970; DeBano and Rice 1973; Savage 1974; DeBano 2000).

Hydrophobicity may also develop after prolonged exposure to petroleum. As early as, Plice (1948) reported on the association of petroleum contamination with the development of soil hydrophobicity. Later, Ellis and Adams (1961), McGill et al. (1981) and Craul (1985) reported on the inability of soil to wet after crude oil contamination.

Li et al. (1997) and Sawatsky and Li (1997) studied soil-water relations in crude oil induced hydrophobic soils. Roy and McGill (1998) characterized hydrophobic soils at crude oil sites in Alberta, Canada. Roy et al. (1999) concluded that constituents derived from petroleum were responsible and Roy and McGill (2000) proposed that the flexible conformation of such constituents modified the expression of hydrophobicity in response to the changing nature of the pore fluids.

1.2 Significance of the Problem

In Alberta, soil hydrophobicity may be a symptom of crude oil spills. The development of hydrophobic soil occurs years to decades after a crude oil spill, when little to no residual petroleum remains in the soil (Roy and McGill 1998). The majority of reported cases occur on productive agricultural land. Soil hydrophobicity is responsible for a reduction in the rate of water infiltration into the soil surface and hence, an increase in surface water redistribution, a decrease in vegetation establishment, and a subsequent increase in soil erosion potential (Roy et al. 1999).

The severity of hydrophobicity is not abated by decades of exposure to natural weathering processes. To further complicate the problem, anecdotal evidence suggests that past attempts to remediate hydrophobic soils have either failed or been only temporarily successful.

1.3 Development of Hydrophobic Soils

1.3.1 Causative Agents

Soil hydrophobicity has been attributed to the presence of organic compounds coating soil particle surfaces (Wallis and Horne 1992). These compounds include metabolic products of basidiomycete fungi (Bond, 1963; Bond and Harris 1964) and actinomycetes (Jex et al. 1985); lipids and waxes from organic matter (Ma'shum et al. 1988; Franco et al. 2000; Horne and McIntosh 2000); and compounds of petroleum hydrocarbon origin (Roy et al. 1999). Inorganic materials are not suspected to be causative agents. Amorphous siloxane groups are probably the most common hydrophobic minerals but their surface density is generally too low to cause soil hydrophobicity (Tschapek 1984). Other hydrophobic minerals include graphite, sulphide, and elemental sulphur but they are present only sporadically in soils (Tschapek 1984).

A coating of amphiphilic organic material has been accepted as the agent responsible for the condition of soil hydrophobicity. However, the causal compounds have not been definitely identified. The approach has been to seek an extractant that renders hydrophobic soils hydrophilic. The compounds extracted by that agent are then identified; still, such identification does not conclusively prove these compounds were the cause of hydrophobicity. Many soils will revert to hydrophobic conditions after extractions of the putative coatings that "cause" hydrophobicity. Roy and McGill (2000) discovered extraction with amphiphilic solvents made hydrophobic soils wettable, however these soils partially regain hydrophobicity with subsequent exposure to non-polar, non-H-bonding solvents. This reversibility of hydrophobicity suggests that even apparently effective amphiphilic solvents do not remove all water-repellent substances from the soil.

Extraction with *iso*propanol/NH_4OH (IPA/NH_4OH) appears to remove putative water-repellent substances from hydrophobic soils whether natural or petroleum-induced. Ma'shum et al. (1988) and Franco et al. (2000) identified unbranched and branched C_{16} to C_{36} fatty acids and alkanes in the IPA/NH_4OH extractions. Horne and McIntosh (2000) identified alkane hydrocarbons (C_{23} to C_{33}), triglycerides and components of humic acids in the IPA/NH_4OH extractions of naturally occurring hydrophobic soils.

Roy et al. (1999) reported that compounds extracted by IPA/NH_4OH from petroleum-induced hydrophobic soil consisted primarily of a homologous series of long-chain and polycyclic aliphatic organic compounds (C_{24} to C_{32}), with a predominance of cycloalkanes, *n*-alkanes and *n*-fatty acids. They concluded that the compounds extracted from petroleum-associated hydrophobic soil are predominately of petroleum origin rather than plant or microbial origin.

Research on fire-induced hydrophobicity has not revealed specific repellent substances responsible for the development of hydrophobic soil (DeBano 2000). However, some studies have indicated that the heating of humic acids may lead to the development of hydrophobicity in soil (Giovannini and Lucchesi 1984).

1.3.2 Processes Leading to the Development of Hydrophobic Soil

Sorption of petroleum compounds to soil particles could generate soil hydrophobicity; both volatile and non-volatile compounds that have resisted biotic and abiotic degradation are potential agents. Causative agents that may sorb to soil from crude oil include interfacially active compounds of asphaltene and resin fractions and high molecular weight non-polar compounds of saturate and aromatic fractions (Roy et al. 1999).

Soil hydrophobicity is not solely a function of the presence of hydrophobic causative agents in the soil; such compounds also occur in soils that to do not display hydrophobicity. The compounds that impart hydrophobicity appear to be amphiphilic; they may change orientation or conformation according to the ionization status of their polar and ionic functional groups. In wettable soils, these compounds tend to have their polar (hydrophilic) ends pointing outwards (Horne and McIntosh 2000). Dehydration may result in re-conformation or re-orientation of the amphiphilic compounds, where the hydrophilic ends orient towards the centre of the soil particle, leaving the hydrophobic sites to face the outside, drier part, of the molecule (Ma'shum and Farmer 1985; Roy and McGill 2000).

Roy (1999) explained that amphiphilic organic molecules interact with the soil mostly through their polar and ionic functional groups, leaving alkyl chain substituents dangling at the soil/water interface. The amphiphilic molecules do not necessarily re-orientate upon dehydration, they may just change shape or conformation.

Conformation of the molecules varies from coiled (minimizing exposed surface area) to stretched (maximizing exposed surface area) depending on soil water properties. The alkyl chains would be expected to stretch in non-polar, non-H-bonding solvents or in air, and coil in polar organic, H-bonding solvents or water (Roy 1999). Therefore, the generation of soil hydrophobicity is a function of both the conformation and number of chains that are exposed at the soil/water interface. The stretched chain conformation at high packing density would be expected to generate severe symptoms of hydrophobicity.

The spreading of hydrophobic soil may occur by the generation of newly coated soil particles, re-conformation or re-orientation of an existing amphiphilic coating, or by mechanical dispersal of existing hydrophobic soil.

1.3.3 Soil and Landscape Properties Related to the Expression of Soil Hydrophobicity

Literature on naturally occurring and fire-induced hydrophobicity relates soil properties to the occurrence of hydrophobicity. There is a positive correlation between hydrophobicity and soil organic matter content (McGhie and Posner 1980; Wallis et al. 1993; McKissock et al. 1998; DeBano 2000). Severe natural hydrophobicity occurs primarily in sandy soils with < 50 g clay kg^{-1} soil (Bond and Harris 1964; Bond 1964; Harper and Gilkes 1994).
Hydrophobicity is determined by the amount of hydrophobic or amphiphilic organic matter available to coat the soil particles and the specific surface area of the soil particles. Soil particles with larger surface areas require larger quantities of organic matter to create severe hydrophobicity, whereas the limited surface area of coarse sands can be readily covered by lower amounts of organic matter. In contrast, clay soils have a larger surface area, and are therefore less likely to encounter sufficient material in the correct orientation or configuration to become hydrophobic.

Hydrophobicity has been reported in soils with > 50 g clay kg^{-1} soil, however more organic carbon is required to induce hydrophobicity than is required in soils with < 50 g clay kg^{-1} (McGhie and Posner 1980; Chan 1992; Harper et al. 2000). McGhie and Posner (1980) state that clays must be aggregated for hydrophobicity to develop, likely because aggregation of clays lowers the exposed surface area of the soil particles.

Natural hydrophobicity may vary with slope position. Wallis et al. (1993) found hydrophobicity to be most pronounced in upper slope positions and least in the depressional positions. Depressional positions tend to be imperfectly or poorly drained, which restricts the expression of hydrophobicity because hydrophobicity is only expressed as soil dries.

1.4 Conclusion

Soil hydrophobicity is a complex phenomenon; it varies greatly in degree of severity, persistence and conditions leading to its occurrence. A coating of amphiphilic organic material has been accepted as the agent responsible for soil hydrophobicity, however the causal agents have not been definitely identified. The generation of hydrophobicity appears to be both a function of the presence of hydrophobic causative agents and the conformation of the amphiphilic organic coating on the soil particles. Hydrophobicity is determined by the amount of amphiphilic organic matter available to coat soil particles and the specific surface area of the soil particles.

The objective of my master's research is to characterize petroleum-associated hydrophobic soil sites in Alberta and to determine if there are identifiable conditions among sites, which may be potential predictors or indicators of hydrophobic soil development. This knowledge is required for the development of appropriate and effective remediation protocols and a scientifically defensible method to prevent the further generation of hydrophobic sites.

We documented conditions at crude oil-associated hydrophobic sites, which may be potential indicators or predictors of hydrophobic soil expression. This research was conducted at the landscape and pedon scale. The landscape conditions within which 27 hydrophobic soil sites exist are documented in chapter 2. The soil pedons, which contain hydrophobic horizons or layers at 12 sites are classified in chapter 3. The relation of soil salinity and carbonates in selected hydrophobic samples to the expression of hydrophobicity as measured by MED is documented in chapter 4. I conclude with an overall synthesis of these results in chapter 5.

1.5 Tables and Figures

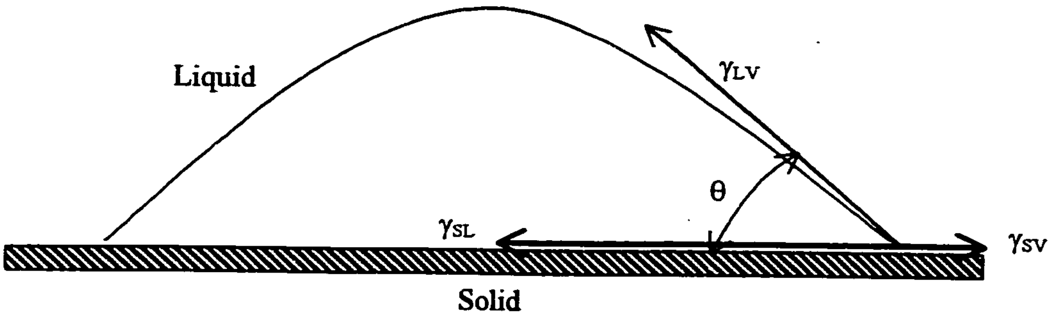

Figure 1-1: **Contact angle of a sessile drop of liquid viewed two dimensionally on a cross- sectional plane (adapted from Ziman 1964) as proposed by Young's equation: $\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta$.**

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Chapter 2: Landscape and Soil Characterization of Hydrophobic Soil Sites[1]

2.1 Introduction

Soil texture, organic carbon content, and topography can be used to predict the susceptibility of soils to develop natural hydrophobicity (Wallis et al. 1993; Harper and Gilkes 1994; Harper et al. 2000). Harper et al. (2000) explained that surface texture could be used to predict the risk of hydrophobic soil development. Hydrophobicity increases in severity with increasing organic carbon contents or decreasing soil surface area. Thus, hydrophobicity is more prevalent in sandy soils, with less than 50 g clay kg^{-1} soil (Bond and Harris 1964; Bond 1969; Harper and Gilkes 1994; Ma'shum et al. 1989). The accumulation of sufficient amounts (approximately 32 to 54 g clay kg^{-1} soil) of organic carbon can induce hydrophobicity in soils that have 50 to 100 g clay kg^{-1} soil (Harper et al. 2000). Hydrophobicity is more apt to be expressed in upper slope positions than in lower lying soils (Wallis et al. 1993). Low-lying soils tend to be imperfectly or poorly drained or tend to receive surface runoff from upper-slopes, which maintains their moisture content longer. Such soils are less likely to appear hydrophobic because as soil moisture content increases added water increasingly interacts by cohesion with soil water, hence water infiltration is not retarded even if it would be under very dry conditions.

Since 1990, soil hydrophobicity has been reported at 40 crude-oil contaminated sites in Alberta, Canada (Roy et al. 2000). Soil hydrophobicity appears to be generated in the presence of petroleum but not all contaminated sites develop this condition. According to Roy and McGill (1998), hydrophobic surface soil no longer has any indications of previous crude oil contamination; however at some sites evidence of oil contamination is present in shallow subsurface horizons. They also reported that crude oil induced hydrophobicity and its related structural degradation occur in the top 10 to 15 cm of the soil profile. They found hydrophobic soils contain smaller-sized aggregates and support sparse plant growth compared to normal adjacent soils.

This chapter reports on the characterization of 27 hydrophobic soil sites in Alberta. The goal was to determine if site characteristics that relate to occurrences of natural hydrophobicity are also associated with hydrophobicity at crude oil spill sites. The conditions we investigated

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[1] This work was part of a larger project. Some of the results were reported in Roy et al. (2000).

included landscape, vegetation and soil properties. We expected to find identifiable landscape conditions that would indicate or predict the development of hydrophobicity. However, we determined that the severity and location of hydrophobic patches is not related to landscape conditions. We found that the absence of vegetation could be used to delineate hydrophobic patches, however not all hydrophobic patches were bare. We expected hydrophobicity to be more severe in sandy textured soils and we expected that the hydrophobic surface soil would be disaggregated and powdery in structure. Instead, we determined that the severity of hydrophobicity is not restricted to a soil textural class and that powdery surface structure is not common to all hydrophobic soils.

2.2 Materials and Methods

2.2.1 Study Area

The 26 hydrophobic locations (27 sites) involved in this study are located in agricultural regions of Alberta; they extend northeast from Calgary to Cold Lake (Figure A-1 in Appendix A). We divided one hydrophobic soil location into two sites because its hydrophobic area spanned two soil orders; Luvisolic and Gleysolic. The latitudes of the locations span 51° 32' N (Township 30) to 54° 36' N (Township 65), and longitudes of 114° 21' W (Range 3 W-5) to 110° 04' W (Range 1 W-4). Elevations of the sites ranged from 450 m to 990 m above sea level.

Sites are located in both the Prairies and Boreal Plains ecozones (Environment Canada 1997). The Moist Mixed Grassland, Mid Boreal Uplands and Aspen Parkland ecoregions represent the Prairies ecozone and the Boreal Plains are represented by the Boreal Transition ecoregion. The 26 locations included representatives of the Chernozemic, Luvisolic, Solonetzic, Regosolic, and Gleysolic soil orders (Table A-1 in Appendix A).

At each hydrophobic location we asked landowners, lease holders, Alberta Environment inspectors and oil company personal an extensive set of questions (Table A-2 in Appendix A). Through these questions we attempted to learn as much as possible about the spill and site management history, land use and agricultural practices involved at each site.

2.2.2 Landscape Description

Landscape Characteristics

The parent geologic material (PGM), surface expression and local groundwater flow system influencing each site were recorded. Sites with Solonetzic soil characteristics were recorded as being in a groundwater discharge areas; sites adjacent to non-saline sloughs were recorded as being in local groundwater recharge areas; and sites that did not appear to be directly influenced by the groundwater where recorded as being in well drained areas. The topographical position of the hydrophobic patches within each site where described. All landscape properties were described according to the Canadian System of Soil Classification.

Vegetation

At 12 representative hydrophobic sites we documented plant species, percent cover and plant health within and at the edges of the hydrophobic patch. We recorded all of the plant species within the hydrophobic patch. At the edge of the patch and adjacent to the patch, we recorded species within three random 0.5 m radius plots. Percent cover was estimated visually and allocated into Braun-Blanquet cover classes, in which the range 0-100 % plant cover is partitioned into six classes, with smaller graduations nearer to the bottom of the scale (Kent and Coker 1992), Table A-3 (in Appendix A) provides details of this approach.

Soil Characteristics

The description of the soil characteristics entailed manual texturing of the surface soil within and adjacent to the hydrophobic patch and the description of the structural conditions of the surface soil. Surface structural conditions were described as being either powdery or aggregated. To be described as aggregated the structure had to contain both micro-aggregates (10 µm – 250 µm) and macro-aggregates (> 250 µm). We opted not to use Canadian System of Soil Classification descriptors such as single grain and granular to describe the surface structure, because it was not possible to determine if clay and silt sized particles were aggregated or single grain and the size of the particles composing the powdery soils were often too fine to be classified as granular. In addition to soil structure the presence or absence of surface crusts was documented.

Powdery hydrophobic surface soils were examined under a scanning electron microscope (SEM) to determine if they contained micro-aggregates. Prior to SEM examination, the soil samples were air-dried and dry-sieved with a 53 μm (270 mesh) and 2 mm (10 mesh) sieve. Soil that passed through each sieve was mounted on pegs with carbon tape and sputter coated with about 20 μm of gold. Before coating the samples with gold, we used an air jet to remove loose soil particles. We used a Jeol JSM-630FXV Scanning Electron Microscope attached to an Energy Dispersive X-Ray Analyzer Kevex 5000. Magnification of 50x – 20,000x was used to produce digital images of the primary and secondary particles in nine soils.

Molarity of ethanol droplet (MED) values and dichloromethane extractable organics (DEO) were determined on the < 53 μm soil fraction, the 53 – 2000 μm fraction and the entire soil. MED and DEO were determined according to the methods described in chapter 3.

2.2.3 Characteristics Associated with Hydrophobicity

Severity of Hydrophobicity

The MED test first proposed by Watson and Letey (1970) and later developed by King (1981) was used to measure soil hydrophobicity. The MED test measures the molarity of ethanol in a droplet of water required for soil infiltration within 10 s. Ethanol lowers the surface tension of water and thus enables infiltration into the soil matrix. The interpretation guidelines provided by King (1981) suggest, soils with a MED index ≤ 1 *M* are not significantly hydrophobic, soils with a MED index of 1.2 *M* – 2.2 *M* are moderately hydrophobic and soils with a MED index ≥ 2.2 *M* are severely hydrophobic.

We assessed soil hydrophobicity using ethanol concentrations of 1.0 *M* intervals in the range of 0.0 – 6.0 *M*. MED indices are routinely measured on air-dried or oven-dried soil; at higher soil moisture contents, MED indices may be unreliable because the water present in the soil attracts the applied droplet of water by forces of cohesion. However, we did not air-dry or oven-dry the soil prior to the MED tests we conducted in the field. We performed triplicate MED tests in the field at three points along a transect dividing the main hydrophobic patch. MED tests were conducted on samples sieved through a 1 mm sieve. We removed the top 1 – 2 mm of surface soil, which often sorbs water; and determined MED on the layer below, which repels water if the soil is dry.

Hardpans and Tar Balls

The presence, size and distribution of hardpans and tar balls were recorded. The term hardpan is used here to mean strongly compacted or indurated soil layers, which may be cemented. They have a greater resistance to penetration than the layers directly above or below. The hardpans discussed in this thesis are cemented layers composed of viscous oil and soil. We dug a 70 cm pit in the center of the worst patch and documented whether or not we located a hardpan layer. Landowners also usually confirmed the presence of hardpans. The term tar balls as used here means soil aggregates scattered on the soil surface that contain visible viscous oil in the form of tar. We recorded the typical diameter of the tar balls.

Delineation of Hydrophobic Patches

Hydrophobic patches at each site were counted and delineated. Landowners and Alberta Environment inspectors helped us determine the general location of the hydrophobic patches. The state and composition of vegetation growing at the site was often but not always a helpful indicator of the extent and depth of surface soil hydrophobicity. Using a hand trowel we removed the top 1 – 2 mm of surface soil and determined if the layer below was hydrophobic by placing a droplet of tap water on the soil. The soil was deemed hydrophobic if the droplet did not penetrate the soil within 10 s. We continued moving away from the center of the patch if the soil did not absorb a droplet of water in 10 s or less. We then marked the patch with flags and measured its area.

2.3 Results

2.3.1 General Site Description

Site use

All sites were located in agricultural areas, but land use varied (Figure 2-1). Most sites were used for cereal and oilseed production (12 sites) or forage (10 sites), 3 sites were battery sites with no agricultural production and one location was a landfarm operation, which consisted of two sites. It was not clear if the forage sites were seeded to help stabilize the soil and prevent spreading of the hydrophobic patches or if forage production decisions were made without consideration of the hydrophobic patches.

Remediation

Efforts had been made to remediate hydrophobicity at some of the sites, however information on the extent and nature of these efforts was not uniformly available. Manure had been applied to three sites; hydrogen peroxide had been applied at two sites and fertilizer was used at a majority of sites. Residues from past manure amendments may have interfered with our soil hydrophobicity assessments at some sites by increasing the MED index.

2.3.2 Landscape and Soil properties

Landscape Properties

Hydrophobic patches occur in soils developed from a variety of PGM, with the majority of the sites located in soils that developed from Morainal parent material; however most of Alberta consists of Morainal parent material (Table 2-1). The surface expression of the sites varied from hummocky to level.

Two of the 26 locations characterized were adjacent to local discharge areas and 6 were located adjacent to local recharge areas (Table 2-2). Hydrophobic patches were found in a variety of slope positions. Of the 26 locations characterized, 11 sites were level, 8 were found in mid-slope positions, 6 were in depressional areas and 2 were located on top of the slope (Table 2-2).

Soil Characteristics

We found that hydrophobicity occurs in soil with a wide range of soil textures, varying from sand to silty clay. Figure 2-2 is a frequency distribution of surface soil textures at the 27 hydrophobic soil sites characterized. These soil textures were determined by hand texturing which resulted in an over-estimation of clay content and under-estimation of sand content compared to particle size analysis subsequently done on 12 of the samples (Table A-3 in Appendix A).

We found that 55 % of the sites had powdery surface structure and of those 60 % had surface crusts (Figure 2-3). We found that 45 % of the sites had an aggregated surface structure (Figure 2-4).

The <53 μm fraction of powdery surface soil contained micro-aggregates and primary soil particles (Figure 2-5). The 53 – 2000 μm fraction contained macro-aggregates (> 250 μm), micro-aggregates (< 250 μm) and primary soil particles (Figure 2-6). The abundance of aggregates versus primary soil particles varied depending on the textural class of the site. Figure 2-6 (left) represents a site with fine-textured soil; there appears to be similar proportions of aggregates and primary soil particles. The aggregates appear rough, which is caused by the agglomeration of soil particles. The primary soil particles have sharp edges and show few to no surface features. Figure 2-6(right) represents a site with coarse-textured soil; it is composed mostly of primary soil particles. A typical micro-aggregate from the < 53 μm fraction is depicted in Figure 2-7; this aggregate appears to be formed by an arrangement of clay domains. A typical macro-aggregate from the 53 – 2000 μm fraction is depicted in Figure 2-8(left); it is composed of an arrangement of clay domains and primary soil particles. It is difficult to determine weather the particle depicted in Figure 2-8(right) is an aggregate or a sand grain that is coated with concentric layers of clay; these particles were common in the 53 – 2000 μm fraction of coarse textured soils. The images of the particle in Figure 2-8(right) and the aggregate in 2-8(left) are taken at different scales, requiring attention to the scale bar when visual comparisons are made. We can conclude that these soil particles are aggregates because they resisted the abrasion of dry sieving.

The < 53 μm fraction of powdery surface soil samples consistently had higher MED (*M*) values and lower DEO (mg/kg) concentrations than the 53 – 2000 μm fraction (Table 2-3 and Table 2-4). The < 53 μm fraction had higher MED (*M*) values than the entire soil and the 53 – 2000 μm fraction had lower MED values than the entire soil (< 53 μm > entire soil > 53 – 2000 μm) (Table 2-3). We found a very slight positive correlation ($R^2 = 0.098$) between MED (*M*) values and DEO (mg/kg) concentrations in the < 53 μm fraction (Figure 2-9). We found no relationship between MED (*M*) values and DEO (mg/kg) concentrations in the 53 – 2000 μm fraction (Figure 2-10).

Vegetation

Vegetation was described by identifying plant species and estimating percent cover. We recorded 13 different plant species adjacent to the hydrophobic patches and 19 species within the hydrophobic patches (Table A-5 in Appendix A). There tended to be greater species diversity within the hydrophobic patches than in the adjacent pristine soil. This is not because hydrophobic soils support a diversity of species but because sites were located on arable land, where weed control prevents species diversity.

All of the weedy species present in the hydrophobic patches were prolific seed producers or have seeds that possess varying degrees of dormancy (Table A-5 in Appendix A). The plant growth in the hydrophobic patches was dominated by the following weedy species: *Cirsium arvense* (Canada thistle), *Chenopodium album* (Lamb's quarter), *Crepis tectorum* (Narrow-leaved hawk's beard), *Fagopyrum tartaricum* (Tartary buckwheat) and *Avena fatua* (Wild oats). These species are all prolific seed producers, which are widely scattered and germinate over an extended period (Alberta Agriculture 1998).

The majority of the patches were bare, however some supported relatively good plant growth (Figure 2-11). Bare patches varied from $< 1\ m^2 - 10^4\ m^2$. Little vegetation was present at sites with hardpan layers.

2.3.3 Characteristics of Hydrophobicity

Hardpans and Tar Balls

Hardpans were found at 13 of the 27 sites investigated. Hardpans in hydrophobic soils have a massive structure; they have a dry rupture resistance class of extremely hard to very rigid. They prevent the penetration of roots and percolation of water. Hardpans were approximately 10 cm thick, tended to be discontinuous and occurred anywhere from just below the soil surface to a depth of 85 cm. All sites with hardpans had powdery surface structure. Soil aggregates containing viscous oil (tar balls) were found at 14 of the 27 sites investigated; their diameter ranged from 0.5 to 10 cm. Six sites had both hardpans and tar balls.

Size of Hydrophobic Patches

Hydrophobic patches ranged from 0.03 to 6.4 hectares. Most sites were less than 1 ha and the median size was 0.38 ha. We found 1 – 8 hydrophobic patches at the 27 sites characterized, with a median of one patch per site.

Severity of Hydrophobicity

We determined MED values in the field on surface soil samples. We found 20 sites were severely hydrophobic (MED values $\geq 2.2\ M$), 7 sites were not severely hydrophobic (MED value $< 2.2\ M$). Ten sites had MED values between 3 and 4 M and 2 sites had MED values $>$ 5 M.

2.4 Discussion

Similar to natural hydrophobicity, petroleum-induced hydrophobicity develops from organic material present in the soil (Roy et al. 1999). However, our data demonstrates that unlike natural hydrophobicity the development of petroleum-induced soil hydrophobicity is not restricted to any particular texture class or group of textural classes. The accumulation of petroleum in these soils was sufficient to completely coat all soil particles regardless of surface area.

Low-lying soils tend to be imperfectly or poorly drained, which restricts the expression of hydrophobicity because hydrophobicity is most strongly expressed as the soil dries (Wallis et al. 1990). However, we found no correlation between topography and location or severity of hydrophobic soil sites. Topography dictates the movement of a crude oil plume and it also controls soil moisture. Crude oil comprises the origin of the repellent organic material responsible for the manifestation of hydrophobic soil (Roy et al. 1999). We could postulate that because crude oil spills tend to migrate down slope, concentrating in low-lying areas and resulting in a higher concentration of oil than in upper slope positions, lower slopes have a greater potential for hydrophobic soil development. However, hydrophobicity only becomes apparent at low soil water contents (King 1981; Wallis et al. 1990), so perhaps observations of varying patch size are due to varying soil moisture deficit from year to year.

Petroleum-induced hydrophobic soils may contain hardpans, tar balls and may have a powdery surface structure. However, these characteristics are not present at all sites. We found no indicators, which predict the occurrence of these characteristics at some sites and not others. Hardpans and tar balls may reflect past efforts to bury layers of oil (hardpans) or patches of oil (tar balls). We could not obtain sufficiently precise site histories to test this hypothesis. The occurrences of hardpans and tar balls are not necessarily related to each other; however results indicate that presence of hardpans and powdery surface structure may be related because all sites that had a powdery surface structure also had a hardpan layer.

Roy and McGill (1998) noted discernible structural degradation of hydrophobic surface soils and after SEM examination and reported that aggregates approximately 100 μm in diameter were scarce. Similarly, we found that the majority of our sites had a powdery surface structure, which contained both micro-aggregates and primary soil particles, however this soil also contained macro-aggregates. We also found that 45 % of the sites had surface soil that contained visible macro-aggregates.

Hydrophobicity is a surface area phenomenon and therefore tends to be more strongly expressed on soil particles that have a lower surface area than those with a high surface area. Therefore, I expected that the < 53 μm fraction would have smaller MED (*M*) values than the 53 - 2000 μm fraction. The < 53 μm fraction is composed of silt and clay particles and micro-aggregates, which have a higher surface area compared to the sand and macro-aggregates in the 53 – 2000 μm fraction. I found that the < 53 μm fraction had higher MED (*M*) values than both the entire soil and the 53 - 2000 μm fraction. These findings could be attributed to two different hypotheses: (1) the entire soil represents a dilution of hydrophobicity (MED values) between the two soil fractions or (2) Natural hydrophobicity develops as a result of small additions of organic carbon, thus soil particles with low surface areas are more susceptible to becoming hydrophobic than particles with high surface areas. However, petroleum associated hydrophobicity develops after a large addition of organic carbon; all the soil particles are coated with hydrophobic material. The finer fraction is more hydrophobic than the coarser fraction, because the residual oil contamination would more strongly adhere to soil particles in the < 53 μm fraction.

As explained in chapter 3, DEO and MED are positively correlated. Therefore we expected that because the < 53 μm fraction had higher MED (*M*) values than the 53 – 2000 μm fraction it would also have a higher concentration of DEO (mg/kg). However, we found that the 53 – 2000 μm fraction had consistently higher concentrations of DEO than the < 53 μm fraction. The 53 – 2000 μm fraction could potentially contain small tar balls, which would inflate the concentration of DEO without increasing hydrophobicity.

Characteristics of Hydrophobic Sites that Impact Investigation

A difficult part of characterizing hydrophobic soil sites is delineating the boundaries of the hydrophobic areas. The absence, species composition and health of vegetation were often good indicators of the boundary of the hydrophobic area. However at some sites, we were unable to detect differences in the abundance, composition or health of the vegetation between the hydrophobic area and adjacent wettable soil. To delineate the boundaries of hydrophobic areas we opted for walking out from the most severe part of the patch. We tested for hydrophobicity using droplets of tap water and if the soil did not absorb the water in 10 s or less we continued moving away from the starting point.

Testing for hydrophobicity in the field is complex. The top 1 – 2 mm of hydrophobic surface soil actually sorbs water, whereas the layer below repels water, if it is dry. This layer of hydrophobic soil was usually 10 to 15 cm thick, and beneath it was usually a layer of moist, wettable soil. Attention to all three of these layers is important to determine the true extent of hydrophobicity.

2.5 Summary and Conclusion

Twenty-seven hydrophobic soil sites were described in this chapter. The results of the macro-scale characterization work can be summarized as follows: (1) all sites were located in agricultural areas, but land used varied, (2) there was no correlation between location and severity of hydrophobic sites and topography or water regime of the site, (3) the development of hydrophobicity is not restricted to any particular soil textural class or group or textural classes, (4) 55 % of the sites had a powdery surface structure composed of micro-aggregates (10 µm to 250 µm in diameter) and 45 % of the sites had an aggregated surface structure, which was composed of both micro- and macro-aggregates (macro-aggregates > 250 µm in diameter), (5) the < 53 µm fraction powdery surface soil consistently had higher MED (*M*) values and lower DEO (mg/kg) concentrations than the 53 – 2000 µm fraction; (6) the majority of the hydrophobic patches were bare, however some supported relatively good plant growth, (7) hardpans were found at 13 of the 27 locations investigated and tar balls were found at 14 sites, six sites had both hardpans and tar balls, (8) hydrophobic patches ranged from 0.03 to 6.4 ha, (9) 20 sites were severely hydrophobic (MED $\geq$ 2.2 *M*) and 7 sites were not severely hydrophobic (MED < 2.2 *M*).

We can conclude that soil hydrophobicity at crude oil spill sites is a complex phenomenon and should not be reduced to a few simplistic generalizations. Unlike natural hydrophobicity, soil textural class and topography are not potential predictors or indicators of the potential for soils to develop hydrophobicity following crude oil contamination. This is probably related to the amount of organic carbon introduced with an oil spill, and the tendency for free oil to flow down slopes and accumulate in low-lying areas.

We found that a powdery surface structure, lack of vegetation and the presence of tar balls and hardpans indicate the presence of hydrophobic soil, however these characteristics were not consistently present at all of the 27 sites characterized.

2.6 Tables and Figures

Table 2-1: Parent geologic material at hydrophobic soil locations.

Parent Geologic Material	Number of Sites
Eolian	3
Fluvial	2
Industrial Mix	1
Lacustrine	5
Morainal	16
Total	**27**

Table 2-2: Landscape properties of hydrophobic soil sites.

Water Regime	Number of Sites	Slope Position	Number of Sites
Local discharge area	2	Top	2
Local recharge area	6	Depression	6
Well drained area	19	Side	8
		No slope	11
Total	**27**	**Total**	**27**

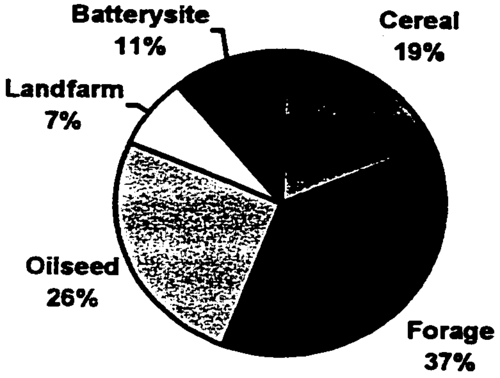

Figure 2-1: Site use at hydrophobic soil locations.

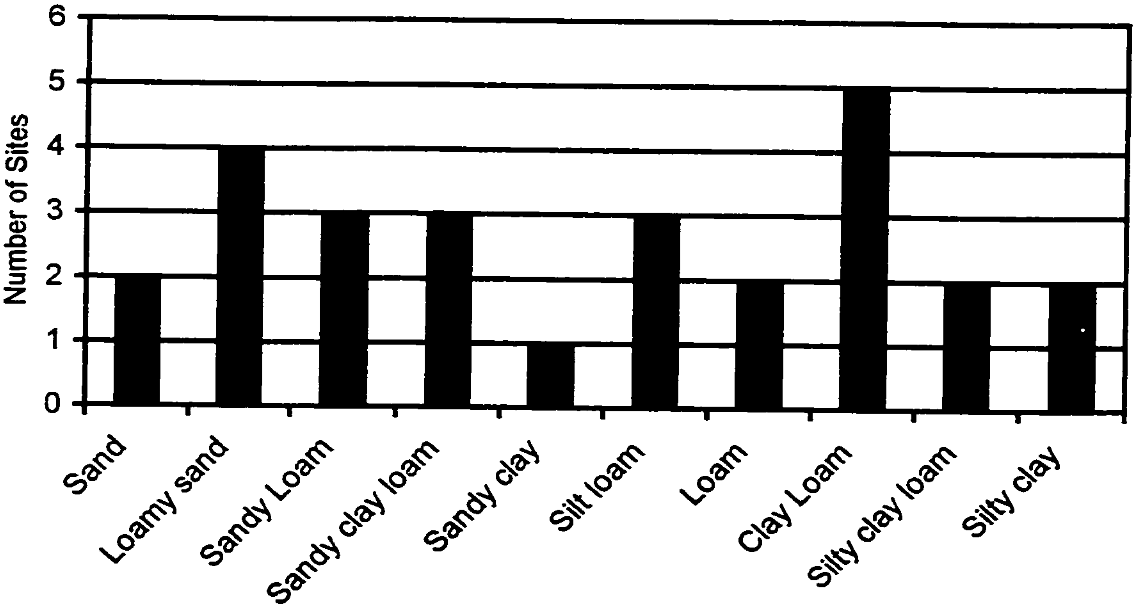

Figure 2-2: Distribution of soil textures among hydrophobic soil sites.

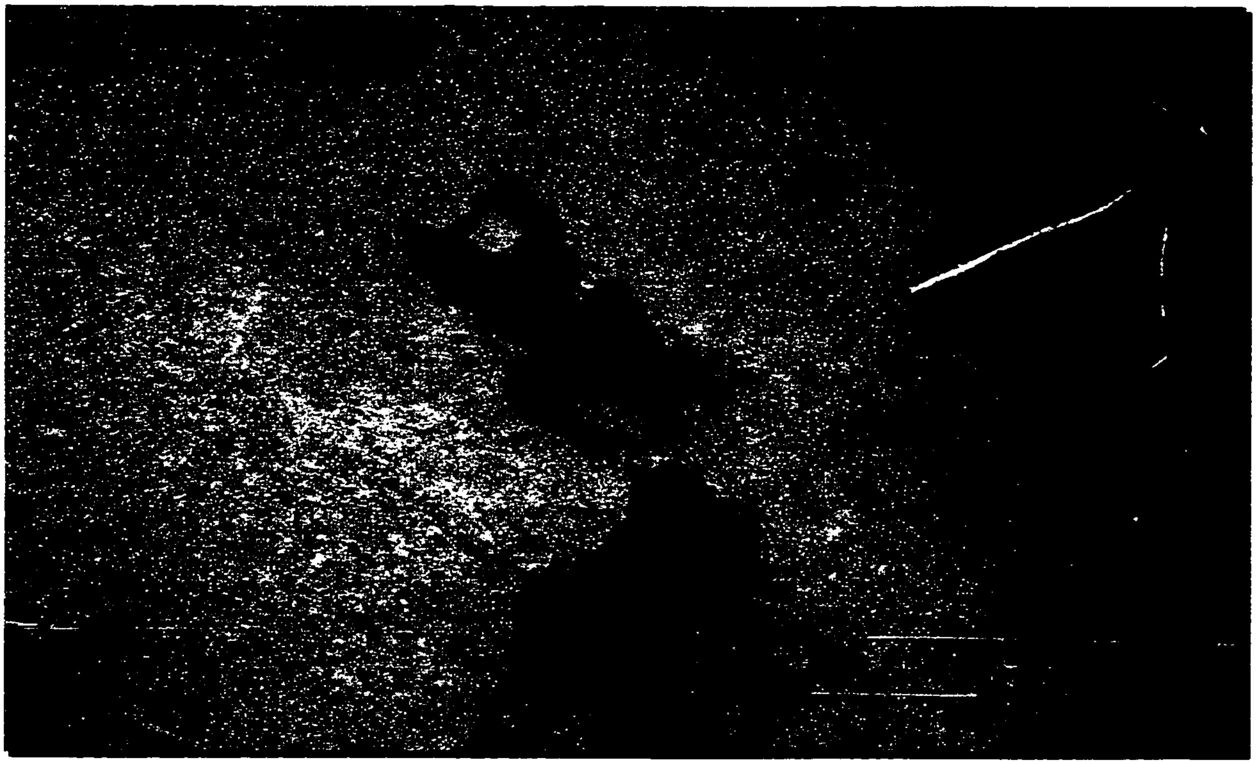

Figure 2-3: Powdery surface structure, found at 55 % of the sites.

Figure 2-4: Aggregated surface structure, found at 45 % of the sites.

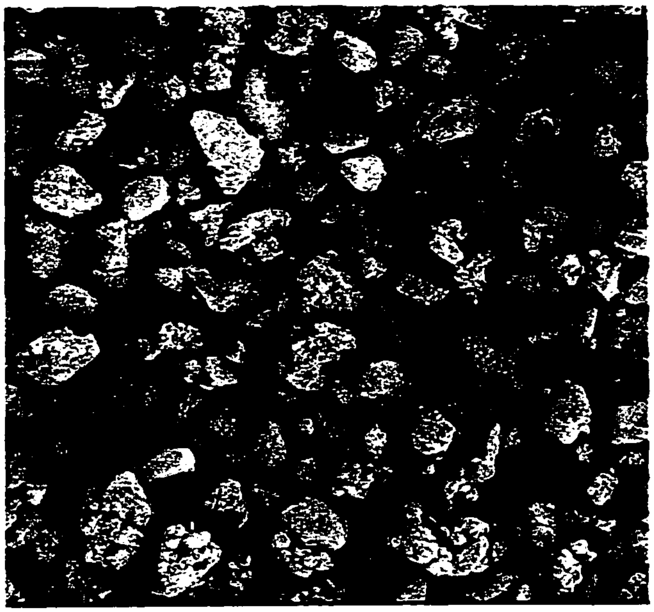

Figure 2-5: Micro-aggregates and primary soil particles contained in the < 53 μm fraction of powdery surface soil. The scale = 10 μm.

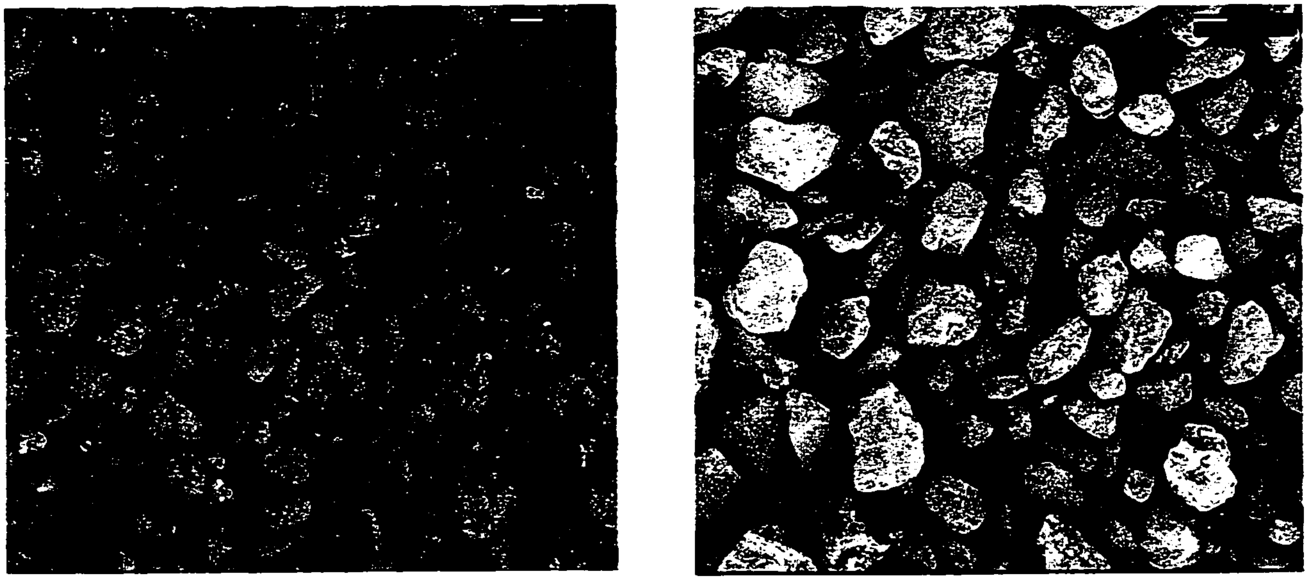

Figure 2-6: Macro-aggregates, micro-aggregates and primary soil particles contained in the 53 to 2000 μm fraction of powdery surface soil. Left: Aggregates and primary soil particles contained in the 53 to 2000 μm fraction of a fine textured site. The scale = 100 μm. Right: Aggregates and primary soil particles contained in the 53 to 2000 μm fraction of a coarse textured site. The scale = 100 μm.

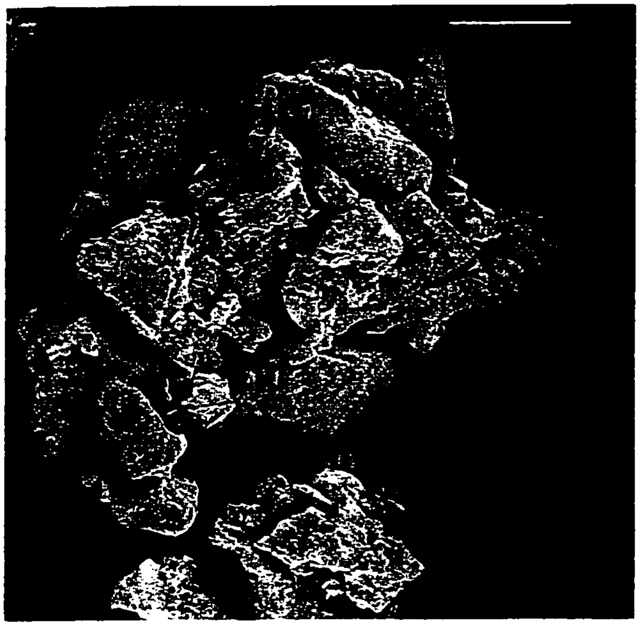

Figure 2-7: Typical micro-aggregate from the < 53 μm fraction of powdery surface soil. This aggregate appears to be formed by an arrangement of clay domains and primary soil particles. The scale = 10 μm.

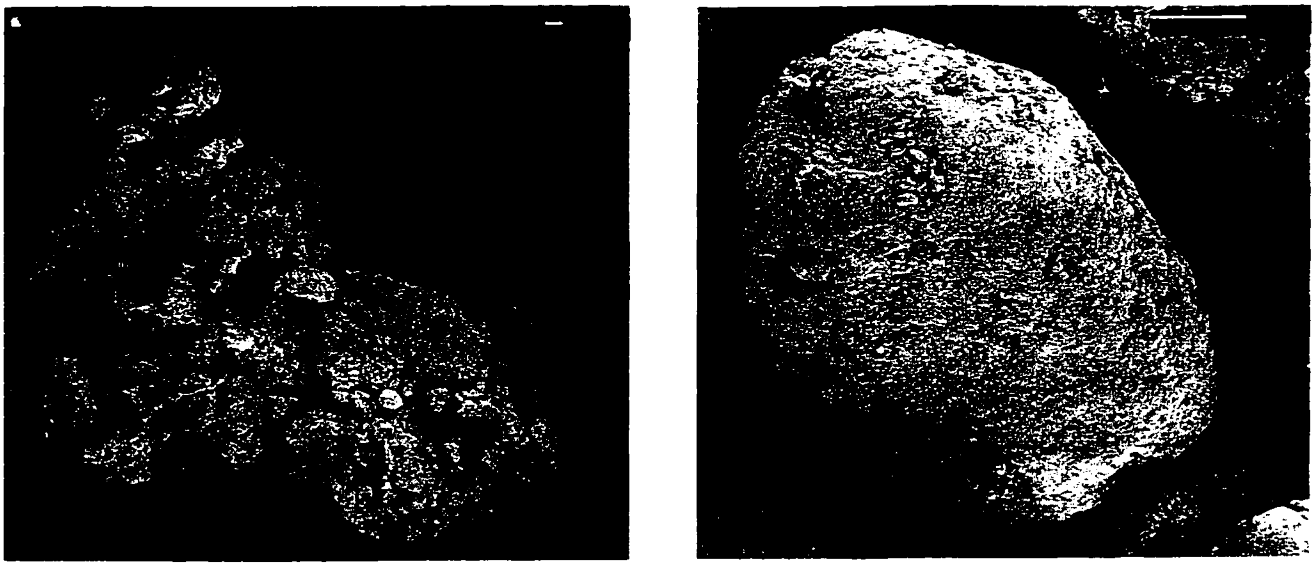

Figure 2-8: Typical macro-aggregates from the 53 to 2000 μm fraction of surface soil. Left: Typical macro-aggregate composed of clay domains and primary soil particles. The scale = 10 μm. Right: An aggregate, sand grain or mini-tar ball; coated with concentric layers of clay. The scale = 100 μm.

Table 2-3: MED (*M*) values for the entire soil, the 53 – 2000 μm fraction and the < 53 μm fraction.

Site Number	MED (*M*)			
	Entire Soil	53 – 2000 μm	< 53 μm	Difference[1]
1	2.9	2.8	3.4	-0.6
3	2.4	2.6	3.0	-0.4
5	3.2	2.8	4.0	-1.2
6	2.8	2.2	3.5	-1.3
7	2.7	2.2	3.2	-1.0
8	4.3	4.1	4.5	-0.4
12	2.9	2	3.8	-1.8
14	3.0	2.8	3.4	-0.6
20	4.7	4.4	4.8	-0.4
23a	3.4	3.0	3.8	-0.8
23b	2.5	2.0	3.1	-1.1
25	3.6	3.4	4.2	-0.8

[1] The difference was calculated by subtracting the < 53 μm fraction from the 53 - 2000 μm fraction

Table 2-4: DEO (mg/kg) concentration for 53 – 2000 μm fraction and the < 53 μm fraction.

Sample	DEO (mg/kg)		
	53 – 2000 μm	< 53 μm	Difference[1]
1	10,908	8,796	2,112
3	5,169	4,698	471
5	14,653	14,597	56
6	9,992	9,211	781
7	41,263	13,983	27,317
8	10,185	9,825	360
12	3,257	2,526	731
14	n/a	N/a	n/a
20	12,1064	18,725	102,339
23a	41,1263	21,677	19,586
23b	13,970	12,901	1,069
25	n/a	21,375	n/a

[1] The difference was calculated by subtracting the < 53 μm fraction from the 53 - 2000 μm fraction

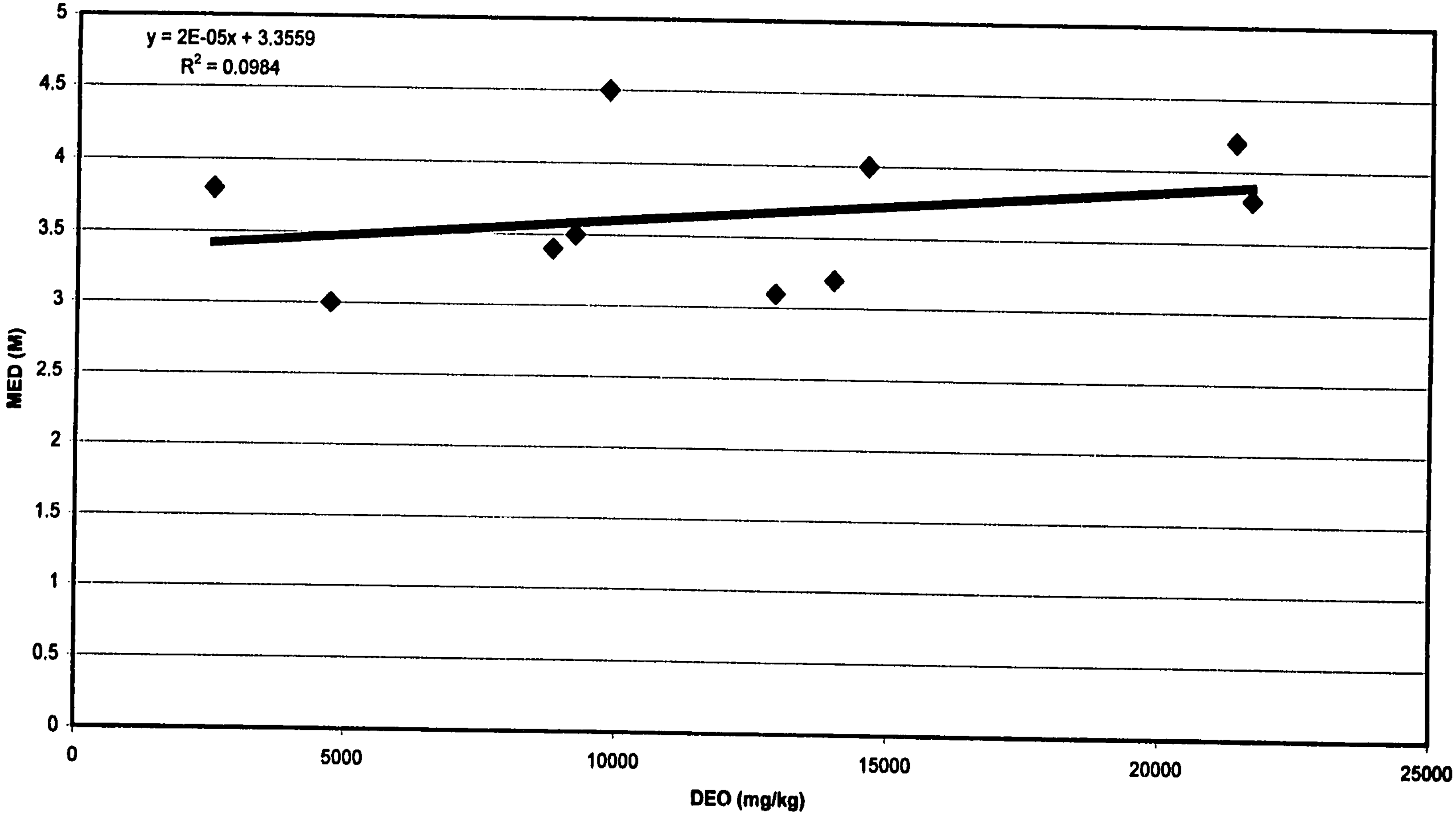

Figure 2-9: Regression of MED (*M*) on DEO (mg/kg) in < 53 μm fraction of powdery surface soil.

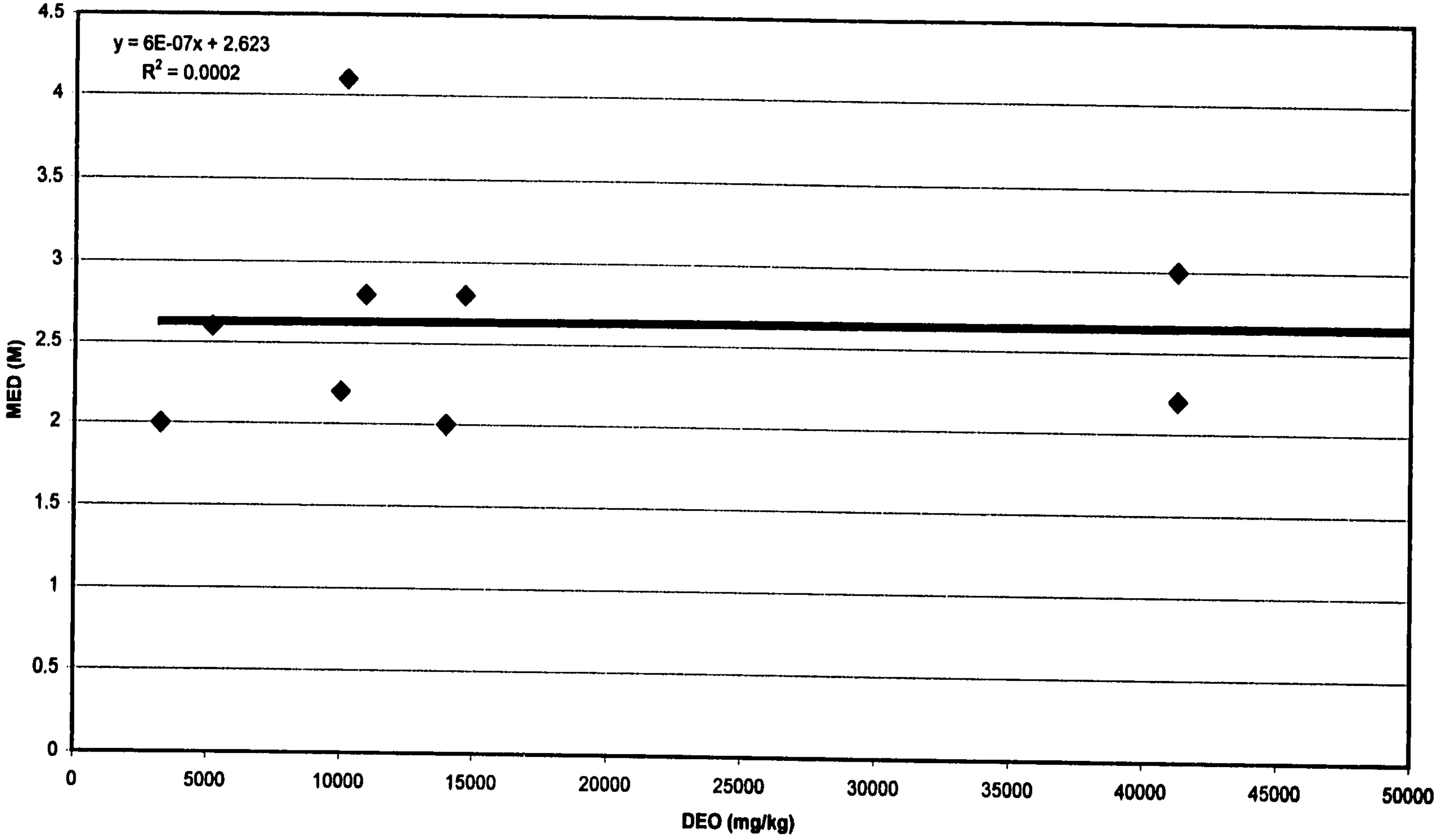

Figure 2-10: Regression of MED (*M*) on DEO (mg/kg) in 53 – 2000 μm fraction of powdery surface soil.

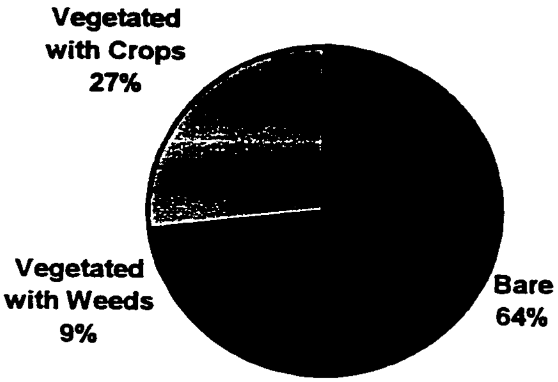

Figure 2-11: Plant growth at hydrophobic soil sites.

2.7 References

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Chapter 3: Characterization of Twelve Hydrophobic and Wettable Soil Pedons in Alberta[1]

3.1 Introduction

Soil hydrophobicity may develop after prolonged exposure of soil to petroleum. Plice (1948) and McGill et al. (1981) reported the association of petroleum contamination with development of soil hydrophobicity. Hydrophobic soils retard or restrict the infiltration of water; they are dry, often have a powdery surface structure, and support sparse plant growth. In chapter 2, we determined that these soils are not restricted to soil order, textural class, or by topography of the landscape. Residual oil contamination, powdery surface structure and the absence of vegetation can be indictors of the presence of hydrophobicity; however these conditions are not true for all hydrophobic sites.

Roy and McGill (1998) found that, in comparison to wettable surface soils, hydrophobic soils were found to have a higher content of mineral nitrogen and total carbon, a comparable pH and slightly lower clay content. They concluded that hydrophobic soils do not differ appreciably from adjacent wettable soils in their inorganic chemistry; they differ mostly in their physical and biological characteristics.

Hydrophobicity is typically thought of as a surface soil condition; influencing the top 10 to 15 cm of the soil (Roy and McGill 1998). Extensive research has been conducted on the water movement through hydrophobic soil profiles (Sawatsky and Li 1997; Ritsema et al. 1997; Dekker and Ritsema 2000). This literature describes the formation of fingered flow patterns through hydrophobic soil. Between these preferential flow paths dry, hydrophobic soil zones and pockets persist (Dekker and Ritsema 2000). Both Ritsema et al. (1997) and Dekker and Ritsema (2000) found that hydrophobicity tended to be confined to the surface soil layers, but zones of hydrophobic soil were found to depths of 50 cm; it is unclear if this research extended deeper than 50 cm in the soil profile.

In this chapter, I report results from detailed examination of soil pedons at 12 of the sites characterized in chapter 2. In the hydrophobic soil pedons we expected to find evidence of relic crude oil contamination in the form of subsurface oil lenses, petroleum odour or the presence of hardpans. Compared to wettable soil pedons, we anticipated a higher amount of

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[1] This work was part of a larger project. Some of the results reported here were previously reported in Roy et al. (2000).

dichloromethane extractable organics (DEO) and total organic carbon (TOC) in the hydrophobic soil pedons. The majority of the sites contained subsurface indicators of previous crude oil contamination events; however, at some sites there were no indicators of any previous subsurface oil contamination. We found a positive correlation between the severity of hydrophobicity and DEO and also developed a regression of DEO on TOC in wettable soils. The detection of hydrophobicity in the field can be extremely difficult and in some cases soil pedons that were wettable and apparently pristine in the field were hydrophobic when dried and analyzed in the laboratory.

3.2 Materials and Methods

3.2.1 Site Selection

Sites were chosen from the 26 locations described in Chapter 2. We chose 12 sites that ranged in soil texture; vegetation establishment; characteristics of hydrophobicity (hardpans, tar balls, surface soil structure); eco-regions; and soil orders. The 12 sites selected contained representatives from the Chernozemic, Gleysolic, Luvisolic, and Solonetzic soil orders. The sites selected extend northeast from Calgary to Cold Lake.

3.2.2 Field Profile Description

The hydrophobic pit was in the middle of the most affected area, and the control pit was outside of the hydrophobic patch, with the same topographical position and aspect as the hydrophobic profile to try to eliminate differences in morphological properties and pedological origin. Control pits were located in apparently wettable soil, which supported healthy plant growth and showed no evidence of field hydrophobicity. Each pit was excavated with a shovel to the C horizon. We used samples from these paired pedons to examine relations among soil hydrophobicity, DEO and TOC, and to examine differences in the physical and chemical characteristics of the hydrophobic and wettable soil pedons.

The soil pedons were described according to the Canadian System of Soil Classification. Descriptions included: horizon designation; horizon thickness; soil texture; structure; colour; mottles; calcareousness; and rooting depth.

Soil samples were collected from each soil horizon and placed in 1 L glass jars. We collected three 1 L random samples of wettable surface soil (0 - 10 cm) and a 5 L sample of hydrophobic surface soil (0 - 10 cm).

3.2.3 Laboratory Analysis

Characterization of Physical Properties

Particle size analysis was performed by the hydrometer method described by McKeague (1978), without pre-treatment for the removal of organic matter or soluble salts. Care was taken to ensure the complete wetting of samples. This entailed mixing the soil samples with sodium hexametaphosphate solution and allowing them to soak overnight. Samples were mixed with a milk-shake mixer for 10 min immediately before analysis. Textural class names were assigned using the criteria from the Canadian System of Soil Classification (1987).

Characterization of Chemical Properties

Electrical conductivity of the samples was determined using a Model 31 Conductivity Bridge (Yellow Springs Instrument Co. Inc.). Prior to taking the reading I mixed 10 g of air-dried soil with 20 ml deionized water in a 60 mL Nalgene bottle, placed it on a reciprocal shaker for 30 min and allowed the samples to settle for 1 h. Shaking the samples on a reciprocal shaker for 30 min ensured complete wetting of the samples.

To determine soil pH I followed the method of Hendershot et al. (1993), in which soil pH is measured on a 2:1 mixture (w:v) soil: 0.01 *M* $CaCl_2$. I used a Corning pH meter (model 10), with a Calomel electrode. Shaking the samples on a reciprocal shaker for 30 min to completely wet the samples.

Total Organic Carbon, Inorganic Carbon and Total Nitrogen

TOC, total carbon (TC) and total nitrogen (TN) were measured on a Carlo Erba NA-1500 series II CN elemental analyzer following the method of Ellert and Janzen (1996). TC and TN were measured on intact samples by high temperature oxidation, followed by gas chromatographic separation and IR detection. TOC was measured after carbonates were removed with HCl. TIC was calculated as the difference between TC and TOC (TIC = TC – TOC).

Extractable Organic Content in Soil

We used dichloromethane extraction to determine the extractable organic content of air-dried soil samples. The moisture content was determined on 20 g of each air-dried sample by placing the samples in the oven at 105 °C for 24 h. Another 20 g of each sample was prepared for determination of the DEO content by mixing the sample with an equal volume of granular anhydrous $MgSO_4$. The soil was subsequently placed in a cellulose thimble and Soxhlet extracted for 6 h at the rate of 10 cycles h^{-1}, using glass-distilled dichloromethane. Paper tissues were used to prevent solids from escaping from the thimble and accumulating in the solvent flasks. The dichloromethane extracts were concentrated on a rotary evaporator, transferred to aluminum dishes, and allowed to dry in a fume hood. The DEO concentration for each soil sample was calculated as follows:

$$DEO \quad = \frac{E}{S-E} 10^{6} \; mg/kg$$

Where E = air-dried extract (g); and S = oven-dried soil (g).

Assessment of Soil Hydrophobicity

The Molarity of Ethanol Droplet (MED) method (Watson and Letey 1970; King 1981) was used to measure soil hydrophobicity. I assessed soil hydrophobicity using ethanol concentrations of 0.2 *M* intervals in the range of 0.0 – 6.0 *M*. Prior to analysis, soil samples were passed through a 1 mm sieve, oven dried at 105 °C for 24 h and cooled in a desiccator. We used the interpretation classes provided by King (1981), which are: MED $\leq 1\,M$ = not significantly hydrophobic; MED from 1.2 *M* – 2.2 *M* = moderately hydrophobic; and MED $\geq$ 2.2 *M* = severely hydrophobic.

3.2.4 Statistical Analyses

Normality Tests

I used means weighted by horizon thickness to combine the data for each profile into A, B and C horizons. This step was necessary to make comparisons between hydrophobic and wettable soil pedons. The Kolmogorov-Smirnov, Anderson-Darling, and Cramér-von Mises tests were used to determine if these data were normally distributed. These tests were preformed using PROC UNIVARIATE in SAS/STAT statistical software (SAS Institute, 1999) and a value of 5 % was selected as the level of significance for all tests.

Pedon Analysis

To analyze differences within physical or chemical variables between hydrophobic and wettable soil pedons I used the non-parametric Wilcoxon signed rank test, performed using PROC NPAR1WAY WILCOXON in SAS/STAT statistical software (SAS Institute 1999). Based on the results of the tests for normality and because of the small sample size, I chose to use the Wilcoxon signed rank test for comparisons of means between hydrophobic and wettable pedons.

Regression Analysis

Regression analysis was conducted using EXCEL statistical software (Microsoft 2000). For the regression of MED on DEO I used samples with a MED > 0 *M* and DEO < 30,000 mg/kg. For the DEO and TOC regression I used samples with a MED = 0 M and DEO < 1,000 mg/kg.

3.3 Results

3.3.1 Pedons Description and Classification

A horizons of the hydrophobic pedons tended to be slightly thinner than the A horizons in the wettable pedons. Compared to wettable soil pedons, structure appears disturbed in the hydrophobic soil pedons (Figure 3-1). At two sites the water table was within 100 cm of the soil surface in both the hydrophobic and wettable soil pedons. Evidence of crude oil contamination, oily hardpans, tar balls, hydrocarbon odour or residual oil lenses, was present at approximately half of the sites. Refer to Appendix B (Table B-1) for complete pedon descriptions and classifications of the 12 sites characterized.

We attempted to dig the wettable soil pit in pristine soil, which had not been contaminated with crude oil. At each site the wettable soil pit was in an area that supported healthy vegetation and had a field determined MED = 0 *M*. After the profile and surface samples were dried, I found lab determined MED > 0 *M* for some of the samples (Table B-2 in Appendix B).

Wilcoxon signed rank tests were used to compare soil parameters in the hydrophobic and wettable soil pedons because approximately 1/3 of the 78 variable x layer combinations were not normally distributed over the 12 sites; of these, 17 were in the surface (0 – 10 cm samples) and A horizons (Table 3-1). We found statistically significant differences between hydrophobic and field wettable pedons for several variable x layer combinations. Most of the differences were observed in the surface layer and A horizon samples (Table 3-2 and 3-3). Only 2 of the 10 variables in the B horizon were significantly different between hydrophobic and field wettable pedons (Table 3-4). No significant differences were detected in the C horizon (Table 3-5).

Particle Size Distribution

In the four soil layers studied, there were no statistically significant differences between the clay contents of the hydrophobic soil samples and the field wettable soil samples (Tables 3-2 – 3-5). The clay content of both the hydrophobic and field wettable soil samples tended to be intermediate (200 – 400 g/kg soil), but some samples had clay contents as low as 35 g/kg (Table B-2 in Appendix B).

Soil pH

Mean pH tended to be slightly higher in all horizons from hydrophobic pedons compared to corresponding wettable pedons (Figure 3-2). However, only in the A horizons were pH values significantly different (Table 3-3). Soil pH increased with increasing depth into the pedon (Figure 3-2). Hydrophobic and wettable soil samples generally had a neutral pH, however the pH of the soil ranged from 3.35 (acidic) to 8.0 (alkaline) (Table B-2 in Appendix B).

Electrical Conductivity

Electrical conductivity was significantly higher in hydrophobic surface layers and hydrophobic A horizons compared to field wettable surface layers and field wettable A horizons (Table 3-2 and Table 3-3). No significant differences in electrical conductivities were detected between hydrophobic and field wettable B or C horizons. The hydrophobic and wettable soil samples had low electrical conductivity values (Table B-2 in Appendix B).

Carbon and Nitrogen Content

I found a significant TC, TOC and TIC difference in hydrophobic and field wettable surface soil (Table 3-2). I did not find a significant TN difference between hydrophobic and wettable surface soil or A horizons. The hydrophobic A horizon had a significantly higher TC and TOC and a significantly lower TIC (Table 3-3).

TOC decreased down the pedon (Figure 3-3). The ratio of TOC/TN (C/N) also decreased down the pedon (Figure 3-4). TOC and C/N ratio tended to be higher in hydrophobic than in wettable soil samples. Hydrophobic samples contained higher DEO (Figure 3-5) contents, which contribute to higher TOC with no concurrent increase in N.

DEO and TOC

Samples from all horizons contained measurable DEO, however not every sample contained petroleum; this provided an opportunity to determine a relationship between DEO and native soil organic matter. For the regression analysis I used samples from wettable soil pits with laboratory-determined MED = 0 *M* and DEO < 1,000 mg/kg and a positive linear relationship emerged. About 72% of the variability in DEO was predictable from the TOC content of the soil (Figure 3-6). The resulting equation DEO (mg/kg) = 17.56 x TOC (g/kg) – 0.28, suggests that approximately 1.8 % of soil TOC is extractable by DEO in samples with MED = 0 *M*.

MED in Relation to DEO

Mean MED values and DEO contents were significantly higher in hydrophobic surface soils than in field wettable surface soils (Table 3-2). In A horizons, the hydrophobic soil had a significantly higher mean MED and mean DEO content than did the field wettable soil (Table 3-3). I found a significant difference in MED and DEO content between the hydrophobic and wettable B horizons (Table 3-4).

MED tended to decrease with increasing depth into the soil pedon (Figures 3-7). However this trend was not found at all sites (Figure 3-8). Typically soil hydrophobicity was a surface condition (Figure 3-8(a)) but it was at times subsurface (Figure 3-8(b)) or throughout the pedon (Figure 3-8(c)).

MED and DEO tended to vary together in moving down the pedon (Figure 3-9), consequently I regressed MED on DEO. Analyses were performed on the data range: MED > 0 *M*; DEO < 30,000 mg/kg. Soil samples with DEO > 30,000 mg/kg were excluded from the regression because they substantially exceed the petroleum content at which petroleum contamination is a more severe problem than hydrophobicity. I found a positive correlation between MED and DEO. The linear equation: MED (*M*) = 0.0001 DEO mg/kg + 1.15 had a coefficient of determination equal to 45 % (Figure 3-10).

Roy et al. (2000) explain that DEO might be distributed in soil as spots that vary in size rather than varying only in number. If this were the case, MED should correlate with $\mathrm{DEO}^{2/3}$ (Roy et al. 2000). We found that the geometric equation: MED (*M*) = 0.24 – 0.00014 DEO (mg/kg) + 0.0083 $\mathrm{DEO}^{2/3}$ (mg/kg) had a coefficient of determination equal to 52 % (Figure 3-11). This relationship allows for variations in size and number of hydrophobic spots, and yields MED = 0.2 *M* at DEO = 0 mg/kg, whereas the linear regression yields MED = 1.2 *M* at DEO = 0 mg/kg.

MED, pH and DEO

To determine if soil pH modified the DEO – MED correlations, I conducted a regression including pH with $\mathrm{DEO}^{2/3}$. I chose to use $\mathrm{DEO}^{2/3}$ rather than DEO because the regression of MED on $\mathrm{DEO}^{2/3}$ had a higher coefficient of determination (52 %) compared to the regression of MED on DEO, which had a coefficient of determination equal to 45 %. The relationship MED = 3.87 - 0.53 pH + 0.00414 $\mathrm{DEO}^{2/3}$ yielded a coefficient of determination equal to 64 % (Figure 3-12).

3.4 Discussion

In a detailed field investigation of the top 30 cm of hydrophobic soil sampled in a grid pattern, Roy et al. (2000) found MED values and DEO contents were significantly higher in the surface (0 - 10 cm depth) than in the subsurface soil (10 - 30 cm depth). Wallis et al. (1990) reported that MED values declined with depth in hydrophobic soil pedons. They found severe hydrophobicity was confined to the top 3 cm of the soil where the carbon content was 51 g/kg. Moderate hydrophobicity was found between 3 and 15 cm depth, and slight hydrophobicity was expressed between 15 and 20 cm depth. Ritsema et al. (1997) and Dekker and Ritsema (2000) found that hydrophobicity tended to be confined to the surface soil layers. However, they found zones and pockets of hydrophobic soil, which extended into the profile to a depth of 50 cm; it is unclear if their profile research extended deeper than 50 cm. Dekker and Ritsema (2000) found that the severity of hydrophobicity decreased with increasing depth into the soil profile.

I also determined that hydrophobicity is predominately a surface soil condition and decreases in severity with increasing depth into the soil. However, two sites had wettable surface soil (top 10 – 15 cm), with a field expressed hydrophobic soil layer directly underneath. This layer was approximately 10 cm thick. I found subsurface hydrophobicity at four sites after laboratory-determination of MED on samples.

Subsurface hydrophobicity has been reported in fire-induced hydrophobic soils, however this is attributed to the heat induced movement of hydrophobic substances downward (DeBano and Rice 1973; Savage 1974; DeBano 2000). I postulate that petroleum-induced hydrophobic soils have the potential to develop subsurface hydrophobicity because of the large addition of crude oil to the soil, which may have occurred below the soil surface or surface spills may have been covered by clean soil during "remediation", leaving the contaminated soil below. However subsurface soils may not be given the opportunity to express hydrophobicity, as is the case with the samples from the B and C horizons, which expressed hydrophobicity only after being dried in the laboratory. It has been widely accepted that soils must dry before hydrophobicity is detectable (Bond 1964; King 1981; Ma'shum and Farmer 1985; Wallis et al. 1990; Ritsema et al. 1997). The B and C horizons in the pedons we studied did not have the opportunity to dry sufficiently.

Variable expression of hydrophobicity can also explain dynamics in patch size. The areas of poor or no crop growth may vary from season to season, depending on the severity of drying (Chan 1992). The influence of drying on the expression of hydrophobicity may relate to the visible expansion or contraction of the patch, in accordance with weather or tillage. Care is needed to distinguish between the presence and expression of hydrophobicity. Sites may appear to be remediated and then revert to their hydrophobic condition after drying. The size of the hydrophobic area may not change, however it may appear to expand or contract.

Roy et al. (2000) found a positive correlation between MED and $DEO^{2/3}$ ($R^2 = 0.72$; $n = 113$) for surface samples taken from a grid pattern at four hydrophobic soil sites. Their regression was done on samples with a DEO < 30,000 mg/kg and MED > 0 *M*. I also conducted a regression using samples from the range MED > 0 *M*; DEO < 30,000 mg/kg from the pedon samples at 12 sites and obtained a positive correlation, however my $R^2 = 0.52$; $n = 46$.

Compared to the surface soil data studied by Roy et al. (2000), the profile MED data appear to be influenced by factors other than DEO alone. Additional variability can be attributed to the wider range of horizons with differing properties. Soil pH increases with depth into the profile, which is correlated with carbonate concentration. Sixty-four percent of the variability in MED was accounted for by soil pH and $DEO^{2/3}$ in combination, compared to the 52 % accounted for by DEO + $DEO^{2/3}$. Therefore, I conclude that, the relationship between MED and DEO may be modified by soil conditions related to pH.

The positive correlation between MED and DEO can be deceptive. DEO extractions do not eliminate soil hydrophobicity (Roy et al. 1999; Roy and McGill 2000), therefore it can be inferred that DEO alone does not cause hydrophobicity. Constituents contained in DEO or constituents related to DEO or their configurations are potentially the causes of hydrophobicity (Roy et al. 1999).

I determined the content of DEO on wettable soil samples with MED = 0 *M*. We believe that these samples had not been contaminated with petroleum. These samples showed no field indications of contamination; they supported healthy vegetation and did not contain residual oil contamination (tar balls and hardpans); they also had oven-dried MED = 0 *M* and DEO contents < 1000 mg/kg. This gave an opportunity to determine if native soil carbon contributes to DEO. We found approximately 72% of the variability in DEO was predictable from TOC content in the soil. This relationship could be useful in establishing protocols to correct DEO values for contributions of native soil carbon when assessing remediation endpoints.

Standard analytical methods for soil physical and chemical properties, which require suspension in water, present numerous disadvantages for the characterization of hydrophobic soils. When analyses require an aqueous phase, extra care had to be taken to mix and wet the soil. Shaking the soil with the aqueous phase for 30 min on a reciprocating shaker seemed to be effective at wetting the soil. However, it was difficult to ensure complete wetting of the soil took place, and it was not possible to determine if the water penetrated or dispersed micro-aggregates. The problem of incomplete wetting may have been most severe in particle size analysis of hydrophobic soil samples. Incomplete dispersion of silt-sized aggregates may have skewed the particle size results. Air trapped in silt-sized aggregates that are not completely wetted could reduce their density and reduce settling velocity; the result would be an over estimation of clay content. Effort was made to overcome such difficulties, but caution should be taken when attempting the analysis of hydrophobic soils.

3.5 Summary and Conclusion

At 12 sites soil pedons within and adjacent to the hydrophobic patch were described and sampled. The results of this work can be summarized as follows: (1) hydrophobic surface soil samples had significantly higher MED, TC, TOC, TIC, electrical conductivity and DEO than wettable surface soil samples; (2) hydrophobic A horizon samples had significantly higher pH, MED, TC, TOC, electrical conductivity and DEO and significantly lower TIC than wettable A horizon samples; (3) samples from the B horizon hydrophobic soil had significantly higher MED values and DEO concentrations that the wettable B horizon samples; (4) C horizon hydrophobic soil samples did not differ significantly from the wettable soil samples in terms of the chemical and physical parameters analyzed; (5) MED and DEO were positively correlated, there correlation was modified by pH: MED (M) = 3.86 - 0.533 pH + 0.0041 $\mathrm{DEO}^{2/3}$(mg/kg) with a coefficient of determination equal to 52 %. (6) Indigenous soil carbon contributed to DEO in apparently pristine samples with an MED = 0 M, such that DEO (mg/kg) = 17.56 x TOC (g/kg) – 0.29 (n=36, $R^2 = 0.72$). This relationship may be useful in establishing how to correct DEO values for contributions of native soil carbon and assessing remediation endpoints.

Hydrophobicity tends to be more strongly expressed as a surface soil condition. This is probably related to the tendency for higher concentration of DEO in the surface soil. Surface soils also have a greater potential to express hydrophobic conditions because they are more apt to dry than subsurface soils; to express hydrophobicity, a soil must dry. We observed only two sites with field expression of subsurface hydrophobicity; however, after laboratory-determination of MED on all samples, subsurface hydrophobicity was detected at four sites. Two of the field-wettable soil pedons were found to be severely hydrophobic after laboratory determination of MED.

3.6 Tables and Figures

Table 3-1: Results normality Tests. Tests were conducted on parameter means weighted by layer thickness for the 12 hydrophobic and 12 field wettable soil pedons.

Parameters	Surface Layer		A horizon	
	Hydrophobic	**Wettable**	**Hydrophobic**	**Wettable**
Thickness	*	*	No	Yes
pH	No	No	No	No
MED	No	Yes	No	Yes
TC	Yes	No	Yes	Yes
TOC	Yes	No	Yes	Yes
TIC	Yes	Yes	Yes	Yes
TN	No	No	No	No
EC	Yes	Yes	No	Yes
Clay	No	No	Yes	Yes
DEO	No	Yes	Yes	Yes

Parameters	B Horizon		C Horizon	
	Hydrophobic	**Wettable**	**Hydrophobic**	**Wettable**
Thickness	Yes	No	Yes	No
pH	No	No	Yes	Yes
MED	Yes	Yes	Yes	*
TC	Yes	Yes	No	Yes
TOC	Yes	Yes	Yes	Yes
TIC	Yes	Yes	Yes	Yes
TN	Yes	Yes	Yes	No
EC	Yes	Yes	Yes	Yes
Clay	No	No	Yes	Yes
DEO	Yes	Yes	Yes	Yes

* Normality tests could not be conducted on the thickness of the surface layer because all samples were taken to a depth of 10 cm. Normality tests could not be conducted on the MED values of the field wettable C horizon samples because all samples had MED = 0.0 *M*.

Yes = normal distribution and No = not normally distributed

Table 3-2: Comparison of surface soil (0 – 10 cm) properties between hydrophobic and field wettable pedons at 12 sites using the Wilcoxon signed rank test.

Parameters	Condition	Mean	Standard Deviation	Degrees of Freedom	Pr > t	Significant Difference $\alpha = 0.05$
pH	Hydrophobic	5.69	0.72	12	0.5375	No
	Wettable	5.46	0.57			
MED (*M*)	Hydrophobic	3.12	0.78	12	<0.0001	Yes
	Wettable	0.52	0.97			
TC (g/kg)	Hydrophobic	50.1	29.5	12	0.0129	Yes
	Wettable	27.8	17.9			
TOC (g/kg)	Hydrophobic	48.9	28.9	12	0.0128	Yes
	Wettable	27.4	17.8			
TIC (g/kg)	Hydrophobic	1.2	1.1	12	0.0043	Yes
	Wettable	0.5	0.6			
TN (g/kg)	Hydrophobic	2.6	0.8	12	0.4257	No
	Wettable	2.3	1.1			
EC (dS/m)	Hydrophobic	36	3.42	12	0.0015	Yes
	Wettable	0.11	0.68			
Clay (g/kg)	Hydrophobic	146.5	62.1	10	0.2252	No
	Wettable	178.6	62.1			
DEO (mg/kg)	Hydrophobic	14,700	12,000	12	0.0002	Yes
	Wettable	2,700	5,300			

Table 3-3: Comparison of A horizon properties between hydrophobic and field wettable pedons at 12 sites using the Wilcoxon signed rank test.

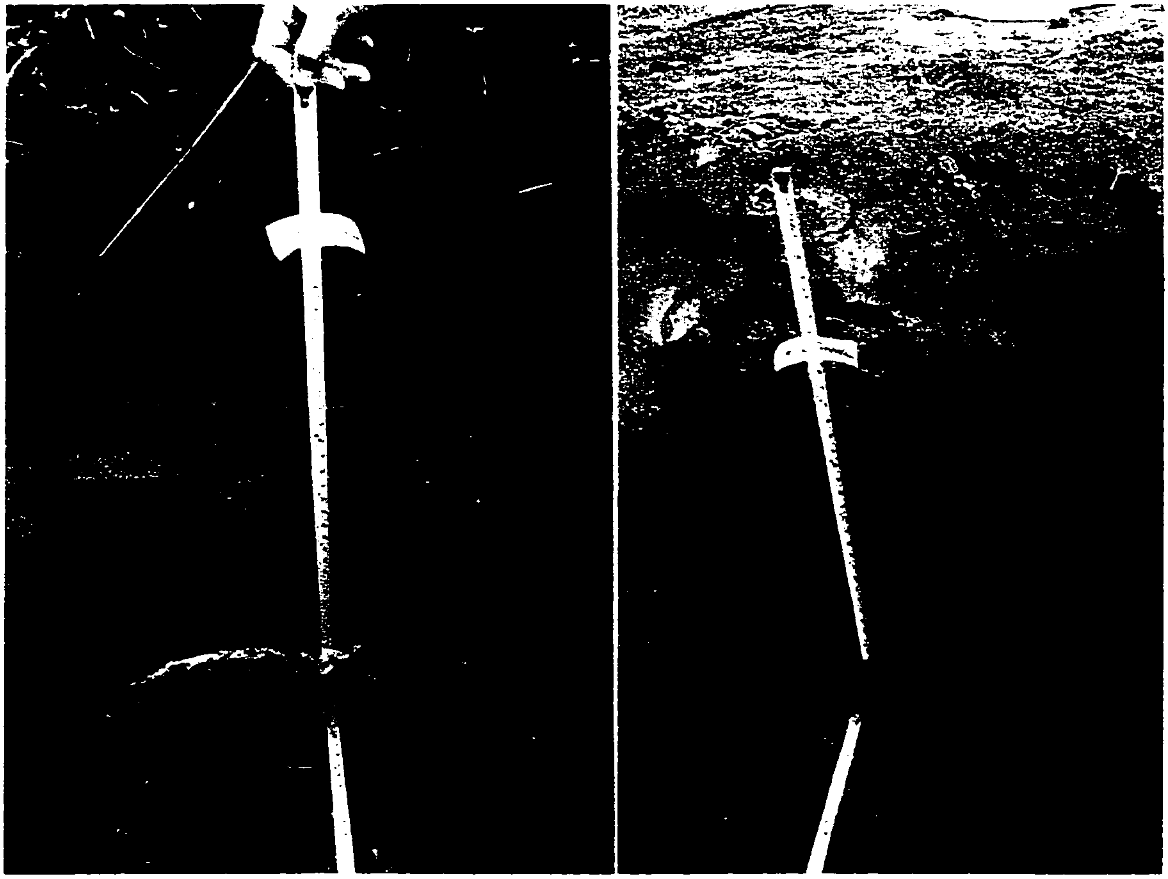
Parameters	Condition	Mean	Standard Deviation	Degrees of Freedom	Pr > t	Significant Difference $\alpha = 0.05$
Thickness (cm)	Hydrophobic	18.77	6.51	12	0.2355	No
	Wettable	22.31	8.41			
pH	Hydrophobic	6.18	0.81	12	0.0511	Yes
	Wettable	5.44	0.99			
MED (*M*)	Hydrophobic	2.95	1.31	12	0.0004	Yes
	Wettable	0.49	0.96			
TC (g/kg)	Hydrophobic	51.9	37.5	12	0.0082	Yes
	Wettable	23.5	12.9			
TOC (g/kg)	Hydrophobic	50.4	36.7	12	0.0111	Yes
	Wettable	23.2	12.8			
TIC (g/kg)	Hydrophobic	1.4	1.5	12	0.0017	Yes
	Wettable	2.6	0.2			
TN (g/kg)	Hydrophobic	2.4	1.0	12	0.2694	No
	Wettable	2.0	0.8			
EC (dS/m)	Hydrophobic	0.24	0.19	11	0.0387	Yes
	Wettable	0.10	0.070			
Clay (g/kg)	Hydrophobic	169.1	38.6	12	0.4058	No
	Wettable	163.9	69.6			
DEO (mg/kg)	Hydrophobic	22,000	2,360	12	0.0002	Yes
	Wettable	2,300	5,400			

Table 3-4: Comparison of B horizon properties between hydrophobic and field wettable pedons at 12 sites using the Wilcoxon signed rank test.

Parameters	Condition	Mean	Standard Deviation	Degrees of Freedom	Pr > t	Significant Difference $\alpha = 0.05$
Thickness (cm)	Hydrophobic	32.30	12.75	9	0.5956	No
	Wettable	41.40	25.97			
pH	Hydrophobic	6.40	1.26	10	0.3244	No
	Wettable	5.89	0.99			
MED (*M*)	Hydrophobic	1.34	1.86	10	0.0290	Yes
	Wettable	0.25	0.82			
TC (g/kg)	Hydrophobic	15.9	16.3	10	0.1597	No
	Wettable	7.9	5.2			
TOC (g/kg)	Hydrophobic	14.0	15.8	10	0.2240	No
	Wettable	7.1	4.4			
TIC (g/kg)	Hydrophobic	1.8	3.0	10	0.1063	No
	Wettable	0.7	1.5			
TN (g/kg)	Hydrophobic	0.9	0.6	10	0.8161	No
	Wettable	0.8	0.3			
EC (dS/m)	Hydrophobic	0.40	0.36	10	0.0611	No
	Wettable	0.22	0.39			
Clay (g/kg)	Hydrophobic	260.4	79.9	10	0.3918	No
	Wettable	248.8	73.8			
DEO (mg/kg)	Hydrophobic	7,900	1,520	10	0.0202	Yes
	Wettable	500	1,300			

Table 3-5: Comparison of C horizon properties between hydrophobic and field wettable pedons at 12 sites using the Wilcoxon signed rank test.

Parameters	Condition	Mean	Standard Deviation	Degrees of Freedom	Pr > t	Significant Difference $\alpha = 0.05$
Thickness (cm)	Hydrophobic	55.3	17.13	10	0.2197	No
	Wettable	48.44	20.09			
pH	Hydrophobic	6.71	1.16	10	0.2239	No
	Wettable	6.46	0.87			
MED (*M*)	Hydrophobic	0.54	1.26	10	0.1478	No
	Wettable	0.00	0.00			
TC (g/kg)	Hydrophobic	7.3	0.68	10	0.7675	No
	Wettable	7.5	0.91			
TOC (g/kg)	Hydrophobic	5.4	0.60	10	0.5539	No
	Wettable	3.3	0.14			
TIC (g/kg)	Hydrophobic	1.9	0.28	10	0.8159	No
	Wettable	4.2	0.83			
TN (g/kg)	Hydrophobic	0.5	0.01	10	0.9728	No
	Wettable	0.5	0.02			
EC (dS/m)	Hydrophobic	0.509	0.67	10	0.2927	No
	Wettable	0.528	1.01			
Clay (g/kg)	Hydrophobic	201.8	82.9	10	0.4118	No
	Wettable	245.9	122.7			
DEO (mg/kg)	Hydrophobic	2,700	5,800	9	0.3119	No
	Wettable	400	1,100			



Wettable Profile

Hydrophobic Profile

Figure 3-1: Wettable and hydrophobic soil profiles. The hydrophobic profiles appear to be more disturbed than the wettable profiles.

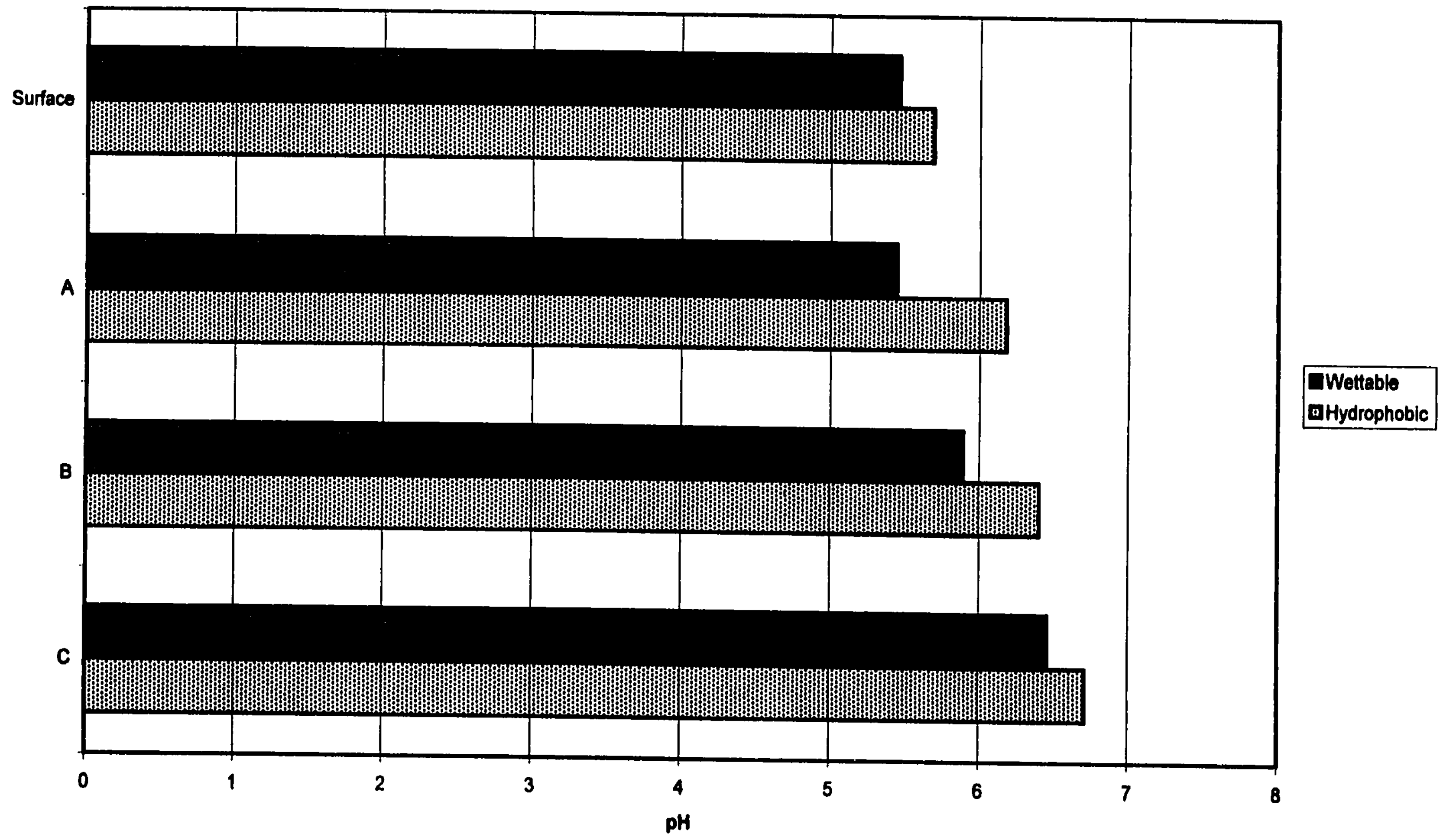


Figure 3-2: Mean pH of wettable and hydrophobic soil samples from surface, A, B and C horizons. Wettable samples are from pits adjacent to the hydrophobic patch, which were wettable in the field and hydrophobic samples are from pits in hydrophobic patches.

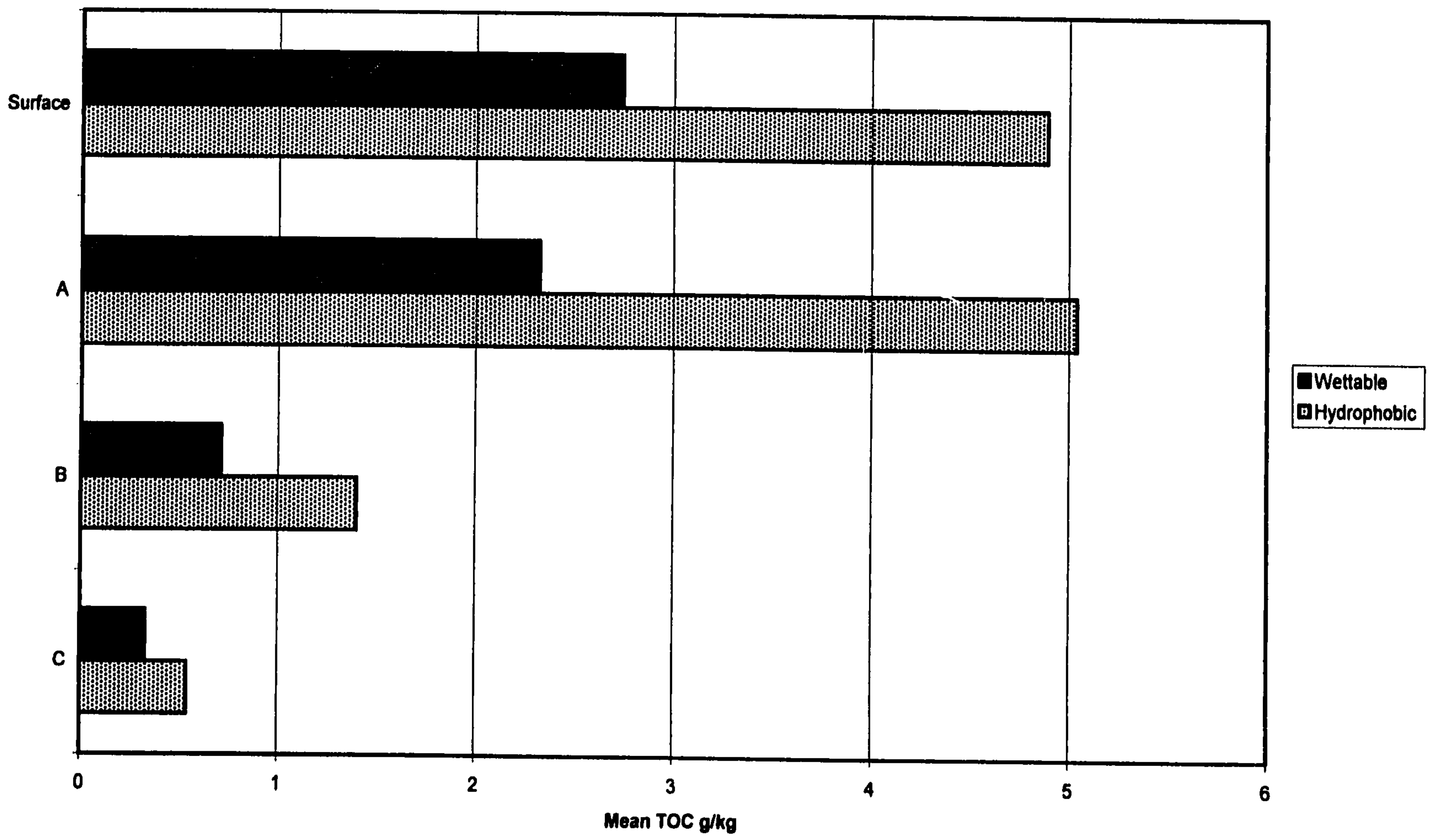


Figure 3-3: Mean TOC in wettable and hydrophobic soils samples from surface, A, B and C horizons. Wettable samples are from pits adjacent to the hydrophobic patch, which were wettable in the field and hydrophobic samples are from pits in hydrophobic patches.

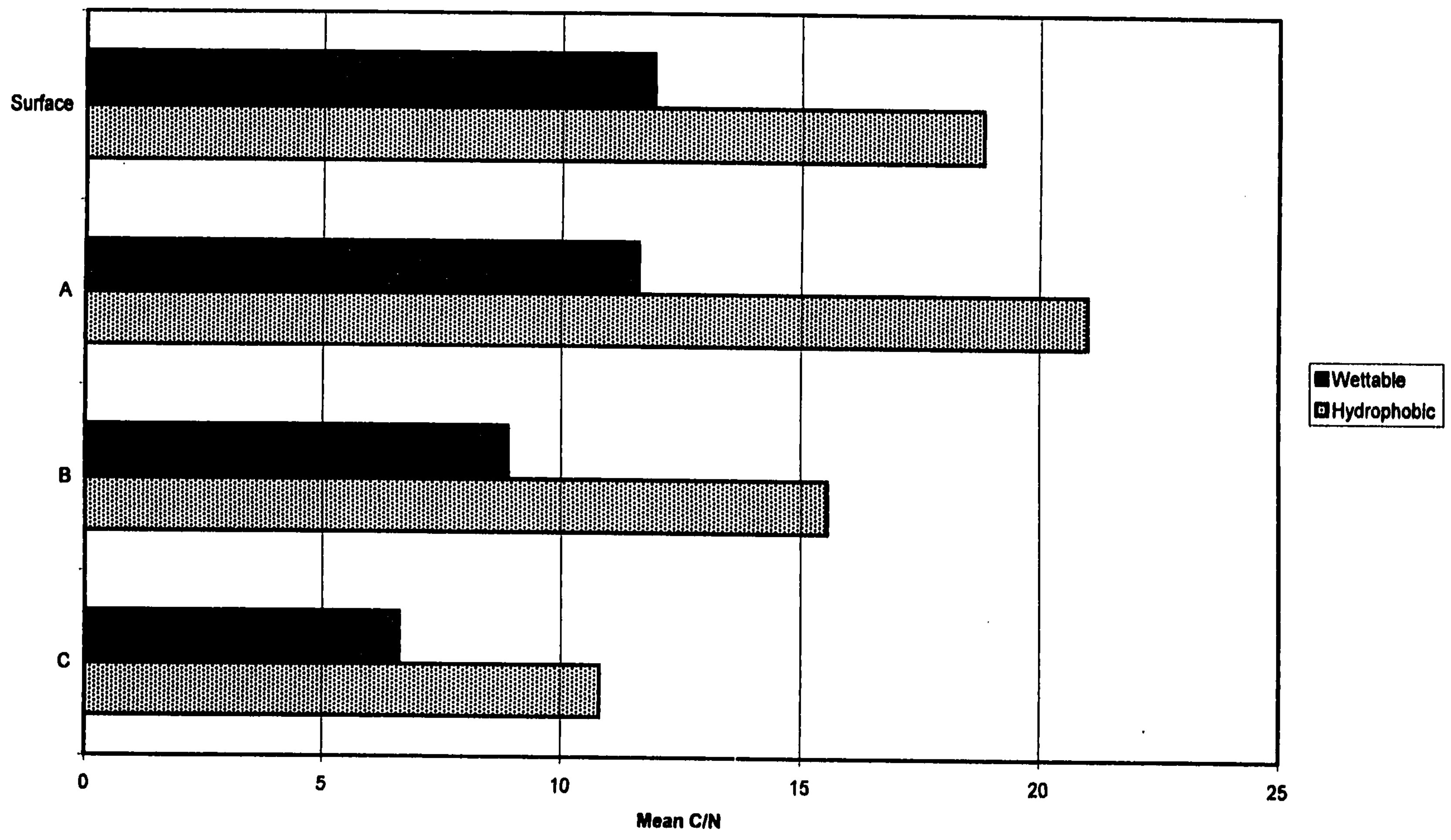


Figure 3-4: Mean ratios of C/N in wettable and hydrophobic soil samples taken from surface, A, B and C horizons. Wettable samples are from pits adjacent to the hydrophobic patch, which were wettable in the field and hydrophobic samples are from pits in hydrophobic patches.

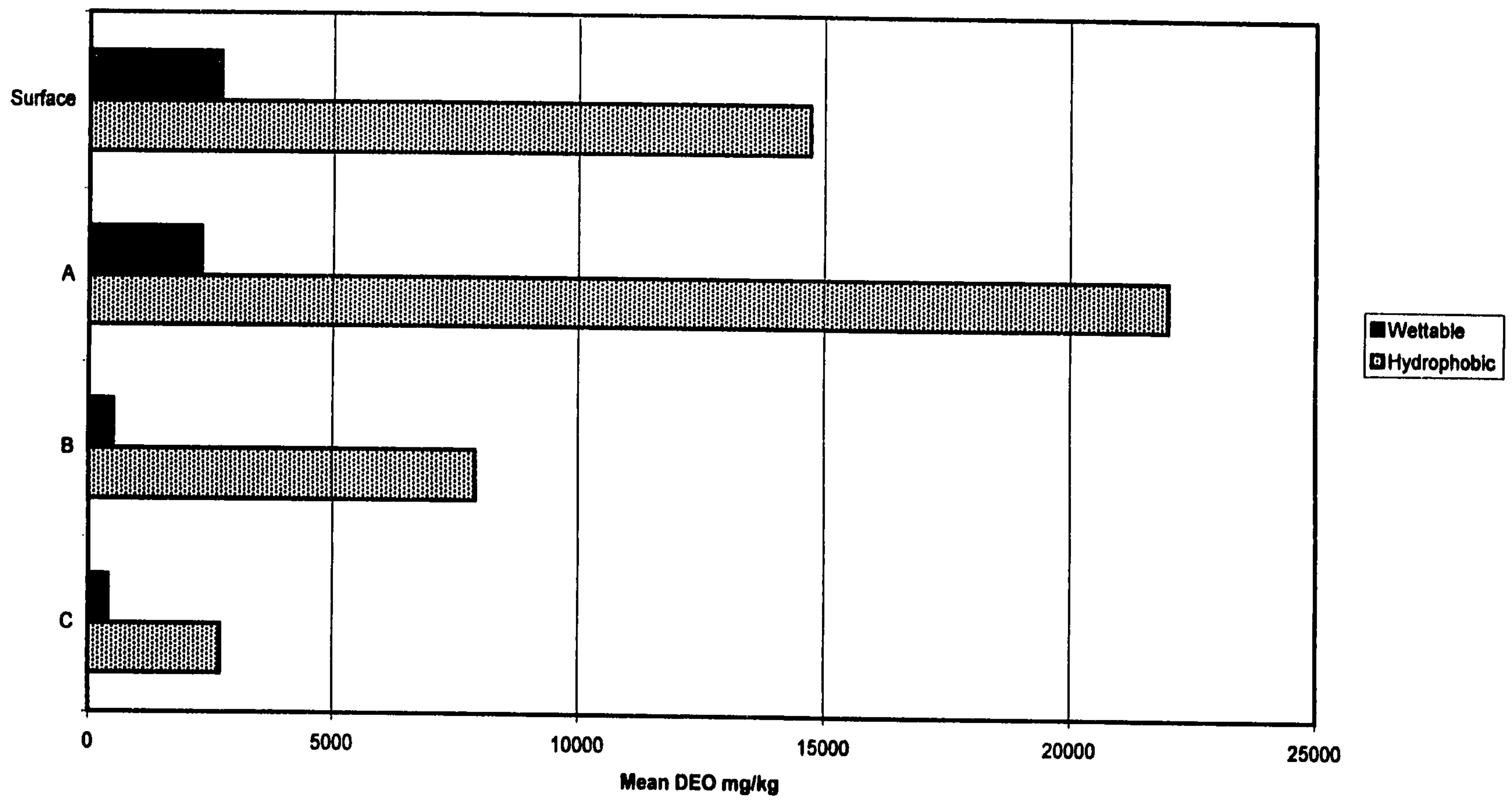


Figure 3-5: Mean Dichloromethane Extractable Organics (DEO) of wettable and hydrophobic soil samples taken from surface, A, B and C horizons. Wettable samples are from pits adjacent to the hydrophobic patch, which were wettable in the field and hydrophobic samples are from pits in hydrophobic patches.

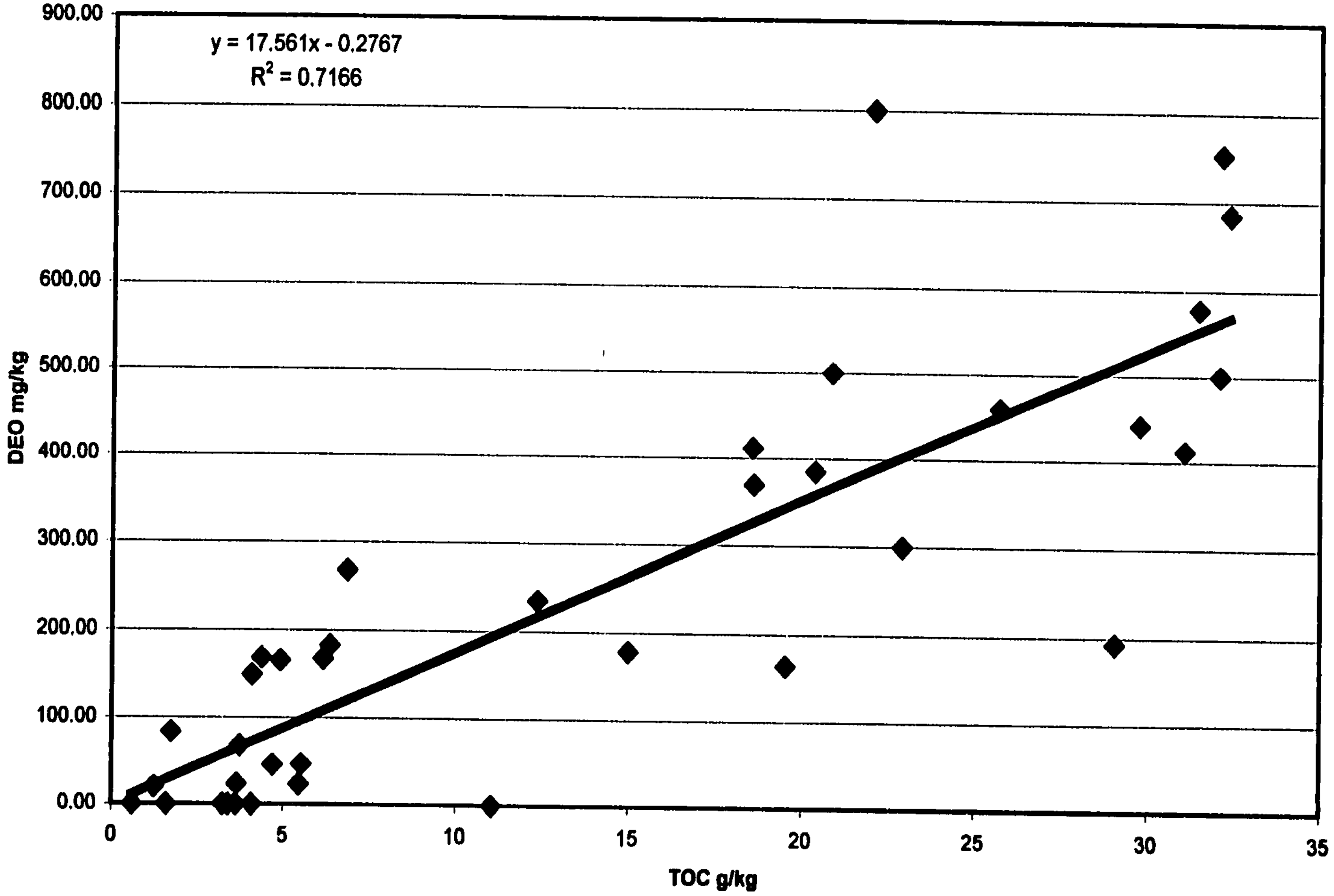


Figure 3-6: Regression of DEO on TOC in samples from wettable soil pits with laboratory determined MED = 0 *M* and DEO < 1,000 mg/kg (n = 36).

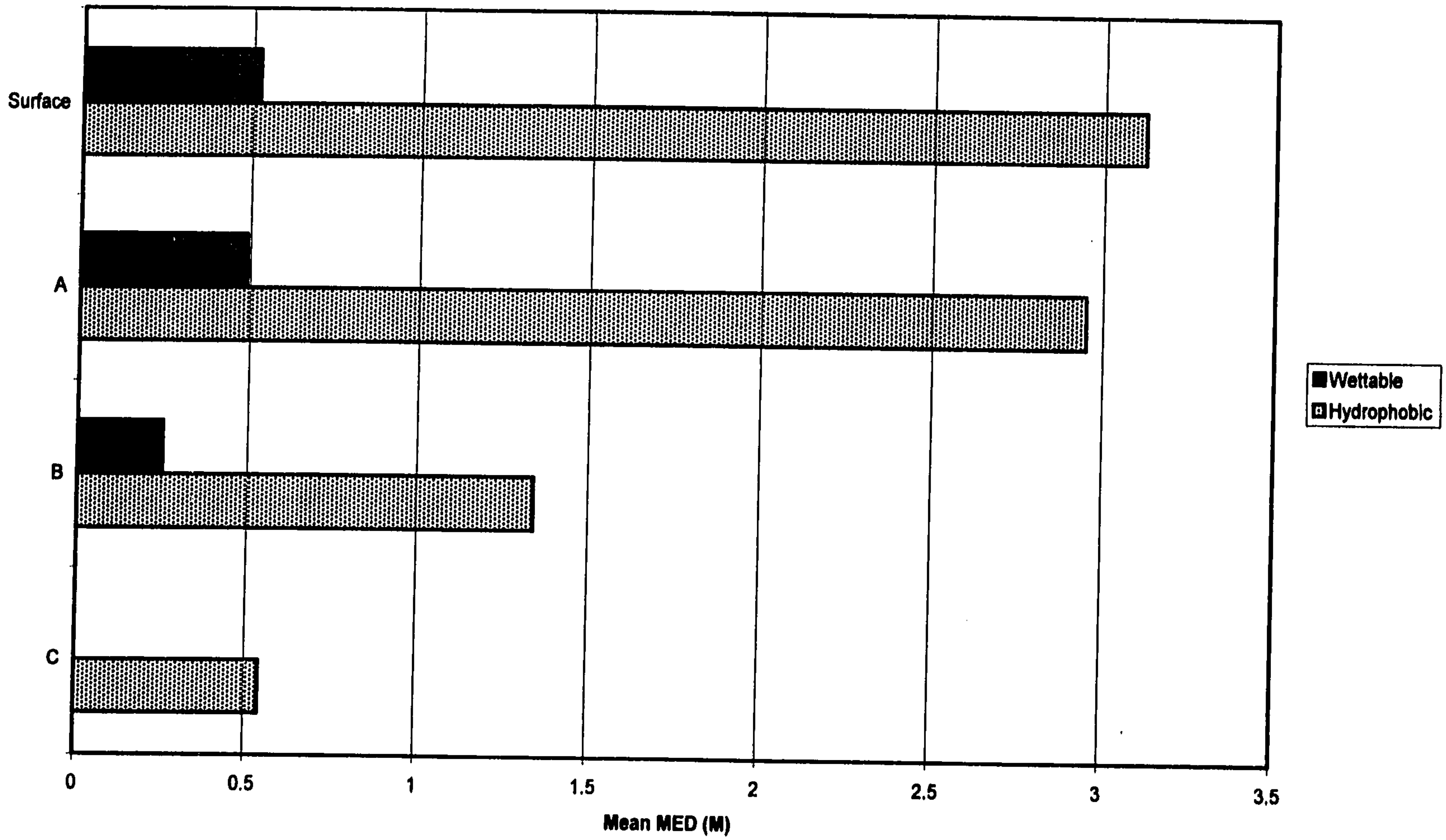


Figure 3-7: Mean MED test values for wettable and hydrophobic soil samples taken from surface, A, B and C horizons. Wettable samples are from pits adjacent to the hydrophobic patch, which were wettable in the field and hydrophobic samples are from pits in hydrophobic patches.

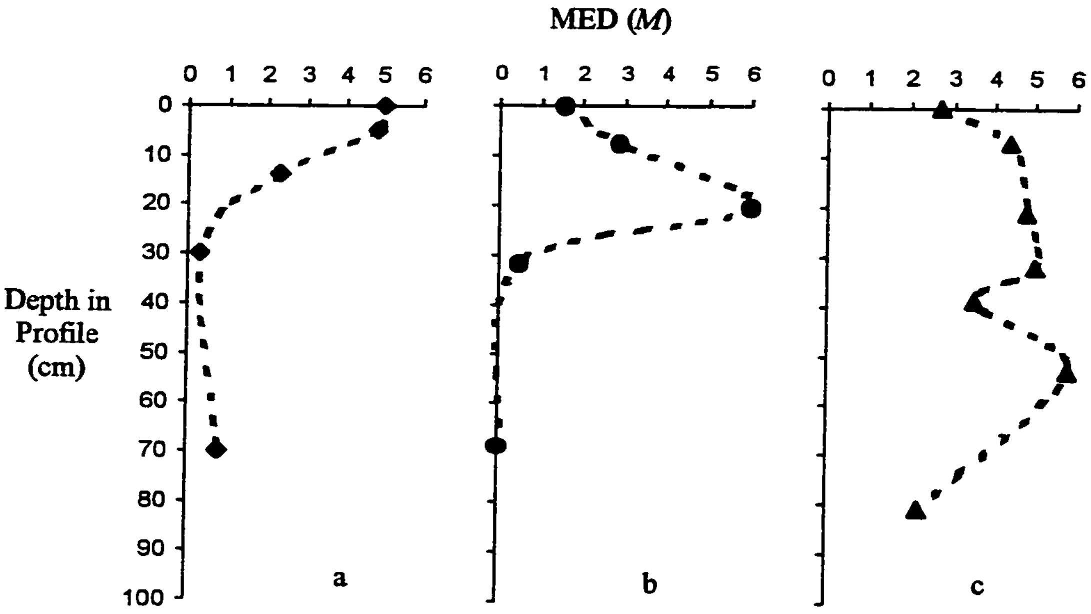


Figure 3-8: Three characteristic expressions of soil hydrophobicity. The pattern of profile (a) was most frequently observed. Two sites had subsurface hydrophobic soil as depicted in profile (b) and two sites had hydrophobicity throughout the entire profile as depicted in profile (c).

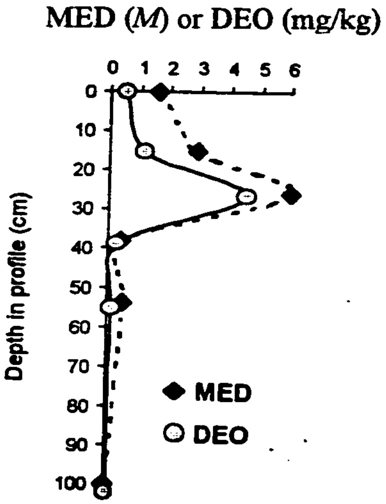


Figure 3-9: A soil profile showing that MED and DEO tended to vary together with depth.

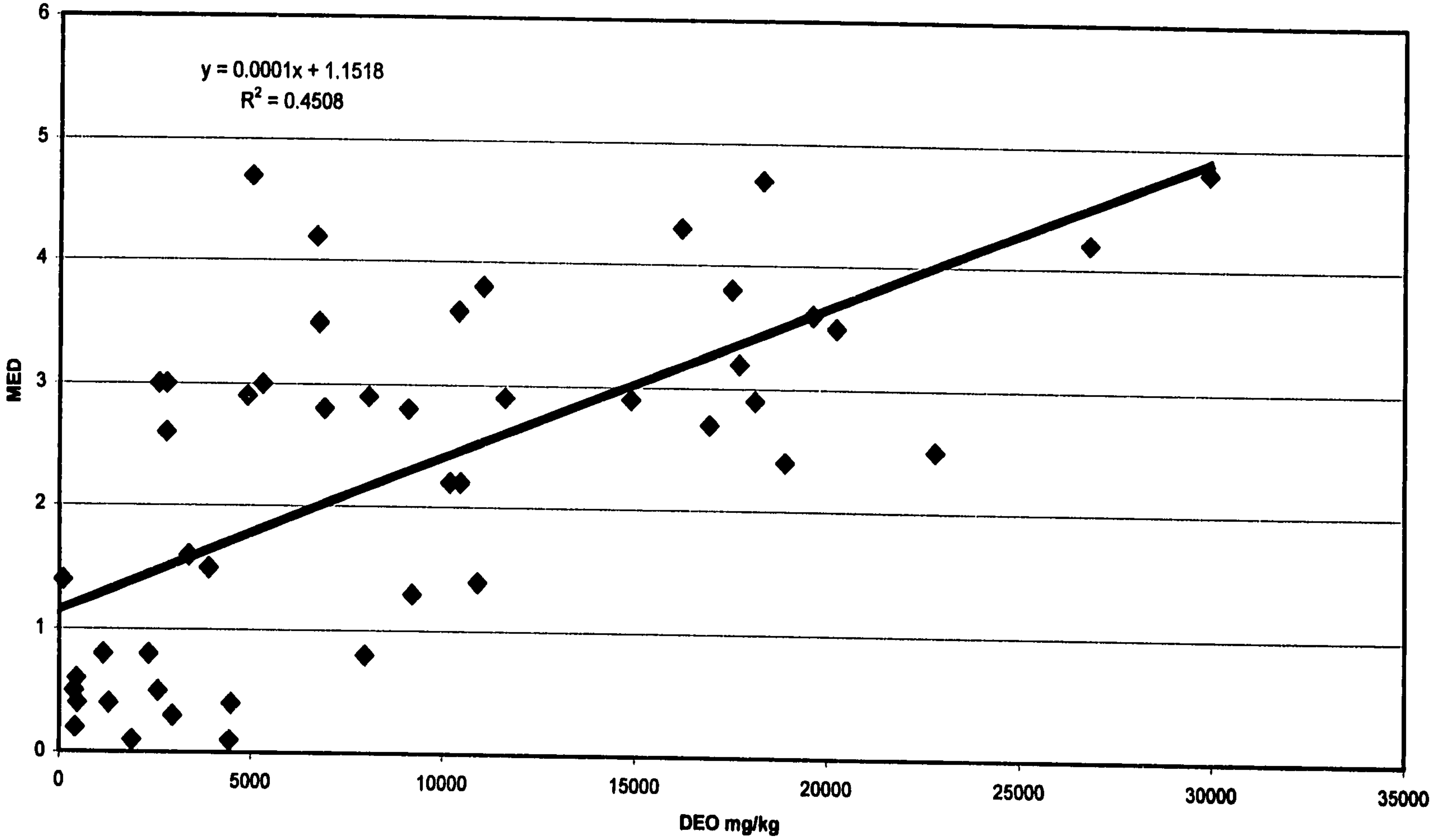


Figure 3-10: Linear regression of MED on DEO in samples from hydrophobic and wettable soil pits with MED > 0 *M* and DEO < 30,000 mg/kg (n = 46).

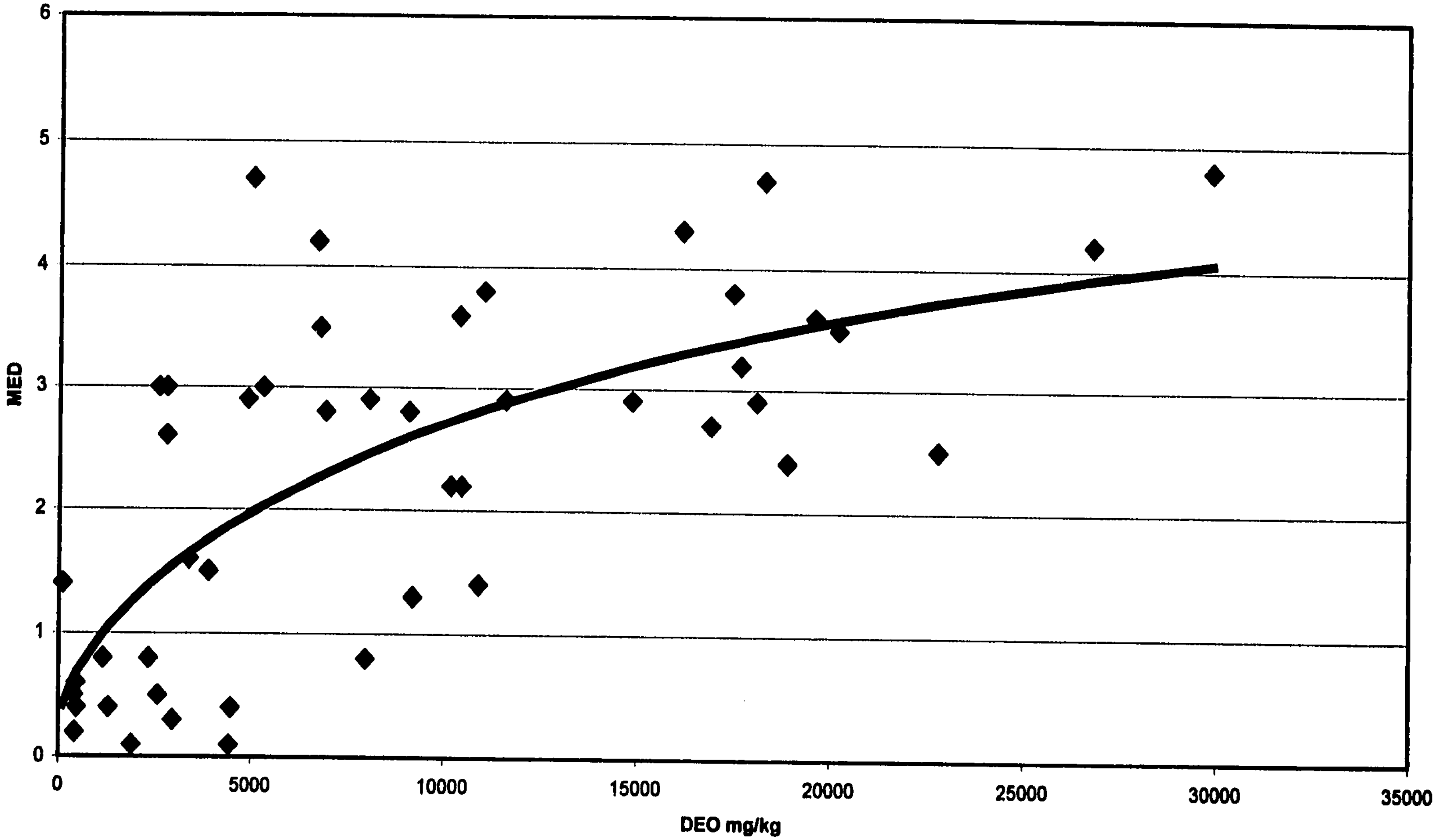


Figure 3-11: Regression of MED on $DEO^{2/3}$ in samples from hydrophobic and wettable soil pedons with MED > 0 *M* and DEO < 30,000 mg/kg. The relationship is MED (*M*) = 0.2454 – 0.00014 DEO (mg/kg) + 0.008304 $DEO^{2/3}$(mg/kg) (n = 46; R^2 = 0.52).

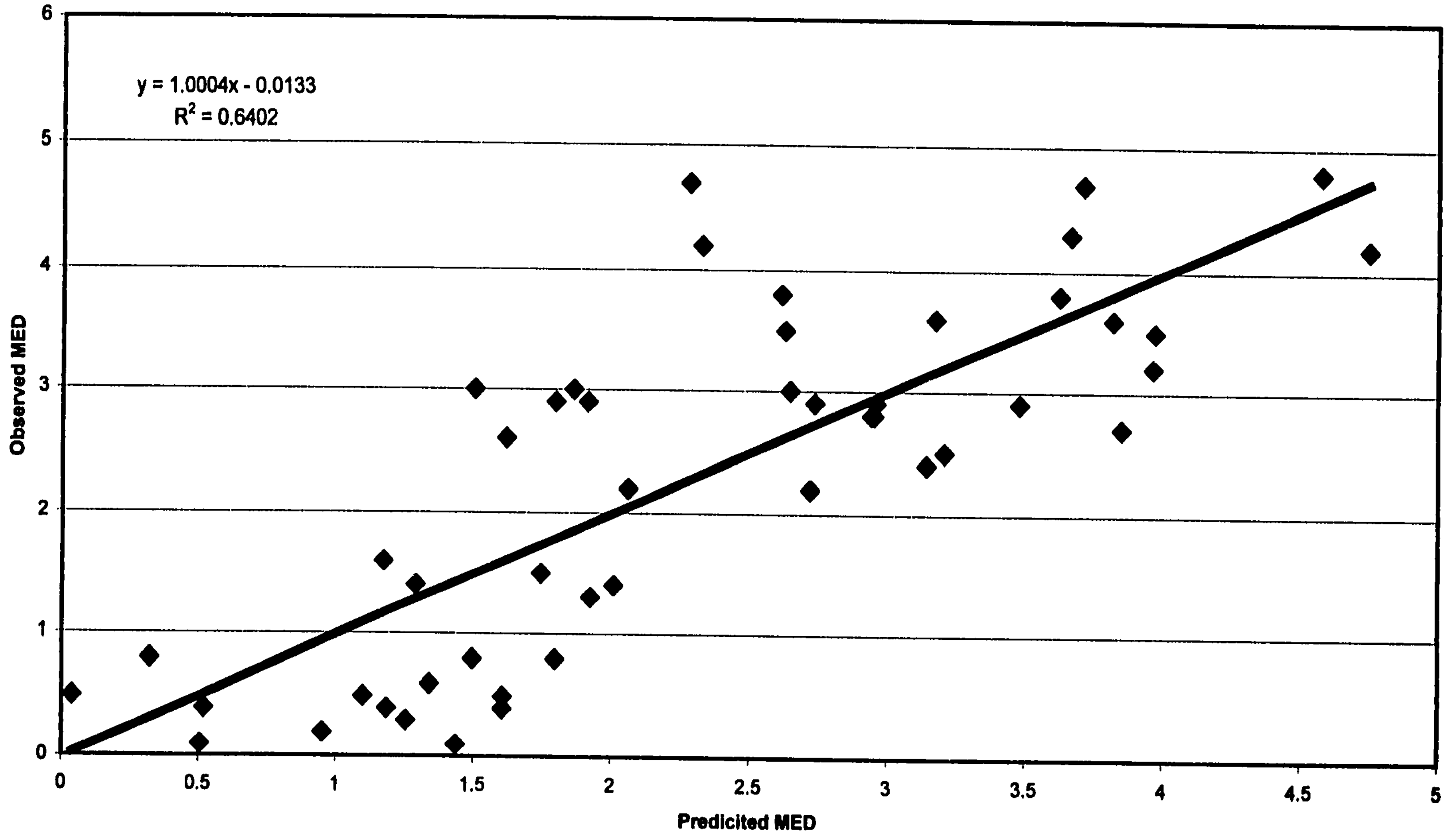


Figure 3-12: Observed MED compared to the predicted MED by the multiple regression of MED on soil pH and $DEO^{2/3}$. The relationship is MED (*M*) = 3.86826 – 0.53343 pH + 0.00414 $DEO^{2/3}$ (mg/kg) and the data range: MED > 0 *M* and DEO 30,000 mg/kg (n = 46).

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Chapter 4: Expression of Soil hydrophobicity in the Presence of Carbonates and Salts.

4.1 Introduction

Bond (1969) reported hydrophobicity in both calcareous and acid sands and found no apparent relation between the acidity or alkalinity of soil and the expression of soil hydrophobicity. We found hydrophobic soils formed from both saline and calcareous parent materials, however we did not detect hydrophobicity in horizons that contained carbonates or salts. The addition of lime to hydrophobic soils may reduce hydrophobicity by providing additional fine material and stimulating the mineralization of the organic compounds responsible for hydrophobicity (Harper et al. 2000). In chapter 3, I concluded that the relationship between molarity of ethanol droplet test (MED) and dichloromethane extractable organics (DEO) may be modified by soil conditions related to pH. I felt it was pertinent to determine if the presence of carbonates or salts prevented the expression of soil hydrophobicity. This information could be valuable in establishing remediation protocols for hydrophobic soils.

My objective was to test the hypothesis that soil hydrophobicity is not expressed in the presence of calcium carbonate ($CaCO_3$) and saline or sodic salts. The testing of this hypothesis entailed two separate experiments. In the first experiment I determined if the removal $CaCO_3$ or salts from soil samples resulted in an increase in soil hydrophobicity. For this experiment I chose samples that had low hydrophobicity and greater than 600 mg/kg DEO. I assumed these samples had the potential to express soil hydrophobicity. In the second experiment, I determined if the addition of $CaCO_3$ or Na_2SO_4 to severely hydrophobic soil samples resulted in a reduction of hydrophobicity.

I expected the removal of carbonates or salts from soil samples would result in an increase in soil hydrophobicity, as determined by the MED test. I expected the addition of $CaCO_3$ or Na_2SO_4 to soil samples would reduce their hydrophobicity.

The removal of carbonates or salts from soil samples did not result in an increase in hydrophobicity. The samples I chose either did not contain enough carbonates or salts to prevent the expression of hydrophobicity, or the samples did not have the potential to express hydrophobicity. The addition of $CaCO_3$ to samples did not result in a significant decrease in hydrophobicity (MED values), however the addition of salts to samples did result in a significant decrease in hydrophobicity (MED values).

4.2 Materials and Methods

The $CaCO_3$ and the salt removal experiments each had 1 treatment, which was replicated 3 times. The $CaCO_3$ addition experiment had 4 treatments, each of which was replicated 3 times. The Na_2SO_4 addition experiment had 3 treatments and 3 replicates.

4.2.1 Sample Selection

For the removal of $CaCO_3$ analysis I chose samples that had carbonates, low hydrophobicity and concentrations of DEO greater than 600 mg/kg soil (Samples 1-5, Table 4-1). The samples I chose for salt removal analysis had an electrical conductivity ≥ 0.5 dS/m, low hydrophobicity and DEO ≥ 600 mg/kg. I did not have any saline samples (≥ 4 dS/m), therefore I chose samples that had a higher electrical conductivity (≥ 0.5 dS/m) than the other samples (Samples 6-10, Table 4-1). I believed that samples with concentrations of DEO $\geq$ 600 mg/kg had the potential to express hydrophobicity, based on conclusions of Roy et al. (2000).

Samples chosen for the addition of carbonates did not have carbonates and they had severe hydrophobicity (MED > 2.2 *M*) (Samples 11-14, Table 4-1). The samples chosen for the addition of Na_2SO_4 also had severe hydrophobicity and an electrical conductivity < 0.2 dS/m (Samples 15-18, Table 4-1). I chose samples with severe hydrophobicity and the absence of carbonates or salts because I wanted to determine if the addition of carbonates or salts would reduce hydrophobicity.

4.2.2 Determination of Gravimetric Quantity of $CaCO_3$ and Salts in Samples

The carbonate content of samples chosen for $CaCO_3$ removal was determined with the approximate gravimetric method described by Goh et al. (1993). Briefly this method entails reacting carbonates in pre-weighed soil samples with acid. The resultant loss in weight from CO_2 released is used to calculate the $CaCO_3$ content.

4.2.3 Removal of $CaCO_3$ or Salts from Selected Samples

I removed carbonates from the soil according to the HCl procedure described by Sheldrick and Wang (1993); however I placed samples in a hot-water bath to speed up the removal of carbonates and centrifuged the samples to remove excess acid instead of using a candle filtration system. I measured the pH of the soil before removing carbonates and left the samples in the hot-water bath until the pH dropped below 5. The centrifuging process involved adding approximately 200 mL of deionized water to each 20 g soil sample and thoroughly mixing on a reciprocal shaker for 10 min. The samples were then centrifuged at 11 000 x g for 10 min. Immediately after centrifuging the supernatant was removed and replaced with 200 mL of deionized water. This process was repeated three times. I placed samples in aluminum dishes and allowed them to air dry.

Salts were removed from the samples by shaking, centrifuging and washing with deionized water, this process was repeated three times.

4.2.4 Addition of $CaCO_3$ or Na_2SO_4 to Selected Samples

The rates selected for $CaCO_3$ addition in each of the four treatments are based on the $CaCO_3$ concentrations in the calcareous classes of the Canadian System of Soil Classification (Table 4-2). The concentrations of Na_2SO_4 added in each of the four treatments are based on the salt contents in the salinity classes of the Canadian System of Soil Classification (Table 4-3). I chose to base the additions on calcareous or salinity classes because I wanted the additions of $CaCO_3$ or Na_2SO_4 to be representative of natural conditions in Alberta. Each soil sample was weighed to 30 g (within 1 %) and placed in aluminum dish. Using a glass-stirring rod, I thoroughly mixed the $CaCO_3$ or Na_2SO_4 into the soil sample. I thoroughly mixed $CaCO_3$ or Na_2SO_4 into each sample prior to mixing in 10 ml of deionized water. The samples were allowed to air dry.

4.2.5 Controls

To determine if the removal of $CaCO_3$ or salts from soil samples increased the hydrophobicity of the samples we compared the MED test values of samples that underwent removal of $CaCO_3$ or salts to two different controls samples. Control C1 samples were not treated. Control C2 samples underwent the centrifuging process outlined above. Both C1 and C2 samples were air-dried.

I compared the MED test values of samples that received no $CaCO_3$ and Na_2SO_4 to two control samples. Control C1 samples received no treatments. For Control C2 we mixed 10 mL of deionized water into soil stirring until it was wet. Both C1 and C2 samples were then air-dried.

4.2.6 Assessment of Soil Hydrophobicity

The MED test was used to measure soil hydrophobicity, as described in chapter 3. Samples were passed through a 1 mm sieve and oven-dried at 105°C for 24 h, then cooled in a dissector prior to MED tests. Light crushing of soil peds and surface crusts was often required to pass the samples through a 1 mm sieve. I gently crushed the samples with a mortar and pestle; abrasion may remove coatings and cause a subsequent reduction in MED (Ma'shum and Farmer 1985; Wallis et al. 1990).

4.2.7 Dichloromethane Extraction

We used dichloromethane extraction to determine the extractable organic content of air-dried soil samples, as described in chapter 3.

4.2.8 Soil pH

Determination of soil pH followed the method of Hendershot et al. (1993), as described in chapter 3.

4.2.9 Soil Electrical Conductivity

Electrical conductivity (and salt content) of the soil samples was determined on a Model 31 Conductivity Bridge (Yellow Springs Instrument Co. Inc.), as described in chapter 3.

4.2.10 Statistical Analyses

We used the Kolmogorov-Smirnov, Anderson-Darling and Cramér-von Mises tests to determine if the data were normally distributed. These tests were performed using PROC UNIVARIATE in SAS/STAT statistical software (SAS Institute 1999). Because the data were normally distributed, I performed an ANOVA using PROC GLM in SAS/STAT statistical software (SAS Institute 1999).

4.3 Results

4.3.1 Carbonate or Salt Removal

The gravimetric carbonate content of samples used in $CaCO_3$ removal analysis is recorded in Table 4-4. The concentration of $CaCO_3$ in the samples ranged from 60 to 479 g/kg (moderate to extreme calcareous classes). In comparison to the MED values of the control C1 and C2 samples, treatment to remove carbonates (Table 4-4) or salts (Table 4-5) did not increase MED values.

4.3.2 $CaCO_3$ and Na_2SO_4 Addition

The addition of $CaCO_3$ did not significantly reduce MED values (Table 4-6). The addition of $CaCO_3$ did not significantly increase the electrical conductivity of the soil samples (Table 4-7), however it did significantly increase the pH of the soil samples (Table 4-8).

The addition of Na_2SO_4 significantly decreased MED values of the treated samples (Table 4-9). There was a significant difference between treatment 1 (1 g/kg Na_2SO_4) and treatment 3 (6 g/kg Na_2SO_4); treatment 2 (4 g/kg Na_2SO_4) and C2; treatments 3 (6 g/kg Na_2SO_4) and C1; and C1 and C2. As expected, the addition of Na_2SO_4 did not significantly alter the soil pH (Table 4-10), but it significantly increased the electrical conductivity (Table 4-11).

Control samples (C2) in both $CaCO_3$ and the Na_2SO_4 were very difficult to completely wet. The wetting of all soil samples became easier with increasing $CaCO_3$ or Na_2SO_4 additions.

4.4 Discussion

The literature on the relationships between carbonates and the degree of hydrophobicity is diverse. Bond (1969) reported hydrophobicity in both calcareous and acid sands and concluded no apparent relation between the acidity or alkalinity of soil and the expression of soil hydrophobicity. In contrast, high pH soil treatments have achieved some alleviation of hydrophobicity in golf greens (Karnock et al. 1993). This could be related to the conclusions of Chen and Schnitzer (1978); they state that liming soil to increase pH enhances the ability of resident fulvic and humic acids to decrease soil hydrophobicity. Both fulvic and humic acid solutions significantly reduce the surface tension of water, which decreases the solid liquid contact angle and subsequently increases water infiltration into hydrophobic soils

(Chen and Schnitzer1978). The reduction in soil hydrophobicity after liming has also been attributed to the addition of fine material and the stimulation of organic matter mineralization (Harper et al. 2000). The reduction in hydrophobicity following the addition of fine material to the soil is related to *claying* of naturally hydrophobic soils, a treatment involving the mixing of large amounts of dispersible clay into hydrophobic soil (McKissock et al. 2000). The addition of fine materials (lime or clay) increases the total surface area of the soil, resulting in a dilution of hydrophobic agents. The stimulation of organic matter mineralization and subsequent reduction in organic compounds responsible for hydrophobicity may explain the reduction in natural hydrophobicity after liming (Wallis and Horne 1992); organic matter has been attributed to the generation of natural hydrophobicity (Bond 1964; McGhie and Posner 1980; Ma'shum et al. 1988; Wallis et al. 1990).

The literature on the relationship between sodium and the degree of hydrophobicity is focused on the application of sodic clays to naturally hydrophobic soils as an amelioration treatment. It has been demonstrated that Na clays are more effective than Ca clays for reducing soil hydrophobicity (Ma'shum et al. 1988; Ward and Oades 1993); this is related to the dispersibility of the clay and its subsequent ability to cover and remain dispersed over the surface of hydrophobic soil particles (Ward and Oades 1993). In contrast, McKissock et al. (2000) determined no relationship between hydrophobicity and exchangeable sodium percentage, suggesting that sodic clays were not more effective than non-sodic clays in reducing hydrophobicity.

I found that the removal of carbonates or salts from selected samples did not result in a significant increase in the severity of hydrophobicity. This could be attributed to three different explanations: (1) there is no relationship between carbonates or salts and soil hydrophobicity; (2) the samples I selected did not contain enough carbonates or salts to prevent or reduce the expression of hydrophobicity; or (3) the samples I selected did not have the potential to express hydrophobicity.

It is possible that there is no relationship between carbonates or salts and soil hydrophobicity, however this seems unlikely. In chapter 2, I reported the presence of hydrophobicity in soils derived from calcareous and saline parent material, however we did not detect hydrophobicity in horizons that contained carbonates or salts. I attributed this to the potential ability of carbonates and salts to hinder the expression of hydrophobicity. This was supported in chapter 3, I found that 63 % of the variability in MED was accounted for by soil pH and

$DEO^{2/3}$ compared to the 52 % accounted for by $DEO^{2/3}$ alone. Therefore I concluded that the relationship between hydrophobicity (MED) and the DEO may be modified by soil conditions related to pH, such as the carbonate content of the soil.

I could hypothesize that the samples I selected did not contain enough carbonates or salts to prevent or reduce hydrophobicity. The samples selected for carbonate removal had carbonate contents ranging from 60 g $CaCO_3$/kg soil (moderately calcareous soil) to 479 g $CaCO_3$/kg soil (extremely calcareous soil) (Table 4-4). These samples effervesced with the application of HCl, however according to the Canadian System of Soil Classification soils with carbonate concentrations ranging from 10 – 60 g/kg are weekly calcareous. The samples selected for salt removal had electrical conductivities ranging from 0.46 – 1.37 dS/m (Table 4-5); I did not have any saline soil samples.

Perhaps the samples I selected did not have the potential to express hydrophobicity. I predicted samples that had values of MED < 2.2 *M* and concentration of DEO > 600 mg/kg had the potential to express severe hydrophobicity upon the removal of carbonates or salts. Roy et al. (2000), concluded that soil samples with DEO < 630 mg/kg can be expected to have an MED $= 0$ *M*, they do not have the potential to express hydrophobicity. I found that samples, which had initial values of MED > 0 *M* showed a slight increase in hydrophobicity following the removal of carbonates or mixing with water treatment. From this I could reason that the samples with MED $= 0$ *M* (independent of DEO concentrations) did not have the potential to express hydrophobicity because the removal of carbonates and salts did not result in an increase in MED.

The addition of $CaCO_3$ did not significantly decrease the hydrophobicity of the soils samples, this can be attributed to thee reasons; (1) as stated by Bond (1969), the alkalinity of the soil does not alter the expression of hydrophobicity; (2) the concentrations of $CaCO_3$ were not sufficient to decrease severe hydrophobicity; (3) $CaCO_3$ is hydrophobic.

The addition of Na_2SO_4 significantly decreased the hydrophobicity of the soil samples; however samples were still severely hydrophobic (MED > 2.2 *M*); therefore I conclude that the concentrations on Na_2SO_4 added to the soil were probably not sufficient to ameliorate severe hydrophobicity. The results of the statistical analyses show a significant difference between treatment 1 (1 g/kg Na_2SO_4) and treatment 3 (6 g/kg Na_2SO_4), treatment 2 (4 g/kg Na_2SO_4) and C2; and treatments 3 (6 g/kg Na_2SO_4) and C1; from this I could infer that the higher the concentration of Na_2SO_4 added to the soil the greater the reduction in hydrophobicity. Results also indicated a significant difference between C1 and C2, thus it appears that force wetting and subsequent air-drying of hydrophobic soil results in a statistically significant reduction in soil hydrophobicity.

4.5 Summary and Conclusion

The objective of the research conducted in this chapter was to test the hypothesis that soil hydrophobicity is not expressed in the presence of $CaCO_3$ and saline or sodic salts. I expected the removal of carbonates or salts from soil samples would result in an increase in soil hydrophobicity and that the addition of $CaCO_3$ or Na_2SO_4 to soil samples would reduce their hydrophobicity. However, the removal of carbonates or salts from soil samples did not result in a statistically significant increase in hydrophobicity. I conclude these results do not support but do not conclusively disprove the hypothesis.

The addition of $CaCO_3$ to samples did not result in a significant decrease in hydrophobicity. Samples become easier to wet upon increasing concentrations of $CaCO_3$ added to the soil.

The addition of Na_2SO_4 to samples did result in a significant decrease in hydrophobicity, however this reduction in hydrophobicity was not sufficient to render the samples not-severely hydrophobic (MED < 2.2 *M*). I speculate that higher concentrations of Na_2SO_4 are required to reduce severe hydrophobicity to moderate or low hydrophobicity.

It is concluded that removal of $CaCO_3$ or salts form samples or adding $CaCO_3$ to samples had no effect on MED. Adding Na_2SO_4 reduced MED, but only marginally.

4.6 Tables and Figures

Table 4-1: Properties of samples selected for removal and addition experiments.

Experiment	Sample	MED (*M*)	DEO (mg/kg)	pH	EC (ds/m)	Clay (g/kg)
$CaCO_3$ removal	1	1.4	10,907	7.3	0.2	195
	2	0.0	1,108	7.3	0.5	200
	3	0.0	551	7.1	0.2	237
	4	0.3	2,962	6.5	0.3	293
	5	0.4	4,435	8.4	0.6	144
Salt removal	6	0.4	1,295	7.2	1.0	316
	7	2.2	10,456	7.1	0.6	247
	8	0.0	1,108	7.3	0.5	200
	9	0.8	7,975	9.6	1.4	70
	10	0.4	4,435	8.4	0.6	144
$CaCO_3$ addition	11	6.0	33,600	7.0	0.1	177
	12	5.0	34,100	8.3	1.0	262
	13	5.8	65,900	7.3	1.1	273
	14	4.2	6,709	5.6	0.1	183
Na_2SO_4 addition	15	6.0	33,600	7.0	0.1	177
	16	4.8	29,943	6.2	0.1	77
	17	4.3	16,189	5.4	0.1	188
	18	4.2	6,709	5.6	0.1	183

Table 4-2: Concentration of $CaCO_3$ added to air-dried soil samples in each treatment.

Treatment	Concentration of $CaCO_3$ (g/kg)	Calcareous Classes
1	30	Weakly calcareous
2	60	Moderately calcareous
3	120	Strongly calcareous
4	260	Very strongly calcareous

Table 4-3: Concentration of Na_2SO_4 added to air-dried soil samples in each treatment.

Treatment	Concentration of Na_2SO_4 (g/kg)	Salinity Classes
1	1.0	Weakly saline
2	4.0	Moderately saline
3	6.0	Strongly saline

Table 4-4: MED values of samples after $CaCO_3$ removal.

Sample	Initial concentration of $CaCO_3$ (g/kg)	DEO (mg/kg)	MED (*M*)		
			C1[a]	C2[b]	Treatment 1 (removal)
1	479	10,900	1.2	1.4	1.3
2	60	1,100	0.0	0.2	0.0
3	89	600	0.0	0.0	0.0
4	374	3,000	0.0	0.0	0.0
5	388	4,400	0.1	0.2	0.16
			No significant difference between treatments ($p = 0.308$)		

[a] C1 = no treatment

[b] C2 = centrifuged

Table 4-5: MED values of samples after salt removal.

Sample	Initial EC (dS/m)	DEO (mg/kg)	MED (*M*)		
			C1[a]	C2[b]	Treatment 1 (removal)
6	0.51	1,300	0.0	0.0	0.0
7	0.56	10,500	1.8	4.2	4.2
8	0.46	1,100	0.0	0.0	0.0
9	1.37	8,000	0.8	0.8	0.8
10	0.55	4,400	0.1	0.1	0.1
			No significant difference between treatments ($p = 0.5417$)		

[a]C1 = no treatment
[b]C2 = centrifuged

Table 4-6: MED values of samples after $CaCO_3$ additions.

Sample	MED (*M*)					
	C1[a]	C2[b]	Treatment 1 (30 g/kg)	Treatment 2 (60 g/kg)	Treatment 3 (120 g/kg)	Treatment 4 (260 g/kg)
11	6.0	5.8	5.7	5.5	5.6	5.4
12	5.1	5.7	4.5	4.2	4.0	3.8
13	5.8	4.6	5.6	5.6	5.5	5.5
14	4.2	4.1	2.9	2.9	2.9	2.9
	No significant difference between treatments ($p = 0.1487$)					

[a]C1 = no treatment
[b]C2 = 10 mL of deionized water

Table 4-7: Electrical conductivity after the additions of $CaCO_3$.

Sample	Electrical conductivity (dS/m)				
	C2[a]	Treatment 1 (30 g/kg)	Treatment 2 (60 g/kg)	Treatment 3 (120 g/kg)	Treatment 4 (260 g/kg)
11	0.25	0.33	0.32	0.37	0.38
12	0.84	0.72	0.71	0.70	0.66
13	0.53	0.66	0.66	0.71	0.74
14	0.05	0.14	0.14	0.13	0.13
	No significant difference between treatments ($p = 0.9947$)				

[a] C2 = 10 mL of deionized water

Table 4-8: Soil pH after the additions of $CaCO_3$.

Sample	pH				
	C2[a]	Treatment 1 (30 g/kg)	Treatment 2 (60 g/kg)	Treatment 3 (120 g/kg)	Treatment 4 (260 g/kg)
11	7.16	7.73	7.95	7.97	7.91
12	8.04	8.57	8.65	8.78	8.85
13	8.14	8.55	8.53	8.61	8.49
14	4.10	8.10	8.16	8.33	8.37
	Significant treatment effect ($p = 0.0007$)[b]				

[a] C2 = 10 ml of deionized water

[b] The pH of C2 is significantly lower than the pH of Treatments 1, 2, 3, and 4.

Table 4-9: MED values of samples after Na_2SO_4 additions.

Sample	MED (M)				
	C1[a]	C2[b]	Treatment 1 (1 g/kg)	Treatment 2 (4 g/kg)	Treatment 3 (6 g/kg)
15	6.0	6.0	5.8	5.73	5.6
16	5.0	5.1	4.8	4.6	4.37
17	5.8	5.7	4.6	3.63	3.5
18	4.2	4.1	3.8	3.6	3.0
	Significant treatment effect (p = 0.0022)[c]				

[a] C1 = no treatment

[b] C2 = 10 mL of deionized water

[c] Treatments 1 and 3; 2 and C2; C1 and 3; C1 and C2 are significantly different from each other.

Table 4-10: Soil pH after the additions of Na_2SO_4.

Sample	pH			
	C2[a]	Treatment 1 (1 g/kg)	Treatment 2 (4 g/kg)	Treatment 3 (6 g/kg)
15	6.6	6.41	6.41	6.40
16	6.64	6.44	6.29	6.46
17	6.02	5.97	5.81	5.74
18	5.93	5.77	5.51	5.77
	No significant difference (Pr > F = 0.5337)			

[a] C2 = 10 ml of deionized water

4.7 References

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Chapter 5: Synthesis

5.1 Synthesis

Existing hydrophobic soil sites may be the result of prior crude oil contamination. Anecdotal evidence suggests these crude oil-contaminated sites were not remediated prior to the development of hydrophobicity. Still, decades later when hydrophobicity manifests itself, these sites present little evidence of crude oil contamination; most of the components of crude oil have either escaped by volatilisation or undergone oxidative or microbial degradation. Unlike naturally occurring hydrophobicity, which tends to be confined to coarse textured soils in upper slope positions, we found that generation of soil hydrophobicity at former crude oil-contaminated sites is not restricted to soil textural class or topographical position. We found that residual oil-contamination; powdery surface structure; and the absence of vegetation can indicate the presence of hydrophobicity; although these conditions are not true for all crude oil associated hydrophobic sites. I determined a positive correlation between molarity of ethanol droplet (MED) values and dichloromethane extractable organics (DEO) concentrations. However, because dichloromethane extractions do not completely eliminate soil hydrophobicity, I cannot conclude that residual oil constituents in DEO induce hydrophobicity. Rather, I must infer that hydrophobicity is not caused by DEO itself but possibly by constituents contained in or related to DEO or their configurations. I found that the relationship between MED and DEO may be modified by altering soil conditions related to pH. However, neither the removal of carbonates from hydrophobic soil samples nor the addition of $CaCO_3$ to samples altered MED. The addition of Na_2SO_4 to severely hydrophobic soil samples reduced MED, but only marginally. I determined that all non-remediated crude oil contaminated sites have the potential to become hydrophobic, but I cannot predict if or when the soil will become hydrophobic.

5.2 Practical Implications

Field investigation of hydrophobic soil is impacted by certain site characteristics. The absence, health, and species composition of vegetation can be good indicators of the boundaries of the hydrophobic area. Yet some sites exhibit no difference in vegetation supported by hydrophobic and wettable soils. To delineate the boundaries of hydrophobic hydrophobicity using droplets of tap water; if the soil does not absorb the droplet in 10 s or less continue stepping away from the starting point.

Field determination of hydrophobicity is complex; the top 1 to 2 mm of hydrophobic surface soil sorbs water, whereas the layer below repels water, if it is dry. This layer of hydrophobic soil tends to be 10 to 15 cm thick and beneath it there is usually a layer of moist, wettable soil. Attention to all three layers is pertinent in determining the true extent of hydrophobicity at the site. To determine the extent of hydrophobicity I recommend measuring MED on oven-dry samples. Moist soils, which have the potential to express hydrophobicity, do not appear hydrophobic because added water coheres to soil water, allowing it to enter the soil.

Variable expression of hydrophobicity can explain dynamics in patch size. The influence of drying on the expression of hydrophobicity may relate to the visible expansion or contraction of the patch. Sites that appear to be remediated may revert to their hydrophobic condition after drying. In this reversion, the actual size of the hydrophobic patch may not change, however, it may appear to contract or expand.

Standard analytical methods for soil physical and chemical properties, which require suspension in water, present numerous disadvantages for the characterization of hydrophobic soils. I recommend shaking the soil with the aqueous phase for 30 min on a reciprocating shaker; this seems to successfully wet the soil. However, we did not determine if the water completely penetrated or dispersed micro-aggregates, and thus ensure complete wetting of the soil took place.

5.3 Recommendations and Future Research

A database on both crude oil spill sites and hydrophobic soil sites would be a valuable aid to future research and remediation efforts related to crude oil associated hydrophobicity. We relied on anecdotal information pertaining to the crude oil contamination and the past dynamics of the hydrophobic areas at each site. Concrete information pertaining to the spill conditions (season, size, and location), any remediation efforts, and the subsequent manifestation of hydrophobic soils would aid in developing protocol to predict, prevent and remediate soil hydrophobicity.

My research determined that the hydrophobic soils associated with crude oil-contamination appear dispersed but are actually composed of both micro-aggregates and primary soil particles. It would be valuable to determine if water repelling agents coat micro-aggregates that contain hydrophilic primary particles; or if the primary particles, which comprise a hydrophobic micro-aggregate, are themselves hydrophobic. If the hydrophobic micro-aggregates are composed of hydrophilic particles then perhaps the dispersion of these aggregates could dilute hydrophobicity by creating new hydrophilic surface area.

Appendix A: Site Description

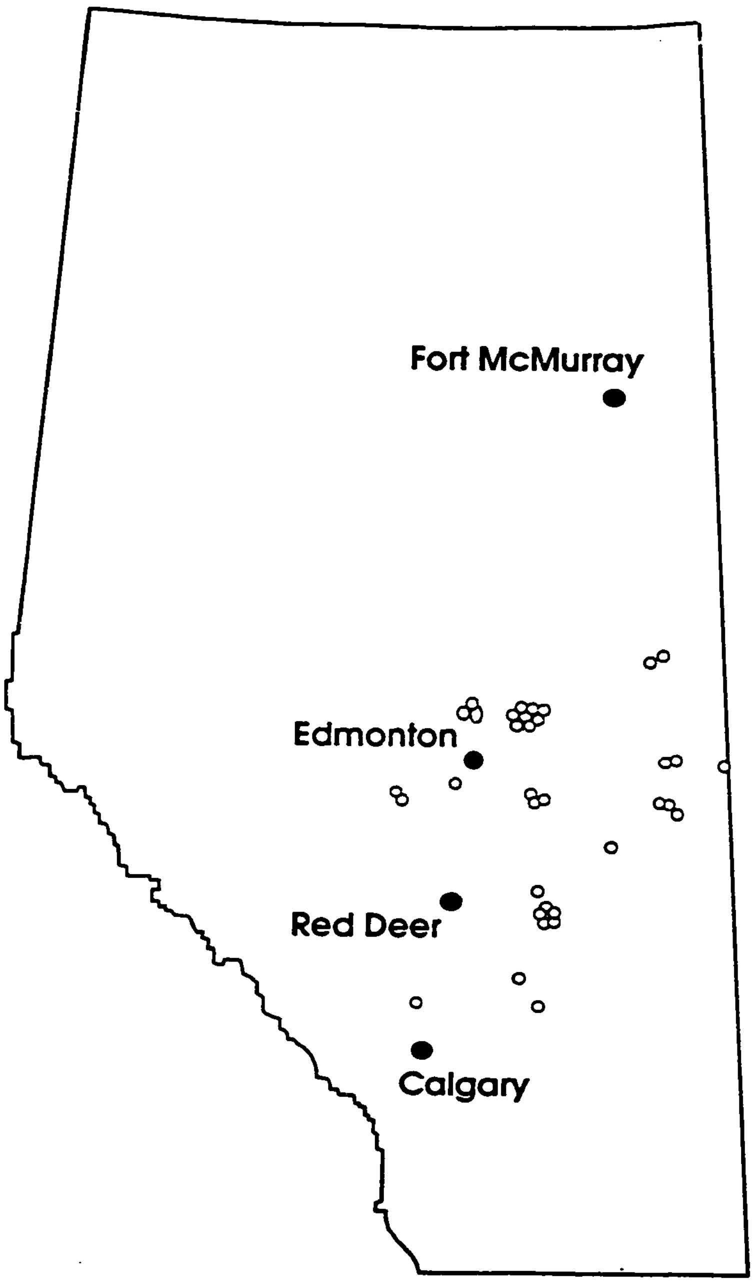

Figure A-1: Map of Alberta: The hydrophobic locations involved in this study extend northeast form Calgary to Cold Lake.

Table A-1: Hydrophobic soil location information.

Site	Ecozone	Ecoregion	Soil Zone	AGRASID Soil Classification	Site Use
1	Prairies	Aspen Parkland	Black Chernozemics	Eluviated Black Chernozem	Cereal
2	Prairies	Moist Mixed Grassland	Dark Brown Chernozemics	Orthic Dark Brown Chernozem	Forage
3	Prairies	Aspen Parkland	Black Chernozemics	Orthic Black Chernozem	Oilseed
4	Prairies	Aspen Parkland	Black Chernozemics	Black Solodized Solonetz	Cereal
5	Prairies	Aspen Parkland	Black Chernozemics	Eluviated Black Chernozem	Cereal
6	Prairies	Aspen Parkland	Black Chernozemics	Orthic Black Chernozem	Cereal
7	Prairies	Aspen Parkland	Black Chernozemics	Orthic Black Chernozem	Forage
8	Prairies	Aspen Parkland	Dark Gray Chernozemics	Orthic Dark Gray Chernozem	Cereal
9	Boreal Plains	Boreal Transition	Gray Luvisols	Gleyed Dark Gray Luvisol	Forage
10	Boreal Plains	Boreal Transition	Gray Luvisols	Orthic Gray Luvisol	Forage
11	Prairies	Aspen Parkland	Black Chernozemics	Black Solodized Solonetz	Oilseed
12	Prairies	Aspen Parkland	Black Chernozemics	Black Solodized Solonetz	Oilseed
13	Prairies	Aspen Parkland	Black Chernozemics	Terric Mesisol Organic	Forage
14	Prairies	Aspen Parkland	Black Chernozemics	Typic Mesisol Organic	Forage
15	Prairies	Aspen Parkland	Dark Gray Chernozemics	Orthic Dark Gray Chernozem	Forage
16	Prairies	Aspen Parkland	Black Chernozemics	Typic Mesisol Organic	Forage
17	Prairies	Aspen Parkland	Black Chernozemics	Eluviated Black Chernozem	Battery
18	Prairies	Aspen Parkland	Black Chernozemics	Orthic Black Chernozem	Battery
19	Prairies	Aspen Parkland	Black Chernozemics	Orthic Black Chernozem	Forage
20	Prairies	Aspen Parkland	Black Chernozemics	Black Solodized Solonetz	Forage
21	Prairies	Aspen Parkland	Black Chernozemics	Orthic Black Chernozem	Oilseed
22	Prairies	Aspen Parkland	Black Chernozemics	Orthic Humic Gleysol	Battery
23 (a.b)	Prairies	Mid Boreal Uplands	Gray Luvisols	Not available	Land-farm
24	Prairies	Moist Mixed Grassland	Dark Brown Chernozemic	Orthic Humic Vertisol	Oilseed
25	Prairies	Aspen Parkland	Black Chernozemics	Orthic Black Chernozem	Oilseed
26	Prairies	Aspen Parkland	Black Chernozemics	Orthic Black Chernozem	Oilseed

Table A-2: Set of questions used to obtain information about sites, from landowners, leaseholders, Alberta Environment inspectors, and company personal.

Amendments applied to the soil	Manure Lime Fertilizer Sterilant (herbicide/pesticide) Detergent
Type of Spill	Surface spill – pipeline, tank failure Subsurface spill – pipeline, tank failure Spill Dimensions
Site use	Battery Landfarm Grazing Arable crops
Remediation following crude oil spill	Burning Cultivation Top soil removal Nothing
Date of spill	Year, season, frequency

Table A-3: Braun-Blanquet cover classes.

Value	Percent-cover
1	Less than 1 %
2	1 – 5 %
3	6 – 25 %
4	26 – 50 %
5	51 – 75 %
6	76 – 100 %

Table A-4: Comparison of soil textural classes determined by particle size analysis and hand texturing.

Site	Soil Textural Class	
	Determined by Particle Size Analysis	Determined by Hand Texturing
1	loam	silty clay
2	sandy loam	silty clay loam
5	sandy loam	clay loam
6	sandy loam	sandy clay
7	sandy loam	loam
8	loam	silt loam
9	loam	clay loam
12	silt loam	clay loam
14	sand	loamy sand
20	sand	loamy sand
23a	silt loam	sandy clay loam
23b	sandy clay loam	sandy clay loam
25	loamy sand	loamy sand

Table A-5: Plant species present at hydrophobic soil sites.

Common Name	Latin Name	Number of sites (out of 12)	Reproduction
Species presents in Hydrophobic Soil Areas			
Bluebur	*Lappula echinata*	1	Seed
Canada thistle	*Cirsium arvense*	6	Seed and sprouting horizontal root stalk
Corn spurry	*Spergula arvensis*	1	Seed
Cow cockle	*Saponaria vaccaria*	1	Seed
Dandelion	*Taraxacum officinale*	1	Seed
Flix weed	*Descurainia sophia*	1	Seed
Foxtail Barely	*Hordeum jubatum*	2	Seed
Green Foxtail	*Setaria viridis*	2	Seed
Horse tail	*Equisetum arvense*	1	Spores and creeping root stalks
Knotweed	*Polygonum aviculare L.*	1	Seed
Lamb's quarters	*Chenopodium album*	7	Seed
Narrow-leaved Hawk's beard	*Crepis tectorum*	4	Seed
Pineapple weed	*Matricaria matricarioides*	3	Seed
Quack grass	*Agropyron repens*	3	Seed and rhizome
Shepherd's purse	*Capsella bursa-pastoris*	2	Seed
Stinkweed	*Thaspi arvense*	2	Seed
Sow thistle	*Sonchus arvensis*	1	Seed and horizontally spreading root stalks
Tartary Buckwheat	*Fagopyrum tartaricum*	7	Seed
Wild oats	*Avena fatua*	4	Seed
Species present in Field-Wettable Soil Areas			
Barely	*Hordeum vulgare*	1	Planted
Canola	*Brassica campestris* *Brassica napus*	3	Planted
Wheat	*Triticum aestivum*	2	Planted
Oats	*Avena sativa*	1	Planted
Alfalfa	*Medicago sativa*	2	Planted
Timothy	*Phleum pratense*	2	Planted
Sheep fescue	*Festuca ovina*	1	Planted
Tartary Buckwheat	*Fagopyrum tartaricum*	2	Seed
Wild oats	*Avena fatua*	1	Seed
Shepherd's purse	*Capsella bursa-pastoris*	2	Seed
Lamb's quarters	*Chenopodium album*	2	Seed
Narrow-leaved Hawk's beard	*Crepis tectorum*	1	Seed
Pineapple weed	*Matricaria matricarioides*	1	Seed
Stinkweed	*Thaspi arvense*	1	Seed
Quack grass	*Agropyron repens*	1	Seed and rhizome
Canada thistle	*Cirsium arvense*	1	Seed and sprouting horizontal root stalk
Dandelion	*Taraxacum officinale*	1	Seed

Appendix B

Table B-1: Pedon Descriptions of the 12 sites characterized in Stage 2. Soil classifications are based on the wettable soil pedons (located adjacent to the hydrophobic soil pedons).

Site 1: Gleyed Calcareous Black Chernozem

Pit location		Outside of hydrophobic patch				
Horizon		Ap	Bm1	Ahb	Bm2	Ckgj
Texture		sandy loam	loam	sandy loam	loam	loam
Moisture		dry-moist	dry-moist	dry-moist	dry-moist	moist-wet
Colour		10YR 2/1 m	10YR 4/3 m	10YR 2/1 m	10YR 4/3 m	10YR 5/3 m
Depth (cm)		0-16	16-29	29-36	36-45	45-100
EC[z] (dS/m)		0.18	0.11	0.17	0.14	0.21
pH (0.01 M $CaCl_2$)		6.9	6.1	7.2	6.9	7.1
Total C (%)		2.10	1.62	3.06	0.95	1.25
Organic C (%)		2.04	1.50	2.91	0.47	0.34
Inorganic C (%)		0.06	0.12	0.15	0.48	0.91
Total N (%)		0.20	0.16	0.25	0.06	0.04
DEO[y] (%)		0.04	0.02	0.02	0	0
MED[x] (*M*)		0	0	0	0	0
Structure	**Primary**	medium granular	coarse blocky	coarse blocky	-	massive
	Secondary	-	medium blocky	medium blocky	-	coarse blocky
	Consistence	Firm	firm	very friable	-	firm
	Grade	Medium	medium	weak	-	medium
Roots	**Abundance**	4-14	1-3	1-3	1-3	1-3
	Diameter (mm)	0.075-1	0.075-1	0.075-1	0.075-1	<0.075
	Orientation	Oblique	oblique	vertical	vertical	vertical
	Distribution	Inped	exped	exped	exped	inped
Boundary	**Sharpness (cm)**	<2	2-5	<2	<2	-
	Form	Smooth	smooth	smooth	smooth	-
Mottles	**Abundance (%)**	<2	<2	<2	<2	2-20
	Diameter (mm)	0.075-1	<5	<5	<5	>15
	Colour	5YR 5/6 m	7.5YR 5/8 m	7.5YR 5/8	7.5YR 5/8	2.5YR 4/8
$CaCO_3$		Absent	moderate	moderate	moderate	strong
Hardpan		Absent	absent	absent	absent	absent
Hydrocarbon Odour		Absent	absent	absent	absent	absent

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[x] Molarity of ethanol droplet (performed in the lab)
[y] Dichloromethane-extractable organics (Soxhlet)

- **continued** -

Pit location		Within hydrophobic patch			
Horizon		A*	B*	C*	Oil layer
Texture		sandy loam	clay	loam	-
Moisture		dry	dry-moist	moist	-
Colour		10YR 2/1d	10YR 4/1 m	10YR 4/1 m	-
Depth (cm)		0-13	13-39	39-85	85-100
EC^z (dS/cm)		0.23	0.21	0.46	-
pH (0.01 *M* $CaCl_2$)		7.3	7.0	8.0	-
Total C (%)		3.34	1.24	1.45	-
Organic C (%)		2.85	0.34	0.72	-
Inorganic C (%)		0.49	0.90	0.73	-
Total N (%)		0.19	0.04	0.06	-
DEO^y (%)		1.09	0.01	0.02	-
MED^x (*M*)		1.4	0.0	0.0	-
Structure	**Primary**	medium granular	very coarse blocky	massive	blocky
	Secondary	-	medium blocky	fine subangular	-
	Consistence	slightly hard	firm	firm	-
	Grade	medium	strong	medium	-
Roots	**Abundance**	4-14	1-3	<1	-
	Diameter (mm)	0.075-1	0.075-1	<0.075	-
	Orientation	oblique	horizontal	horizontal	-
	Distribution	inped/exped	exped	exped	-
Boundary	**Sharpness (cm)**	<2	<2	-	-
	Form	smooth	smooth	-	-
Mottles	**Abundance (%)**	<2	<2	>20	-
	Diameter (mm)	<5	<5	>15	-
	Colour	7.5YR 4/6 m	7.5YR 4/6 m	5YR 4/6 m	-
$CaCO_3$		moderate	strong	strong	absent
Hardpan		absent	absent	absent	present
Hydrocarbon Odour		absent	absent	absent	at 85 cm

[*] Mixed or otherwise disturbed horizon
[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

Site 3: Gleyed Calcareous Black Chernozem

Pit location		Outside of hydrophobic patch				
Horizon		Ap	Ah	Bmgj	Bmkgj	Cskgj
Texture		loam	Loam	loam	silt loam	silt loam
Moisture		dry	dry-moist	dry-moist	dry-moist	dry-moist
Colour		10YR 3/1 d	10YR 2/1 m	10YR 4/2 m	10YR 5/4 m	10YR 5/3 m
Depth (cm)		0-18	18-35	35-44	44-56	56-100
EC[z] (dS/m)		0.23	0.34	1.22	1.52	3.04
pH (0.01 *M* $CaCl_2$)		6.6	7.5	7.3	7.3	7.7
Total C (%)		3.28	2.06	1.19	1.32	1.05
Organic C (%)		3.24	1.95	1.11	0.55	0.37
Inorganic C (%)		0.04	0.10	0.09	0.76	0.68
Total N (%)		0.31	0.21	0.14	0.09	0.08
DEO[y] (%)		0.07	0.02	0	0	0
MED[x] (*M*)		0	0	0	0	0
Structure	**Primary**	coarse granular	Blocky	blocky	blocky	massive
	Secondary	-	medium subangular blocky	medium blocky	coarse blocky	medium subangular blocky
	Consistence	slightly hard	Firm	very friable	friable	friable
	Grade	medium	Medium	strong	strong	medium
Roots	**Abundance**	4-14	4-14	4-14	4-14	1-3
	Diameter (mm)	<0.075	<0.075	<0.075	0.075-1	0.075-1
	Orientation	vertical	Vertical	vertical	vertical	vertical
	Distribution	inped	Inped	exped	exped	exped
Boundary	**Sharpness (cm)**	2-5	5-15	2-5	2-5	-
	Form	wavy	Wavy	wavy	wavy	-
Mottles	**Abundance (%)**	0	<2	2-20	2-20	2-20
	Diameter (mm)	-	<5	<5	<5	<5
	Colour	-	10YR 4/6	10YR 4/6	7.5YR 4/4	2.5YR 3/6
$CaCO_3$		absent	absent	absent	strong	strong
Hardpan		absent	absent	absent	absent	absent
Hydrocarbon Odour		absent	absent	absent	absent	absent
Miscellaneous		-	-	-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued-

Pit location		Within hydrophobic patch				
Horizon		A1*	A2*	B1*	B*	C*
Texture		loam	loam	clay loam	clay loam	loam
EC^z (dS/m)		0.24	0.10	1.00	1.05	1.67
Moisture		Dry	dry-moist	dry-moist	dry-moist	dry-moist
Colour		10YR 4/2 d	10YR 3/2 m	10YR 3/2 m	2.5YR 4/4 m	2.5YR 5/4 m
Depth (cm)		0-15	15-26	26-38	38-54	54-100
pH (0.01 M CaCl$_2$)		7.0	7.0	7.2	7.6	7.6
Total C (%)		3.81	4.39	0.88	1.01	0.78
Organic C (%)		3.69	4.13	0.87	0.96	0.27
Inorganic C (%)		0.13	0.26	0.01	0.05	0.51
Total N (%)		0.25	0.16	0.11	0.11	0.05
DEO^y (%)		0.81	3.36	0.13	0.04	0
MED^x (M)		2.9	6.0	0.4	0.5	0
Structure	**Primary**	fine granular	fine prismatic	coarse columnar	coarse columnar	massive
	Secondary	-	-	medium blocky	medium blocky	-
	Consistence	Loose	very friable	Friable	friable	very friable
	Grade	Weak	medium	medium	medium	medium
Roots	**Abundance**	>14	<1	0	0	0
	Diameter (mm)	<0.075	0.075-1	-	-	-
	Orientation	vertical	oblique	-	-	-
	Distribution	inped/exped	exped	-	-	-
Boundary	**Sharpness (cm)**	<2	2-5	-	-	-
	Form	Wavy	wavy	-	-	-
Mottles	**Abundance (%)**	0	0	0	<2	2-20
	Diameter (mm)	-	-	-	>15	5-15
	Colour	-	-	-	7.5YR 4/6	7.5YR 4/6
CaCO$_3$		Absent	absent	absent	strong	strong
Hardpan		Absent	absent	absent	absent	absent
Hydrocarbon Odour		Absent	slight	absent	absent	absent
Miscellaneous		-	oily	-	-	sand lenses

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 5: Eluviated Black Chernozem

Pit location		Outside of hydrophobic patch					
Horizon		Ap	Ahe1	Ahe2	Ae	Bt	C
Texture		loam	loam	loam	silt loam	sandy clay loam	clay loam
Moisture		-	-	-	-	-	-
Colour		2/1 10YR	2/1 10YR	4/2 10YR	5/3 10YR	4/4 10YR	5/3 10YR
Depth (cm)		0-5	5-20	20-31	31-40	40-61	61-100
EC^z (dS/m)		0.12	0.08	-	0.09	0.08	0.05
pH (0.01 *M* $CaCl_2$)		-	5.3	-	6.2	5.9	6.6
Total C (%)		3.15	2.57	-	0.41	0.38	0.12
Organic C (%)		3.11	2.57	-	0.41	0.37	0.13
Inorganic C (%)		0.04	0	-	0.01	0	0
Total N (%)		0.28	0.23	-	0.07	0.07	0.03
DEO^y (%)		0.04	0.05	-	0.20	0.01	0
MED^x (*M*)		0	0	-	0	0	0
Structure	**Primary**	fine granular	fine platy	medium platy	medium platy	fine subangui. blocky	massive
	Secondary	-	-	-	-	-	-
	Consistence	-	-	-	-	-	-
	Grade	Weak	weak	weak	weak	medium	medium
Roots	**Abundance**	4-14	4-14	4-14	4-14	1-3	1-3
	Diameter (mm)	1-2	1-2	1-2	1-2	1-2	<0.075
	Orientation	Vertical	vertical	vertical	vertical	vertical	horizontal
	Distribution	inped	exped	exped	exped	inped	exped
Boundary	**Sharpness (cm)**	<2	2-5	<2	2-5	2-5	-
	Form	smooth	wavy	smooth	smooth	smooth	-
Mottles	**Abundance (%)**	0	0	0	0	0	0
	Diameter (mm)	-	-	-	-	-	-
	Colour	-	-	-	-	-	-
$CaCO_3$		absent	absent	absent	absent	absent	absent
Hardpan		absent	absent	absent	absent	absent	absent
Hydrocarbon Odour		absent	absent	absent	absent	absent	absent
Miscellaneous		-	-	-	-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch				
Horizon		A1*	hardpan	A2*	B*	C*
Texture		loam	-	clay loam	silt loam	loam
Moisture		-	-	-	-	-
Colour		10YR 3/3	7.5YR 2/0	10YR 4/2	10YR 4/3	10YR 3/4
Depth (cm)		0-9	9-25	25-34	34-60	60-100
EC[z] (dS/m)		0.51	-	0.12	0.17	0.30
pH (0.01 *M* CaCl$_2$)		5.3	-	6.5	5.9	7.2
Total C (%)		6.68	-	1.98	0.52	0.42
Organic C (%)		6.62	-	1.96	0.51	0.41
Inorganic C (%)		0.06	-	0.02	0.01	0.02
Total N (%)		0.39	-	0.18	0.07	0.06
DEO[y] (%)		2.68	-	0.14	0	0
MED[x] (*M*)		4.2	-	0	0	0
Structure	**Primary**	-	-	medium platy	fine subangular blocky	medium subangular blocky
	Secondary	-	-	-	-	-
	Consistence	-	-	-	-	-
	Grade	massive	massive	medium	medium	medium
Roots	**Abundance**	>14	>14	4-14	4-14	1-3
	Diameter (mm)	1-2	1-2	1-2	1-2	1-2
	Orientation	vertical	vertical	vertical	vertical	vertical
	Distribution	inped	exped	inped	inped	exped
Boundary	**Sharpness (cm)**	<2	2-5	2-5	2-5	-
	Form	smooth	wavy	wavy	wavy	-
Mottles	**Abundance (%)**	0	0	0	0	2-20
	Diameter (mm)	-	-	-	-	<5
	Colour	-	-	-	-	5YR 4/6
CaCO$_3$		absent	absent	absent	absent	absent
Hardpan		absent	present	absent	absent	absent
Hydrocarbon Odour		absent	present	absent	absent	absent
Miscellaneous		-	-	-	-	-

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 6: Eluviated Black Chernozem

Pit location		Outside of hydrophobic patch				
Horizon		Ap	Ah	Ae	Btj	Csk
Texture		Loam	-	loam	loam	clay loam
Moisture		dry	dry	dry	Dry	Dry
Colour		-	-	-	-	-
Depth (cm)		0-12	12-21	21-29	29-67	67-100
EC[z] (dS/m)		0.14	-	0.08	0.18	1.98
pH (0.01 *M* CaCl$_2$)		5.8	-	6.4	7.0	7.2
Total C (%)		4.15	-	1.25	0.63	3.26
Organic C (%)		4.06	-	1.24	0.62	0.49
Inorganic C (%)		0.10	-	0.02	0.01	2.77
Total N (%)		0.36	-	0.14	0.08	0.07
DEO[y] (%)		0.19	-	0.02	0.02	0.02
MED[x] (*M*)		0.1	-	0	0	0
Structure	**Primary**	medium subangular blocky	fine subangular blocky	medium platy	fine prismatic	fine subangular blocky
	Secondary	-	-	-	-	-
	Consistence	-	-	-	-	-
	Grade	strong	strong	weak	weak	weak
Roots	**Abundance**	4-14	4-14	4-14	1-3	1-3
	Diameter (mm)	1-2	1-2	1-2	0.075-1	0.075-1
	Orientation	vertical	vertical	oblique	oblique	oblique
	Distribution	inped	inped	exped	inped/exped	inped/exped
Boundary	**Sharpness (cm)**	<2	<2	2-5	5-15	-
	Form	wavy	wavy	wavy	wavy	-
Mottles	**Abundance (%)**	0	0	0	0	0
	Diameter (mm)	-	-	-	-	-
	Colour	-	-	-	-	-
CaCO$_3$		absent	weak	weak	weak	moderate
Hardpan		absent	absent	absent	absent	absent
Hydrocarbon Odour		absent	absent	absent	absent	absent
Miscellaneous		-	-	-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch					
Horizon		A1*	A2*	B*	C1*	C2*	C3*
Texture		loam	loam	clay loam	clay loam	-	-
Moisture		-	-	-	-	-	-
Colour		-	-	-	-	-	-
Depth (cm)		0-6	6-12	12-34	34-50	50-65	85-100
EC^z (dS/m)		0	-	0.20	1.98	-	-
pH (0.01 *M* $CaCl_2$)		6.0	-	6.6	7.1	-	-
Total C (%)		5.00	-	0.99	0.98	-	-
Organic C (%)		4.93	-	0.98	0.37	-	-
Inorganic C (%)		0.06	-	0.01	0.61	-	-
Total N (%)		0.32	-	0.12	0.05	-	-
DEO^y (%)		1.81	-	0.03	0.01	-	-
MED^x (*M*)		2.9	-	0	0	-	-
Structure	**Primary**	medium blocky	fine platy	fine prismatic	-	-	fine blocky
	Secondary	-	-	-	-	-	-
	Consistence	-	-	-	-	-	-
	Grade	medium	weak	strong	-	-	weak
Roots	**Abundance**	1-3	1-3	4-14	1-3	<1	<1
	Diameter (mm)	0.075-1	0.075-1	1-2	0.075-1	0.075-1	0.075-1
	Orientation	vertical	vertical	vertical	vertical	oblique	vertical
	Distribution	inped	inped	exped	inped	inped	inped
Boundary	**Sharpness (cm)**	<2	2-5	2-5	2-5	2-5	-
	Form	wavy	smooth	wavy	wavy	wavy	-
Mottles	**Abundance (%)**	0	0	0	0	0	0
	Diameter (mm)	-	-	-	-	-	-
	Colour	-	-	-	-	-	-
$CaCO_3$		weak	weak	weak	moderate	moderate	strong
Hardpan		absent	absent	absent	absent	absent	absent
Hydrocarbon Odour		absent	absent	absent	absent	absent	absent
Miscellaneous		-	-	-	-	-	-

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 7: Orthic Black Chernozem

Pit location		Outside of hydrophobic patch		
Horizon		Ap	Bm	Ck
Texture		loam	clay loam	clay
Moisture		-	-	-
Colour		-	-	-
Depth (cm)		0-14	14-80	80-100
EC^z (dS/m)		0.11	0.08	0.14
pH (0.01 M $CaCl_2$)		5.7	6.8	6.5
Total C (%)		3.19	0.42	0.61
Organic C (%)		3.15	0.41	0.44
Inorganic C (%)		0.04	0.01	0.18
Total N (%)		0.30	0.06	0.06
DEO^y (%)		0.06	0.01	0.02
MED^x (M)		0	0	0
Structure	**Primary**	medium subangular blocky	medium blocky	medium blocky
	Secondary	-	-	-
	Consistence	-	-	-
	Grade	strong	medium	medium
Roots	**Abundance**	4-14	4-14	4-14
	Diameter (mm)	1-2	1-2	0.075-1
	Orientation	vertical	oblique	oblique
	Distribution	inped	exped	inped
Boundary	**Sharpness (cm)**	5-15	2-5	-
	Form	broken	irregular	-
Mottles	**Abundance (%)**	0	0	0
	Diameter (mm)	-	-	-
	Colour	-	-	-
$CaCO_3$		absent	absent	strong
Hardpan		absent	absent	absent
Hydrocarbon Odour		absent	absent	absent
Miscellaneous		-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch					
Horizon		A*	B1*	B2*	B3*	B4*	C*
Texture		loam	clay loam	loam	sand	silt loam	loam
Moisture		-	-	-	-	-	-
Colour		-	-	-	-	-	-
Depth (cm)		0-14	14-28	28-35	35-43	43-63	63-100
EC[z] (dS/m)		0.09	0.34	1.02	0.15	1.07	0.57
pH (0.01 M $CaCl_2$)		6.2	8.2	8.3	5.6	7.3	7.1
Total C (%)		6.59	3.70	3.24	6.89	7.85	0.63
Organic C (%)		6.47	3.52	3.09	6.19	7.19	0.60
Inorganic C (%)		0.12	0.17	0.15	0.70	0.66	0.04
Total N (%)		0.24	0.09	0.08	0.08	0.15	0.05
DEO[y] (%)		6.62	3.09	3.41	9.11	6.59	1.05
MED[x] (*M*)		4.4	4.8	5.0	3.5	5.8	2.2
Structure	**Primary**	-	-	-	-	-	fine prismatic
	Secondary	-	-	-	-	-	-
	Consistence	-	-	-	-	-	-
	Grade						medium
Roots	**Abundance**	0	0	0	0	0	1-3
	Diameter (mm)	-	-	-	-	-	0.075-1
	Orientation	-	-	-	-	-	random
	Distribution	-	-	-	-	-	inped
Boundary	**Sharpness (cm)**	2-5	2-5	2-5	2-5	2-5	-
	Form	wavy	wavy	wavy	wavy	wavy	-
Mottles	**Abundance (%)**	0	0	0	0	0	<2
	Diameter (mm)	-	-	-	-	-	<5
	Colour	-	-	-	-	-	-
$CaCO_3$		absent	absent	absent	absent	absent	absent
Hardpan		absent	absent	absent	absent	absent	absent
Hydrocarbon Odour		yes	yes	yes	yes	yes	yes
Miscellaneous		Hydrocarbon contamination extends to > 95 cm; solid to 63 cm and fingers to 95 cm					

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 8: Gleyed Black Chernozem

Pit location		Outside of hydrophobic patch			
Horizon		Ap	Bm	Bmgj	Cg
Texture		loam	loam	clay loam	loam
Moisture		wet	wet	Wet	wet
Colour		10YR 2/1 m	10YR 3/2 m	10YR 5/2 m	10YR 5/2 m
Depth (cm)		0-30	30-40	40-56	56-100
EC[z] (dS/m)		0.12	0.57	0.07	0.06
pH (0.01 *M* $CaCl_2$)		5.5	5.3	5.9	6.4
Total C (%)		6.16	2.82	0.88	0.46
Organic C (%)		6.14	2.74	0.87	0.45
Inorganic C (%)		0.02	0.08	0	0.01
Total N (%)		0.37	0.23	0.07	0.06
DEO[y] (%)		2.02	0.50	0.39	0.35
MED[x] (*M*)		3.5	4.7	1.5	0
Structure	**Primary**	fine granular	fine granular	medium subangular blocky	fine granular
	Secondary	-	-	-	-
	Consistence	-	-	-	-
	Grade	medium	medium	weak	medium
Roots	**Abundance**	4-14	4-14	4-14	1-3
	Diameter (mm)	<0.075	<0.075	<0.075	<0.075
	Orientation	vertical	vertical	vertical	vertical
	Distribution	inped	inped	inped	inped
Boundary	**Sharpness (cm)**	2-5	5-15	5-15	-
	Form	wavy	wavy	wavy	-
Mottles	**Abundance (%)**	0	<2	2-20	>20
	Diameter (mm)	-	<5	<5	<5
	Colour	-	10YR 4/6	10YR 4/6	10YR 4/6
$CaCO_3$		absent	absent	absent	absent
Hardpan		absent	absent	absent	absent
Hydrocarbon Odour		absent	absent	absent	absent
Miscellaneous		-	-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch			
Horizon		A*	B1*	B2*	C*
Texture		silt loam	silt loam	loam	sandy loam
Moisture		dry	dry	wet	very wet
Colour		10YR 2/2 d	10YR 3/3 d	10YR 4/1 m	10YR 4/0 m
Depth (cm)		0-10	10-18	18-41	41-100
EC[z] (dS/m)		0.28	0.06	0.30	0.16
pH (0.01 *M* CaCl$_2$)		6.2	5.8	7.1	6.7
Total C (%)		5.75	1.22	0.84	2.41
Organic C (%)		5.67	1.20	0.83	2.25
Inorganic C (%)		0.08	0.02	0.01	0.16
Total N (%)		0.33	0.09	0.09	0.06
DEO[y] (%)		1.10	1.02	0.92	2.58
MED[x] (*M*)		3.8	2.2	1.3	3.8
Structure	**Primary**	massive	fine blocky	fine subangular blocky	medium subangular blocky
	Secondary	-	-	-	-
	Consistence	-	-	-	-
	Grade	-	-	-	-
Roots	**Abundance**	<1	<1	<1	0
	Diameter (mm)	<0.075	<0.075	<0.075	-
	Orientation	vertical	vertical	vertical	-
	Distribution	inped	inped	inped	-
Boundary	**Sharpness (cm)**	<2	<2	<2	-
	Form	smooth	smooth	smooth	-
Mottles	**Abundance (%)**	0	<2	2-20	2-20
	Diameter (mm)	-	5-15	<5	<5
	Colour	-	10YR 5/8	10YR 4/6	10YR 4/4
CaCO$_3$		absent	absent	absent	absent
Hardpan		absent	present	absent	absent
Hydrocarbon Odour		strong	strong	strong	strong
Miscellaneous		Strongly gleyed, lenses of hydrocarbons to water table (90 cm)			

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 9: Dark Gray Luvisol

Pit location		Outside of hydrophobic patch		
Horizon		Ap	Bt	C
Texture		clay loam	clay loam	loam
Moisture		dry-moist	moist-wet	moist-wet
Colour		10YR 3/2 m	10YR 5/3 m	10YR 5/2 m
Depth (cm)		0-20	20-58	58-100
EC[z] (dS/m)		0.04	0.06	0.04
pH (0.01 M CaCl$_2$)		5.0	4.5	4.2
Total C (%)		1.88	0.37	0.41
Organic C (%)		1.86	0.36	0.41
Inorganic C (%)		0.02	0.01	0
Total N (%)		0.17	0.06	0.06
DEO[y] (%)		0.04	0	0
MED[x] (M)		0	0	0
Structure	**Primary**	medium granular	very coarse columnar	very coarse columnar
	Secondary	-	fine subangular blocky	medium blocky
	Consistence	slightly hard	friable	firm
	Grade	medium	medium	strong
Roots	**Abundance**	4-14	4-14	4-14
	Diameter (mm)	0.075-1	0.075-1	0.075-1
	Orientation	oblique	horizontal	horizontal
	Distribution	inped	inped	exped
Boundary	**Sharpness (cm)**	<2	2-5	-
	Form	smooth	wavy	-
Mottles	**Abundance (%)**	0	0	0
	Diameter (mm)	-	-	-
	Colour	-	-	-
CaCO$_3$		absent	absent	absent
Hardpan		absent	absent	absent
Hydrocarbon Odour		absent	absent	absent
Miscellaneous		-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch		
Horizon		A*	B*	C*
Texture		loam	Loam	loam
Moisture		dry	dry-moist	moist-wet
Colour		10YR 3/3 d	10YR 5/3 m	10YR 4/2 m
Depth (cm)		0-20	20-53	53-100
EC[z] (dS/m)		0.07	0.05	0.05
pH (0.01 *M* $CaCl_2$)		4.9	4.3	4.4
Total C (%)		1.99	0.50	0.53
Organic C (%)		1.96	0.49	0.52
Inorganic C (%)		0.03	0.01	0.01
Total N (%)		0.17	0.06	0.06
DEO[y] (%)		0.10	0.02	0.01
MED[x] (*M*)		0	0	0
Structure	**Primary**	fine granular	fine blocky	medium blocky
	Secondary	-	coarse columnar	coarse columnar
	Consistence	soft	very friable	friable
	Grade	weak	weak	medium
Roots	**Abundance**	>14	1-3	<1
	Diameter (mm)	2-5	0.075-1	<0.075
	Orientation	oblique	horizontal	horizontal
	Distribution	inped/exped	exped	exped
Boundary	**Sharpness (cm)**	<2	2-5	-
	Form	smooth	wavy	-
Mottles	**Abundance (%)**	0	0	0
	Diameter (mm)	-	-	-
	Colour	-	-	-
$CaCO_3$		absent	absent	absent
Hardpan		absent	absent	absent
Hydrocarbon Odour		absent	absent	absent
Miscellaneous		-	-	-

* Mixed or otherwise disturbed horizon
[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

Site 12: Orthic Gray Luvisol

Pit location		Outside of hydrophobic patch				
Horizon		Ap	Ae	Bt1	Bt2	Ck
Texture		clay loam	silt loam	silty clay	clay loam	loam
Moisture		dry	dry	moist-wet	moist-wet	moist-wet
Colour		10YR 4/3 d	10YR 5/2 d	10YR 4/2 d	10YR 4/2 d	10YR 4/6 d
Depth (cm)		0-12	12-14	14-18	18-25	25-100
EC[z] (dS/m)		0.08	0.06	0.10	0.09	0.17
pH (0.01 M CaCl$_2$)		5.3	6.4	5.8	6.7	6.3
Total C (%)		3.32	1.22	0.65	0.40	0.53
Organic C (%)		3.31	1.20	0.64	0.39	0.41
Inorganic C (%)		0.01	0.02	0.02	0.01	0.12
Total N (%)		0.27	0.11	0.08	0.06	0.05
DEO[y] (%)		0.23	0.45	0.02	0.01	0.01
MED[x] (M)		0.8	0.4	0	-	0
Structure	Primary	fine granular	fine platy	fine blocky	medium blocky	medium blocky
	Secondary	-	-	-	-	-
	Consistence	-	-	-	-	-
	Grade	strong	strong	-	-	-
Roots	Abundance	4-14	4-14	4-14	4-14	1-3
	Diameter (mm)	0.075-1	<0.075	<0.075	<0.075	<0.075
	Orientation	vertical	vertical	vertical	random	random
	Distribution	inped	inped	inped	inped	inped
Boundary	Sharpness (cm)	<2	<2	5-15	2-5	-
	Form	wavy	smooth	wavy	wavy	-
Mottles	Abundance (%)	0	0	0	0	0
	Diameter (mm)	-	-	-	-	-
	Colour	-	-	-	-	-
CaCO$_3$		absent	absent	absent	absent	strong
Hardpan		absent	absent	absent	absent	absent
Hydrocarbon Odour		absent	absent	absent	absent	absent
Miscellaneous		-	-	-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch			
Horizon		A*	B1*	B2*	C*
Texture		loam	loam	-	Loam
Moisture		-	-	-	-
Colour		10YR 5/3 d	10YR 3/2 m	10YR 6/2 m	10YR 5/2 m
Depth (cm)		0-17	17-22	22-36	36-100
EC^z (dS/m)		0.68	0.31	-	0.46
pH (0.01 *M* $CaCl_2$)		5.1	6.1	-	7.3
Total C (%)		4.43	4.12	-	0.39
Organic C (%)		4.34	4.04	-	0.36
Inorganic C (%)		0.09	0.08	-	0.03
Total N (%)		0.26	0.25	-	0.06
DEO^y (%)		0.68	1.16	-	0.11
MED^x (*M*)		3.5	2.9	-	0
Structure	**Primary**	massive	medium blocky	fine prismatic	very coarse columnar
	Secondary	-	-	-	-
	Consistence	-	-	-	-
	Grade	-	-	-	-
Roots	**Abundance**	0	1-3	1-3	1-3
	Diameter (mm)	-	<0.075	<0.075	<0.075
	Orientation	-	vertical	Vertical	vertical
	Distribution	-	inped	inped	inped
Boundary	**Sharpness (cm)**	-	<2	<2	-
	Form	-	wavy	smooth	-
Mottles	**Abundance (%)**	0	0	0	0
	Diameter (mm)	-	-	-	-
	Colour	-	-	-	-
$CaCO_3$		absent	absent	absent	strong
Hardpan		absent	absent	absent	absent
Hydrocarbon Odour		absent	yes	yes	yes
Miscellaneous		-	hydrocarbon plume in B and C horizons		

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 14: Rego Black Chernozem

Pit location		Outside of hydrophobic patch	
Horizon		Ap	C1
Texture		sandy loam	sand
Moisture		dry	dry
Colour		10YR 3/2 d	10YR 5/8 d
Depth (cm)		0-20	20-100
EC[z] (dS/m)		0.08	0.03
pH (0.01 M $CaCl_2$)		5.9	6.7
Total C (%)		1.77	0.06
Organic C (%)		1.76	0.06
Inorganic C (%)		0.01	0
Total N (%)		0.16	0.02
DEO[y] (%)		0.04	0
MED[x] (M)		0.2	0
Structure	Primary	massive	massive
	Secondary	-	-
	Consistence	-	-
	Grade	-	-
Roots	Abundance	>14	4-14
	Diameter (mm)	0.075-1	<0.075
	Orientation	vertical	vertical
	Distribution	-	-
Boundary	Sharpness (cm)	<2	-
	Form	wavy	-
Mottles	Abundance (%)	0	0
	Diameter (mm)	-	-
	Colour	-	-
$CaCO_3$		absent	absent
Hardpan		absent	present
Hydrocarbon Odour		absent	absent
Miscellaneous		Recorded a C2 horizon, but did not sample	

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch	
Horizon		A*	C*
Texture		sandy loam	sand
Moisture		dry	dry
Colour		10YR 3/2 d	10YR 4/4 d
Depth (cm)		0-30	30-100
EC[z] (dS/m)		0.05	0.03
pH (0.01 *M* $CaCl_2$)		5.3	4.9
Total C (%)		1.58	0.08
Organic C (%)		1.55	0.07
Inorganic C (%)		0.03	0.01
Total N (%)		0.11	0.02
DEO[y] (%)		0.28	0
MED[x] (*M*)		3.0	0
Structure	**Primary**	massive	medium blocky
	Secondary	-	-
	Consistence	-	-
	Grade	-	medium
Roots	**Abundance**	<2	4-14
	Diameter (mm)	0.075-1	0.075-1
	Orientation	vertical	oblique
	Distribution	Inped	inped
Boundary	**Sharpness (cm)**	-	-
	Form	-	-
Mottles	**Abundance (%)**	0	0
	Diameter (mm)	-	-
	Colour	-	-
$CaCO_3$		absent	absent
Hardpan		absent	absent
Hydrocarbon Odour		absent	absent
Miscellaneous		-	

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 20: Gleyed Black Chernozem

Pit location		Outside of hydrophobic patch		
Horizon		Ah	Bm	Cg
Texture		sand	loamy sand	loamy sand
Moisture		moist-wet	moist-wet	moist-wet
Colour		10YR 2/1 m	10YR 3/2 m	10YR 4/3 m
Depth (cm)		0-20	20-37	37-100
EC^z (dS/m)		0.08	0.03	0.03
pH (0.01 *M* $CaCl_2$)		5.5	6.3	6.4
Total C (%)		1.30	0.55	0.17
Organic C (%)		1.29	0.55	0.16
Inorganic C (%)		0.01	0	0.01
Total N (%)		0.11	0.06	0.04
DEO^y (%)		0.05	0	0
MED^x (*M*)		0.4	0	0
Structure	**Primary**	massive	massive	massive
	Secondary	-	-	-
	Consistence	-	-	-
	Grade	massive	massive	massive
Roots	**Abundance**	>14	1-3	1-3
	Diameter (mm)	0.075-1	<0.075	<0.075
	Orientation	vertical	vertical	vertical
	Distribution	inped	inped	inped
Boundary	**Sharpness (cm)**	5-15	>15	-
	Form	wavy	irregular	-
Mottles	**Abundance (%)**	0	<2	>20
	Diameter (mm)	-	5-15	>15
	Colour	-	10YR 4/6	10YR 4/6
$CaCO_3$		absent	absent	absent
Hardpan		absent	absent	absent
Hydrocarbon Odour		absent	absent	absent
Miscellaneous		-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch	
Horizon		A*	C*
Texture		sand	sand
Moisture		dry-moist	moist-wet
Colour		10YR 2/2 m	10YR 5/3 m
Depth (cm)		0-14	14-100
EC^z (dS/m)		0.06	0.08
pH (0.01 *M* $CaCl_2$)		6.2	7.6
Total C (%)		3.03	0.12
Organic C (%)		3.00	0.12
Inorganic C (%)		0.03	0
Total N (%)		0.11	0.03
DEO^y (%)		2.99	0
MED^x (*M*)		4.8	0
Structure	**Primary**	massive	massive
	Secondary	-	-
	Consistence	-	-
	Grade	massive	massive
Roots	**Abundance**	>14	0
	Diameter (mm)	<0.075	-
	Orientation	vertical	-
	Distribution	inped	-
Boundary	**Sharpness (cm)**	<2	-
	Form	smooth	-
Mottles	**Abundance (%)**	0	>20
	Diameter (mm)	-	>15
	Colour	-	10YR 5/8
$CaCO_3$		absent	absent
Hardpan		present	present
Hydrocarbon Odour		absent	absent
Miscellaneous		Roots do not penetrate hard pan	

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 23: Dark Gray Luvisol

Pit location		Outside of hydrophobic patch		
Horizon		Ahe	Ae	Btgj
Texture		loam	loam	sandy loam
Moisture		moist	dry	dry
Colour		-	-	-
Depth (cm)		0-2	2-18	18-100
EC[z] (dS/m)		0.10	0.04	0.04
pH (0.01 *M* $CaCl_2$)		4.6	5.2	4.7
Total C (%)		7.16	0.81	0.70
Organic C (%)		7.14	0.80	0.69
Inorganic C (%)		0.02	0.01	0.01
Total N (%)		0.59	0.07	0.06
DEO[y] (%)		0.69	0.05	0.03
MED[x] (*M*)		2.8	0.6	0
Structure	**Primary**	fine platy	coarse platy	medium subangular blocky
	Secondary	-	-	fine subangular blocky
	Consistence	-	-	-
	Grade	weak	strong	strong
Roots	**Abundance**	all roots in LFH	0	0
	Diameter (mm)	-	-	-
	Orientation	-	-	-
	Distribution	-	-	-
Boundary	**Sharpness (cm)**	2-5	<2	-
	Form	wavy	smooth	-
Mottles	**Abundance (%)**	0	0	2-20
	Diameter (mm)	-	-	<5
	Colour	-	-	-
$CaCO_3$		absent	absent	absent
Hardpan		absent	absent	absent
Hydrocarbon Odour		absent	absent	absent
Miscellaneous		-	-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

Site 23a: Orthic Humic Gleysol

Pit location		Within hydrophobic patch			
Horizon		Ap*	Bkg1*	Bkg2*	Ckg*
Texture		sandy loam	silt loam	loam	loam
Moisture		dry	moist-wet	moist-wet	moist-wet
Colour		10YR 3/1 d	10YR 4/2 m	2.5Y 4/2 m	2.5y 3/2 m
Depth (cm)		0-29	29-44	44-80	80-100
EC[z] (dS/m)		0.40	0.21	0.09	0.14
pH (0.01 *M* CaCl$_2$)		7.3	7.1	6.5	6.8
Total C (%)		13.57	0.63	0.23	0.34
Organic C (%)		13.25	0.62	0.23	0.23
Inorganic C (%)		0.31	0.01	0.01	0.11
Total N (%)		0.47	0.06	0.03	0.04
DEO[y] (%)		8.96	0.06	0	0.01
MED[x] (*M*)		3.3	0	0	0
Structure	**Primary**	fine granular	coarse blocky	coarse blocky	massive
	Secondary	-	fine blocky	medium blocky	-
	Consistence	loose	firm	firm	firm
	Grade	weak	medium	strong	medium
Roots	**Abundance**	<1	<1	<1	0
	Diameter (mm)	<0.075	1-2	1-2	-
	Orientation	vertical	horizontal	horizontal	-
	Distribution	inped	exped	exped	-
Boundary	**Sharpness (cm)**	<2	2-5	2-5	-
	Form	smooth	wavy	wavy	-
Mottles	**Abundance (%)**	0	>20	>20	>20
	Diameter (mm)	-	5-15	5-15	<5
	Colour	-	5/6 7.5 YR	4.8 2.5 YR	4.8 2.5 YR
CaCO$_3$		absent	strong	strong	strong
Hardpan		absent	absent	absent	absent
Hydrocarbon Odour		absent	absent	absent	absent
Miscellaneous		-	-	-	-

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 23b: Gleyed Dark Gray Luvisol

Pit location		Within hydrophobic patch				
Horizon		Ap*	Aej*	Btgj*	Bgj*	Cg*
Texture		sandy loam	sandy loam	sandy clay loam	sandy loam	-
Moisture		dry	dry-moist	moist	moist	moist-wet
Colour		10YR 4/2 d	10YR 3/1 m	5Y 4/2 m	5Y 2.5 m	5Y 2.4/2 m
Depth (cm)		0-10	10-23	23-34	34-51	51-100
EC^z (dS/m)		0.45	0.38	0.32	1.37	0.55
pH (0.01 *M* $CaCl_2$)		6.8	7.4	6.5	9.8	8.4
Total C (%)		9.86	14.01	0.94	1.94	1.14
Organic C (%)		8.94	14.11	0.55	1.29	0.61
Inorganic C (%)		0.93	0	0.39	0.65	0.53
Total N (%)		0.31	0.28	0.05	0.06	0.04
DEO^y (%)		1.89	3.67	0.30	0.80	0.44
MED^x (*M*)		2.4	2.3	0.3	0.8	0.1
Structure	**Primary**	fine granular	fine granular	medium subangular blocky	medium subangular blocky	massive
	Secondary	-	fine subangular blocky	-	fine subangular blocky	-
	Consistence	-	-	firm	loose	-
	Grade	massive	massive	medium	weak	massive
Roots	**Abundance**	<1	0	0	0	0
	Diameter (mm)	<0.075	-	-	-	-
	Orientation	-	-	-	-	-
	Distribution	-	-	-	-	-
Boundary	**Sharpness (cm)**	2-5	<2	<2	2-5	-
	Form	wavy	smooth	smooth	wavy	-
Mottles	**Abundance (%)**	0	0	2-20	2-20	>20
	Diameter (mm) (mm)	-	-	< 5	< 5	> 15
	Colour	-	-	10YR 3/2	10YR 5/4	10YR 4/4
$CaCO_3$		absent	absent	weak	weak	weak
Hardpan		absent	absent	absent	absent	absent
Hydrocarbon Odour		absent	absent	absent	absent	absent

* Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)

Site 25: Rego Black Chernozem

Pit location		Outside of hydrophobic patch	
Horizon		Ap	C
Texture		sandy loam	sandy clay loam
Moisture		dry-moist	moist-wet
Colour		10YR 3/3 m	10YR 4/4 m
Depth (cm)		0-16	16-100
EC^z (dS/m)		0.17	0.08
pH (0.01 *M* $CaCl_2$)		6.1	6.2
Total C (%)		1.89	0.18
Organic C (%)		1.86	0.17
Inorganic C (%)		0.03	0
Total N (%)		0.15	0.03
DEO^y (%)		0.04	0.01
MED^x (*M*)		0	0
Structure	**Primary**	fine granular	medium blocky
	Secondary	-	-
	Consistence	friable	firm
	Grade	weak	medium
Roots	**Abundance**	>14	<1
	Diameter (mm)	1-2	<0.075
	Orientation	oblique	vertical
	Distribution	inped	exped
Boundary	**Sharpness (cm)**	<2	-
	Form	wavy	-
Mottles	**Abundance (%)**	0	0
	Diameter (mm)	-	-
	Colour	-	-
$CaCO_3$		absent	absent
Hardpan		absent	absent
Hydrocarbon Odour		absent	absent
Miscellaneous		-	-

[z] Electrical conductivity (2:1 v/w, water:soil ratio)
[y] Dichloromethane-extractable organics (Soxhlet)
[x] Molarity of ethanol droplet (performed in the lab)

- continued -

Pit location		Within hydrophobic patch	
Horizon		A*	C*
Texture		sandy loam	loam
Moisture		Dry	moist-wet
Colour		10YR 3/3 d	10YR 4/4 m
Depth (cm)		0-18	18-100
EC^z (dS/m)		0.18	0.14
pH (0.01 M $CaCl_2$)		5.8	5.9
Total C (%)		1.55	0.26
Organic C (%)		1.54	0.27
Inorganic C (%)		0.02	0
Total N (%)		0.14	0.05
DEO^y (%)		0.28	0.01
MED^x (M)		2.6	0
Structure	**Primary**	medium granular	medium subangular blocky
	Secondary	-	-
	Consistence	weak	friable
	Grade	weak	medium
Roots	**Abundance**	4-14	<1
	Diameter (mm)	<0.075	<0.075
	Orientation	oblique	vertical
	Distribution	inped	exped
Boundary	**Sharpness (cm)**	2-5	-
	Form	Irregular	-
Mottles	**Abundance (%)**	0	0
	Diameter (mm)	-	-
	Colour	-	-
$CaCO_3$		Absent	absent
Hardpan		Absent	absent
Hydrocarbon Odour		Absent	absent
Miscellaneous		-	-

[*] Mixed or otherwise disturbed horizon

[z] Electrical conductivity (2:1 v/w, water:soil ratio)

[y] Dichloromethane-extractable organics (Soxhlet)

[x] Molarity of ethanol droplet (performed in the lab)