UNIVERSITY OF ALBERTA

SOIL WATER REPELLENCY AT OLD CRUDE OIL SPILL SITES

BY

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ABSTRACT

My doctoral research focussed on soils that develop severe and persistent water-repellent character several years or decades following contamination by crude oil. These water-repellent soils no longer look, feel or smell like they contain any oil, but they remain dry even under heavy rainfalls and support sparse plant growth. The underlying objective of my research was to identify the causative agents and the processes leading to the development of soil water repellency at old crude oil spill sites.

Characterization of three water-repellent soils revealed that they are not salt-affected, nitrogen-deficient, nor sterile. Viable soil microorganisms subsist in them, although they are likely inactive due to limited access to water and dissolved nutrients. An extraction procedure had to be found that would remove soil water repellency completely and not destroy causative agents in the process. Soxhlet extraction with *iso*propanol/15.7 *M* NH_4OH (7:3, v/v) (IPA/NH_4OH) met these criteria and was used to isolate putative causative agents for further characterization. Isolated putative causative agents were identified as consisting predominantly of homologous series of straight-chain and polycyclic aliphatic hydrocarbons (C_{12} to C_{34}), including petroleum biomarkers (i.e. hopanes). From this evidence, I concluded that causative agents of soil water repellency are petroleum residues and not products of microbial origin. I subsequently found that sequential extraction alternating between amphiphilic and nonhydrogen-bonding solvents eliminates and in turn restores soil water repellency.

My research indicates that soil water repellency is not simply caused by the presence of hydrophobic organic molecules in soil. My data and literature reports on the conformational flexibility of insoluble organic molecules lead me to conclude that soil water repellency is a function of the packing density and tail conformation of amphiphilic organic molecules forming the outermost layer of soil particle surfaces. Intact or partially oxidized amphiphilic molecules of petroleum origin appear to be the causative agents of soil water repellency at old crude oil spill sites. Two possibly synergistic mechanisms are proposed to explain how the sorption of vapour- or liquid-phase petroleum hydrocarbons may have initiated the development of soil water repellency at old crude oil spill sites.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

GLOSSARY OF TERMS

a.m.u.	atomic mass unit
AW	acid-washed
BRU	Bruderheim site
^{13}C-NMR	solid-state ^{13}C nuclear magnetic resonance spectroscopy
CCH	cyclohexane
CEC	cation exchange capacity
$CHCl_3$	chloroform
CPMAS	cross-polarisation magic-angle spinning
CW	control wettable
DCM	dichloromethane
DEV	Devon site
ELL	Ellerslie site
GC/CI/MS	gas chromatography/mass spectroscopy (chemical ionisation mode)
GC/EI/MS	gas chromatography/mass spectroscopy (electron impact ionisation mode)
INAA	instrumental neutron activation analysis
IPA	*iso*propanol
IPA/CH_3COOH	*iso*propanol/5.2 *M* acetic acid (7:3, v/v)
IPA/NH_4OH	*iso*propanol/14.8 *M* ammonia (7:3, v/v)
MED	molarity of ethanol droplet
MWD	mean weight diameter
NW	water-repellent (nonwettable) soil
PW	pristine wettable soil
r.c.f.	relative centrifugal force (× g) = $0.00001118 \times N_m^2 \times r$, where N_m is rotational velocity (r.p.m.) and r is radius of rotation (cm)
RIC	relative ion count
S	spreading coefficient ($mJ \cdot m^{-2}$ or $mN \cdot m^{-1}$)
SDS	sodium dodecyl sulphate
SFE	supercritical fluid extraction
VOCs	volatile organic compounds
W_A	work of adhesion ($mJ \cdot m^{-2}$ or $mN \cdot m^{-1}$)
W_C	work of cohesion ($mJ \cdot m^{-2}$ or $mN \cdot m^{-1}$)
γ_l	free energy of the liquid/air interface ($mJ \cdot m^{-2}$ or $mN \cdot m^{-1}$)
γ_s	free energy of the solid/air interface ($mJ \cdot m^{-2}$ or $mN \cdot m^{-1}$)
$\gamma_{s/l}$	free energy of the solid/liquid interface ($mJ \cdot m^{-2}$ or $mN \cdot m^{-1}$)
θ	contact angle in the liquid phase at the line of three-phase contact (°)

CHAPTER 1

Current state of knowledge regarding the cause of soil water repellency[1]

GENERAL INTRODUCTION

Occurrence and significance of the problem

Soil water repellency is encountered in diverse ecosystems in many parts of the world. Most literature reports are of naturally-occurring or fire-induced soil water repellency, but there have also been a few reports of pollution-induced soil water repellency. Well-documented cases of naturally-occurring soil water repellency are found in Southern Australia. There, about five million hectares of sandy pasture soils have gradually developed recurring water repellency following the clearing of native vegetation (Blackwell 1993). Naturally-occurring soil water repellency has also been reported from other environments, including golf sand greens and citrus groves in the United States (Jamison 1942; Miller and Wilkinson 1977), coastal sand dunes in the Netherlands and New Zealand (Dekker *et al.* 1998; Wallis *et al.* 1991), and forested soils in Japan and Canada (Nakaya *et al.* 1977; Barrett and Slaymaker 1989). Fire-induced soil water repellency seems to be as widely distributed geographically. It has been encountered in Portugal, Italy, the United States, and South Africa (Scholl 1975; Giovannini *et al.* 1987; Scott and van Wyk 1990; Doerr *et al.* 1998). Pollution-induced water repellency is less well documented, but Ellis and Adams (1961) and Craul (1985) have reported it. It usually develops following prolonged exposure of soil to liquid- or vapour-phase petroleum hydrocarbons.

The condition described as soil water repellency in the literature varies greatly in its degree of severity and persistence. Some reports describe soil water repellency that is short-lived (e.g. seasonal), while others deal with water repellency that persists unabated for several decades. Some reports are of soils that absorb water with varying reduced infiltration rates, whereas others are of soils that remain dry even under heavy rainfalls.

Soil water repellency inhibits or retards plant growth. It disturbs the hydrological balance of ecosystems and prevents soil organisms from contributing efficiently to energy flow and nutrient cycling. Bare, dry

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[1] A version of this chapter has been submitted for publication in the European Journal of Soil Science. Roy, J.L. and W.B. McGill. Current state of knowledge regarding the cause of soil water repellency.

and often disaggregated water-repellent soils are also highly susceptible to dispersal by erosion. Dispersal of water-repellent soil poses a threat to the productivity of surrounding soil.

WHAT IS SOIL WETTABILITY?

Soil water repellency is poor soil wettability. In order to understand what is soil water repellency, it is necessary to understand what is soil wettability. Wetting refers to the displacement of a fluid, liquid or gas by another immiscible fluid, a liquid, over the surface of a solid. In soil wettability studies, the solid is mineral soil particles and their organic coating, the displaced fluid is air, and the wetting fluid is water and whatever organic and inorganic solutes it may contain.

Two possible configurations can be adopted by water and air in contact with soil. Water may spread without limit, displacing air from the entire available surface area of the solid, a situation corresponding to a contact angle (θ) of 0°. Alternatively, water may move over the soil surface, displace air in the process, but finally come to a halt when the contact angle between the liquid/air, solid/air and solid/liquid interface reaches a finite value $\theta > 0^\circ$. In the first instance, the soil readily absorbs water droplets and is thus said to be readily wettable or normal soil. In the second one, the soil does not readily absorb water and so is referred to as water-repellent or nonwettable soil. As we will see later, the meaning of 'readily' is usually arbitrarily defined.

Water displaces air over the surface of soil when the force of attraction of water molecules for the soil surface is greater than the force of attraction of water molecules for one another. Wettability is thus determined by the balance of adhesive forces between the liquid and solid and cohesive forces in the liquid. Adhesive forces measure the tendency of the liquid to spread over the soil surface, whereas cohesive forces measure the tendency of drops of liquid to ball up. Adhesive and cohesive forces are expressions of capillary tensions having units of force per unit length. Because the capillary tension of a surface or interface is numerically equal to the free energy per unit area of that surface or interface ($\mathrm{mN \cdot m^{-1} = mJ \cdot m^{-2}}$), adhesive and cohesive forces are sometimes also referred to as work of adhesion and work of cohesion and expressed in units of energy per unit of area.

Spontaneous spreading of water over the soil surface occurs when the work of adhesion (W_A) is greater than the work of cohesion (W_C) (in $\mathrm{mJ \cdot m^{-2}}$ or $\mathrm{mN \cdot m^{-1}}$). The difference between W_A and W_C is known as the spreading coefficient (S). W_A, W_C and S can be expressed in terms of surface energy ($\mathrm{mJ \cdot m^{-2}}$) or surface tension ($\mathrm{mN \cdot m^{-1}}$):

$$W_A = \gamma_s + \gamma_l - \gamma_{s/l} \tag{1}$$

$$W_C = 2\gamma_\ell \qquad (2)$$

$$S = W_A - W_C = \gamma_s + \gamma_\ell - \gamma_{s/\ell} - 2\gamma_\ell = \gamma_s - \gamma_\ell - \gamma_{s/\ell} \qquad (3)$$

γ_s is the surface free energy of the solid in contact with air, γ_ℓ is the surface free energy of the liquid in contact with air, and $\gamma_{s/\ell}$ is the surface free energy of the solid in contact with the liquid. Equation (4) illustrates how the contact angle (θ) is determined by competition between W_A and W_C forces (Johnson and Dettre 1993). The first part of this equation is known as Young's equation:

$$\cos\theta = (\gamma_s - \gamma_{s/\ell})/\gamma_\ell = (2W_A/W_C) - 1 \qquad (4)$$

The necessary condition for spontaneous wetting to take place is simply that the process shall involve a reduction in free energy (Burdon 1949). Wetting thus takes place only as long as $S > 0$. At equilibrium, the contact angle is static and the spreading coefficient can only be negative or zero (Johnson and Dettre 1993). It is only under nonequilibrum conditions that the spreading coefficient can be positive and the process of wetting observed. The spreading coefficient is positive, for example, when adsorption of water vapour molecules initially occurs at the soil/air interface.

It is often thought that formation of a water vapour film precedes the spreading of liquid water over solid surfaces. This has been called the distillation theory of spreading (Burdon 1949). There is no evidence that this is a universal mechanism, but the possibility of its existence has been discussed by other workers (Kistler 1993; Blake 1993). The distillation theory of spreading is not readily explained by Equation (3). This is because formation of a film of adsorbed water vapour molecules on the soil surface would eventually bring S to zero or to a negative value before any wetting has taken place. According to some workers, the forces driving the wetting process are cohesive and viscous interactions between the thickening film of vapour molecules and the liquid front. The wetting process is driven in the first place by changes of phase of water molecules from the liquid to the gaseous phase. This is then followed by changes from the gaseous to the liquid phase as more water vapour molecules condense onto the adsorbed vapour film and by growing cohesive forces and viscous interactions between the condensed vapour film and liquid-phase molecules at the wetting front line.

The theoretical relationships presented above are of little practical use in predicting the wetting behaviour of soil. This is because classical theory of capillarity assumes ideal solid surfaces and does not predict the occurrence of contact angle variation over time. Nevertheless, they provide valuable insight into the forces that determine soil wettability. For example, it is often said that the only requirement for good soil wetting is that the solid surface tension be larger than the liquid surface tension. Equation (3) shows that this is a necessary, but not sufficient condition. For spontaneous wetting to take place, the soil surface tension must exceed the summed tension of the liquid surface and of the liquid/solid interface. The liquid/solid interfacial tension typically has a value that is intermediate between that of the solid surface and that of the liquid surface (Shaw 1980).

Most soils absorb water readily. What is not well known is why and how they do it. Both readily wettable and water-repellent soils adsorb water vapour molecules (Miyamoto *et al.* 1972). The presence of adsorbed water vapour molecules on the soil surface may thus be a necessary condition for good soil wetting, but it is obviously not a sufficient one. It may be that good soil wetting requires a high surface density or thick packing of adsorbed water vapour molecules ahead of the wetting front line. A greater surface density of hydrophobic moieties might, for instance, prevent formation of such densely packed films in water-repellent soil. Even readily wettable soils, however, would be expected to contain at least some hydrophobic organic surface groups having low affinity for liquid- or vapour-phase water molecules. Such surface groups commonly occur in soil in the form of long alkyl chain substituents in humic and nonhumic organic material and siloxane groups on dehydroxylated silica surfaces. The fact that wetting occurs spontaneously in most soils is an indication that the entire surface area available for liquid-soil interactions does not have to be equally hydrophilic or uniformly coated with a film of adsorbed water vapour molecules for soil wetting to take place.

Naturally-occurring water-repellent soils do not seem to obey the distillation theory of spreading. These soils adsorb water molecules from the vapour phase, but not from the liquid phase (Miyamoto *et al.* 1972). Adsorption of water vapour molecules in these soils is thus not sufficient in itself to give rise to good soil wetting. It is usually assumed that water vapour molecules sorb to soil through the same interaction mechanisms as liquid water molecules do (i.e. mostly by dipole and H bonding interactions). The evidence presented by Miyamoto *et al.* (1972) thus indicates that water molecules in the liquid phase do not spread on the soil surface not because there are no effective short-range soil-liquid attraction forces, but because these attraction forces are weaker than cohesive forces in the liquid. It suggests that the difference between readily wettable and water-repellent soil lies in the packing density of their hydrophilic surface groups. Formation of a continuous film of adsorbed water vapour may require longer on surfaces that are characterised by a low surface density of hydrophilic groups. In some soils, this may allow complete evaporation of the liquid phase before a continuous film has had time to form. This would explain why a slightly water-repellent soil will often absorb a standard size water droplet before it has had time to evaporate completely whereas a severely water-repellent soil usually will not.

Theoretical models of wetting usually assume uniform and constant solid surface properties. However, not all units of surface area in soil can be expected at any time to have the same free energy. If, as Zisman (1964), Fink (1970) and Ma'Shum *et al.* (1988) have suggested, it is a good approximation to state that the outermost molecular groups on the surface of a solid determine its wettability, then the packing density and spatial distribution of high- and low-energy molecular groups on heterogeneous soil surfaces must also contribute to determining wettability. There may be a critical ratio of hydrophobic to hydrophilic surface area and a critical spatial distribution of these areas at a certain scale that affects wetting thermodynamics, which is not currently accounted for by theoretical thermodynamics. To date, the mechanism by which a wetting line advances on a solid surface remains only partially resolved.

It would be interesting to know what is the smallest scale of resolution at which there is a specific fraction of the soil surface area that must bear hydrophobic moieties in order to generate macroscale water repellency symptoms. By macroscale water repellency symptoms, I mean observable by sight and touch after addition of water to soil, or quantifiable by water droplet penetration tests. One study has shown that the mixing of one hydrophobic sand grain with nine hydrophilic ones produces water-repellent sand, whereas the mixing of one hydrophobic sand grain with 99 hydrophilic ones does not (Bauters *et al.* 1998). A ratio of 1:9 hydrophobic to hydrophilic units of surface area at the scale of a few square millimetres may thus be more than enough to produce macroscale water repellency symptoms in most soils; but is this ratio the same as that to be expected of the smallest unit of surface area that is the seat of water repellency symptoms? In order to arrive at an explanation of how soil water repellency develops, researchers need to be able to determine what is the smallest scale of resolution at which the ratio of hydrophobic to hydrophilic surface area (or average solid surface tension) is an indicator of macroscale soil water repellency symptoms. This information is not yet available.

HOW IS SOIL WATER REPELLENCY MEASURED ?

The contact angle (θ) is a measure of wettability. It is the macroscopically observable consequence of molecular-level interactions. A small contact angle means high wettability and a large contact angle means poor wettability. Theoretically, a 90° contact angle marks the division between infiltration and noninfiltration of water into porous soil (Fink 1976). If the contact angle is less than 90°, soil is wettable enough for spontaneous wetting to occur. If the contact angle has a value ranging from 90 to 180°, different degrees of water repellency are displayed by the soil. In practice, a contact angle greater than 90° is required to assure complete water runoff. Reliable contact angle data are difficult to obtain experimentally and are thus rarely used as absolute measures of soil water repellency. Instead, soil water repellency is usually assessed by recording how soil responds to contact with water.

There are several reasons why semiempirical assessments of soil water repellency are usually favoured over direct and indirect contact angle measurements. The most important one is that theoretically valid contact angle measurements are impossible to make in natural soil. Theories of wetting, such as the

Young equation, are usually formulated based on an ideal solid surface model. This ideal surface is smooth, homogeneous and nondeformable, and the angle formed at the liquid/solid interface is static and independent of gravity (Johnson and Dettre 1993). The surface area of a soil, however, is typically rough, heterogeneous and deformable (e.g. surface solubility) and contact angle measurements made on it typically decrease with increasing contact time. Consequently, contact angle measurements made on soil are usually difficult to reconcile with what is manifested as macroscale soil water repellency.

Soil is usually considered readily wettable if it completely absorbs water droplets within a few seconds, usually 10 or less. Soils that do not absorb water droplets within a few seconds are considered water-repellent and ranked according to the severity of their water repellency symptoms using different assessment procedures and corresponding arbitrary scales. Soil water repellency is most commonly assessed by the water droplet penetration time (WDPT) test and the molarity of ethanol droplet (MED) tests. Measurements of capillary rise and water-entry pressure are also used by some researchers to calculate contact-angle data and rank water-repellent soils according to these data. The WDPT test is performed by monitoring the time that it takes for complete penetration of water droplets into soil. The MED test is performed by identifying the aqueous ethanol solution of highest surface tension to allow complete droplet absorption into soil within 10 s. The WDPT and MED tests obey the same theoretical principles and have the same flaws that other water repellency assessment procedures have. Their main advantage is that they are simpler to perform.

The WDPT and MED tests have a sound theoretical basis. In the original WDPT test, the time required for droplet imbibition by the soil is recorded as an index of soil water repellency. This test accounts for the dynamism of contact angle values in soil, but it does not entail artificial modification of system conditions. In the MED test, the time required for droplet imbibition is set at 10 s and it is the surface tension of the wetting liquid that is varied and used as the indicator of soil water repellency. The MED test thus also accounts to a certain extent for the time-dependence of contact angle values in soil, but the time of observation is limited to 10 s and system conditions are modified so as to favour spontaneous wetting. This is achieved by increasing the ethanol concentration in the liquid, which lowers the free energy of the liquid surface and of the liquid/solid interface when liquid is brought into contact with soil. The aqueous ethanol concentrations used usually range from 0 to 6 M (surface tension range of ≈ 72 to 32 $\mathrm{mN \cdot m^{-1}}$) because most water-repellent soils absorb droplets of ≤ 6 M ethanol concentration within less than 10 s.

WDPT and MED test results obtained on the same soil do not usually bear a high correlation coefficient. This is to be expected because soil/water/air systems cannot be validly compared to soil/aqueous ethanol/air systems without accounting for differences in the nature of their solid-liquid molecular interactions. The submicroscopic physics, kinetics, and thermodynamics of wetting in soil/liquid/air systems are largely determined by these solid-liquid interactions. It is well known that soil does not interact with ethanol the same way as it interacts with water. For example, some organic and inorganic compounds on soil particle surfaces are more soluble in ethanol than they are in water. When the wetting liquid dissolves organic or inorganic compounds present at the soil surface, system thermodynamics are affected because the surface free energy of the liquid, solid and liquid/solid interface undergoes a change in the process. Liquid-soil interactions do not invalidate estimates of solid surface tension obtained by the WDPT test any more than they invalidate those obtained using the MED test. They only make estimates of solid surface tension obtained by these two separate tests not directly comparable.

It is not clearly known to what extent conditions under which droplet penetration tests are performed can vary without affecting the results. It would nevertheless seem prudent to standardise the procedure. The droplet size used should be uniform and large enough so that the liquid-solid contact area encompasses some of the largest-sized geometrical heterogeneities of the soil surface (i.e. macropores). This is necessary because there is evidence that roughness at the surface of solids affects the thermodynamics of wetting (Johnson and Dettre 1964). The soil should be sieved to pass at least a 2-mm sieve to reduce the range of geometrical heterogeneities found at the soil surface. The soil surface should be levelled by gentle shaking to prevent droplets from rolling off the point of placement during the assessment of soil water repellency. The soil, test liquid and air should be at the same temperature and this temperature reported with the results as it affects wetting thermodynamics.

The soil moisture potential seems to be by far the most important source of variability in soil water repellency assessments. I discuss in a later section why soil moisture interferes with measurements of soil water repellency. Here, I only recommend that the soil be air-dried prior to the assessment of soil water repellency to minimise the risk of soil water-test liquid interactions. It is also acceptable to perform MED tests on soil that is oven-dried (105 °C, 24 h) *from the air-dried state* when oven-drying does not cause a statistically significant increase or decrease in soil water repellency. Oven-dried soil should of course be allowed to cool to the test temperature before it is brought into contact with the test liquid. Oven-drying should always be preceded by air-drying because oven-drying soil from the moist state introduces variability in soil water repellency assessments that is not readily explained by available theoretical and experimental evidence (Ma'Shum and Farmer 1985; Dekker *et al.* 1998). Water repellency assessments made on oven-dried soil should be favoured when their results are less variable than those obtained on air-dried soil.

Systematic conversions of results obtained with one water repellency assessment procedure (e.g. capillary rise) into results of another kind of assessment procedures (e.g. WDPT) should be made only when it is known that they were obtained at a fixed and similar soil moisture potential. By fixing the soil moisture potential to the air-dry range, King (1981) was able to detect high correlations ($r^2 \geq 0.75$; n = 25 to 101) between the results of MED, WDPT, infiltration and capillary rise test results.

WHAT IS KNOWN ABOUT THE CAUSE OF SOIL WATER REPELLENCY ?

Several plausible sources of causative agents of soil water repellency have been proposed in the past. Originally suggested by consideration of circumstantial evidence, some have also earned support based on experimental evidence. Still, the question of the cause of soil water repellency remains only partially resolved. This is because a mechanism by which proposed causative agents impart water repellency to soil has never been satisfactorily demonstrated.

A few decades ago, DeBano (1969) pointed out that all that was known with reasonable certainty about the causative agents of soil water repellency was that they are hydrophobic organic compounds. This is still largely true today, although investigations over the past decades have increased our awareness of the complexity of the soil water repellency problem. Wallis and Horne (1992) recently reviewed the literature documenting various aspects of the problem of soil water repellency. Such a review is not repeated here. My intent, rather, is to describe some of the difficulties that are encountered in investigations into the cause of soil water repellency. This is followed by a discussion of established facts and findings which, in my opinion, contributed most significantly to the improvement of our understanding of the probable causes of soil water repellency.

Technical difficulties encountered in investigations into the cause of soil water repellency

The most common procedure that is used to identify causative agents of soil water repellency consists in characterising organic compounds whose removal from soil has reduced the severity of soil water repellency symptoms and in testing these compounds for ability to impart water repellency to readily wettable soil. There are several known limitations associated with the interpretation of outcomes resulting from the use of this investigative approach. A few of them are listed below:

1. *A nondestructive extraction method that removes soil water repellency completely and irreversibly has never been identified*

Complete elimination of water repellency symptoms should not be taken as a guarantee of complete or even substantial removal of causative agents of soil water repellency. This is because soil water repellency can often be restored by physical treatment that entails no addition of hydrophobic organic compounds to soil. For example, McGhie and Posner (1980) observed that chloroform extraction restores water repellency in hot water-extracted water-repellent soil. Ma'Shum and Farmer (1985) found that re-wetting and air-drying restores water repellency in freeze-dried water-repellent soil.

Extraction solvents that have been reported to eliminate soil water repellency completely have generally not been shown to do so irreversibly. For example, Ma'Shum *et al.* (1988) did not test if water repellency eliminated by Soxhlet extraction with *iso*propanol:15.7 *M* aqueous ammonia (7:3, v/v) (IPA/NH_4OH) could not be partially restored by subsequent extraction with chloroform or re-wetting followed by air- or oven-drying. When soil water repellency can be restored by physical treatment, one should be cautious in inferring that any causative agents have been removed from water-repellent soil.

2. *A wide variety of organic compounds that occur naturally in readily wettable soil can impart transient water repellency to readily wettable soil*

There is currently no published valid test to confirm that proposed causative agents have been correctly identified. Testing solutions or suspensions of proposed causative agents for ability to generate soil water repellency when added to readily wettable soil does not provide the conclusive evidence that is normally expected from such tests. This is because a wide variety of organic constituents of readily wettable soils possess the ability to impart water repellency when added to soil using the habitual test procedure. For example, Horne and McIntosh (1998) recently reported that organic material extracted from water-repellent or readily wettable soils using IPA/NH_4OH imparts a similar degree of water repellency when added to soil. Such results confirm that IPA/NH_4OH extracts hydrophobic organic material from soil, but not necessarily that it extracts causative agents of *naturally-occurring* soil water repellency.

Soil water repellency has been induced using a wide variety of organic matter sources, including comminuted plant litter (McGhie and Posner 1980), particulate soil organic matter (Franco *et al.* 1995), and solvent extract obtained from soils (Ma'Shum *et al.* 1988) or from plant residues lying on the soil surface (Doerr *et al.* 1998). The same success rate, however, has also been obtained with material removed from readily wettable soil and with commercially available sources of hydrophobic organic material. For example, Ma'Shum *et al.* (1988) induced soil water repellency by adding cetyl alcohol, palmitic acid and tristearin to soil. Franco *et al.* (1995) obtained similar results with cetyl palmitate, and Fink (1970, 1976) with silicone materials and mixtures of a petroleum resin dust-suppressant oil and paraffin wax.

Any material possessing some hydrophobic character may be expected to impart water repellency when applied to soil in sufficient quantity. This is because organisation of dissolved or suspended organic molecules occurs upon sorption onto soil and solvent evaporation (i.e. phase separation and crystallisation) (Muthukumar *et al.* 1997). This organisation typically favours exposure of nonpolar moieties at the fluid/solid interface because organic molecules interact with soil more strongly through their hydrophilic, polar functional or ionic groups (e.g. through cation exchange, protonation, ligand exchange, H bonding and van der Waals interactions) (Sposito 1984). Hydrophobic nonpolar moieties that can only interact with the soil through weak van der Waals forces consequently tend to be left dangling at the outer layer of the organic coating. The packing density of nonpolar moieties at the outermost layer of the soil surface is often thought to be what ultimately determines the severity of water repellency symptoms that are induced by addition of hydrophobic organic material to soil.

Organic material that imparts water repellency when added to soil in solution or suspension often does not cause water repellency in the soil from which it was obtained (e.g. material obtained from readily wettable soil). This is probably because organisation is not so pronounced in natural soils where additions of hydrophobic organic material occur by small increments and spatial distribution is expected to be less uniform.

3. *Soil water repellency that is generated by fresh addition of hydrophobic organic compounds is not generally tested for resistance to extraction*

Naturally-occurring soil water repellency is not easily eliminated by nondestructive extraction procedures. This fact suggests that its causative agents are either strongly sorbed to soil or too complex to dissolve in commonly used extraction solvents. Ability to induce water repellency symptoms in soil should not be the only criterion used to obtain experimental confirmation of the correct identification of causative agents of soil water repellency. Hydrophobic organic compounds that can impart water repellency to soil under controlled laboratory conditions should also be assessed for ability to pass the test of equal resistance to nondestructive extraction procedures. Jamison (1942) used this argument to test and reject the hypothesis that the paraffin spray oil used as pesticide carrier to fight diseases in citrus groves is the cause of soil water repellency under citrus trees. He was able to generate soil water repellency by adding paraffin oil emulsion to soil at the rate of 3.2 ml dry oil per kg soil. However, when he compared the resilience of water repellency symptoms in the oiled soil and a naturally-occurring water-repellent soil, he found that extraction with ether completely eliminated water repellency in the oiled soil, but did not reduce it in the naturally-occurring water-repellent soil. His conclusion was that the water repellency condition induced by oil application differs from that which develops in the field.

Naturally-occurring and artificially induced soil water repellency may differ in recalcitrance because their causative agents differ in chemical structure. This would indicate that the target causative agents of naturally-occurring soil water repellency have not been correctly identified. Alternatively, they may have the same chemical structure, but display unequal resistance to extraction because of different ageing times in the soil. Many organic compounds appear to acquire increased recalcitrance with increasing time of residence in the soil (Alexander 1995). Whether and why causative agents of naturally-occurring and artificially induced water repellency display unequal recalcitrance should be given greater consideration in the future.

It is a universal problem in investigations of the causative agents of soil water repellency that proposed causative agents are usually only tested for ability to generate transient soil water repellency. This is an important limitation considering that organic substances that can impart chronic water repellency to soil are possibly only a subset of those that can impart transient water repellency to soil. Ideally, not only the resistance to extraction, but also the persistence of artificially induced soil water repellency symptoms should be monitored over relatively long periods of time and under exposure to natural or simulated weathering factors. Some researchers investigating hydrophobic organic substances for use in water harvesting have found such tests to be informative (Fink 1976).

4. *Soil water repellency symptoms can be eliminated without removal of any compounds from soil and generated without addition of any compounds to soil*

Soil that is water-repellent in the air-dried or oven-dried state can be made readily wettable by force-wetting followed by freeze-drying (Ma'Shum and Farmer 1985). Such results are repeatable and have given rise to the statement that soil water repellency can be eliminated without removal of any organic compounds from soil. Freeze-dried soil is made water-repellent again if it is re-wetted and then air- or oven-dried. Water-repellent soils that have been rendered wettable by extraction with hot water can also regain their water repellency following treatment with chloroform (McGhie and Posner 1980). These observations have given rise to the statement that soil water repellency can be restored without addition of any organic compounds to soil.

Such observations have at least one important practical implication. It is that mixtures of organic compounds whose removal from water-repellent soil reduces soil water repellency may consist entirely of innocuous organic compounds, or of a mix of innocuous compounds and causative agents of soil water repellency. They indicate that reduction in soil water repellency cannot be interpreted as confirmation of removal of causative agents, just as increase in soil water repellency cannot be interpreted as confirmation of addition of causative agents of naturally-occurring soil water repellency.

5. *There is currently no published reliable test that can be used to distinguish between causative agents of soil water repellency and innocuous organic compounds in extracts obtained from water-repellent soil*

I have discussed why it is imprudent to infer that causative agents have been removed based on the results of extraction procedures that cause reductions in soil water repellency. In addition, I have described how testing putative causative agents for ability to impart water repellency to readily wettable soil can be misleading. There is yet another analytical problem associated with the identification of causative agents of naturally-occurring soil water repellency. It is that their chemical structure is not known and that their presence in extract obtained from water-repellent soil cannot be confirmed experimentally. Extracts obtained from water-repellent soil typically contain an unmanageably large mixture of organic compounds, most of which cannot be characterised by gas chromatography/mass spectroscopy (GC/MS). Compounds that are successfully characterised are typically indistinguishable, at least qualitatively, from compounds that occur naturally in most soils. For example, long-chain fatty acids such as those that Wander (1949) and Ma'Shum *et al.* (1988) have isolated from water-repellent soil have also been isolated from readily wettable soil by Schulten and Schnitzer (1990). Without knowledge of the chemical structure of causative agents of naturally-occurring soil water repellency, characterisation of organic extracts obtained from water-repellent soil are best used to detect quantitative aberrations between their content of hydrophobic organic material and that of extracts obtained from readily wettable soils.

PROCESSES LEADING TO THE DEVELOPMENT OF SOIL WATER REPELLENCY

I will now discuss what is known from theory and from experiment about the probable causes of soil water repellency under three main themes. Available evidence suggests that two sequential processes are needed to give rise to soil water repellency. These are: (1) accumulation of hydrophobic organic material in soil and (2) re-distribution and re-organisation of this material in soil. A third process, (3) stabilisation of the hydrophobic organic material, seems to be required to ensure persistence of induced water repellency symptoms.

1. Accumulation of hydrophobic organic material in soil

Water-repellent soils must differ from adjacent normal soils by having a larger a fraction of their total surface area that is constituted of hydrophobic moieties. This hypothesis is consistent with wettability theories and with available evidence pointing to the role of hydrophobic organic material as causative agents of soil water repellency. It entails that water-repellent soils contain organic molecules having hydrophobic moieties (e.g. alkyl chain substituents at least two C atoms long), which can impart water repellency to soil. Organic molecules containing one or more hydrophobic moieties are hereafter referred to as hydrophobic organic substances because at least part of their molecule displays hydrophobic character.

First, the established facts. There is compelling evidence that soil water repellency is caused by organic rather than inorganic hydrophobic material. Firstly, with the exception of siloxane groups on dehydroxylated quartz surfaces, there are virtually no hydrophobic mineral surfaces in soil (Tschapek 1984). Secondly, there is no indication that water-repellent and adjacent readily wettable soils differ in mineralogical composition. Thirdly, heating soil at high temperatures for prolonged periods of time seems to be the only effective way to eliminate soil water repellency permanently (Nakaya *et al.* 1977; Giovannini and Lucchesi 1984). It has also been amply demonstrated that water-repellent soils contain hydrophobic organic substances that can impart water repellency to soil. Franco *et al.* (1995) isolated water-repellent particulate organic matter from nonwettable sand that imparts water repellency when added to readily wettable soil. They also detected the presence of a hydrophobic coating containing aliphatic organic material on the surface of nonwettable sand grains. McGhie and Posner (1980) generated soil water repellency by adding hydrophobic, comminuted plant litter to soil. Doerr *et al.* (1998) achieved the same result with ethanol extracts of pine and eucalyptus forest litter. Wander (1949) and Ma'Shum *et al.* (1988) have isolated long-chain fatty acids from water-repellent sandy soils and induced water repellency by adding solutions of these acids to readily wettable soil.

It is generally accepted that soil water repellency is caused by organic material that has hydrophobic properties. The current state of knowledge, however, leaves many unresolved questions. For example, it is not known why most soils are readily wettable even though they also contain hydrophobic organic substances than can impart water repellency to soil (Schnitzer *et al.* 1986; Dinel *et al.* 1990). It is obvious that presence of hydrophobic organic compounds in soil is a necessary, but not sufficient, condition for repellency expression.

Now, the unresolved issues. Theory predicts that water-repellent soils contain a greater ratio of hydrophobic to hydrophilic surface area, or lower average solid surface tension, than readily wettable soils do. What is not known is what minimal ratio of hydrophobic:hydrophilic surface area results in macroscale repellency expression or at what scale this critical ratio is of practical significance. It is usually assumed that hydrophobic and hydrophilic organic substances have achieved a more or less spatially uniform packing density that exceeds this hypothetical critical ratio in water-repellent soils. However, the nature of the quantitative relationship between hydrophobic fractional coverage and induced soil water repellency symptoms remains poorly defined.

Research has indicated that addition of hydrophobic organic compounds to soil can give rise to soil water repellency. For example, Fink (1970) observed that increasing the rate of addition of dissolved hydrophobic organic material to soil increased the severity of induced water repellency symptoms. He noted also that, consistent with theory, this trend prevailed only up to the concentration required to form a compact monolayer over the entire surface area of soil particles. Ma'Shum *et al.* (1988), in contrast, reported that maximal water repellency was induced in a soil by increasing the rate of addition of cetyl alcohol to that theoretically equivalent to over 21-fold the compact monolayer concentration. They proposed that cetyl alcohol molecules coating both sand grains and water droplets were required to induce maximal soil water repellency. Nonuniform coverage was dismissed by the authors on the grounds that discontinuities in the coating were not detectable. However, because they did not describe the detection protocol that was used, this possible alternative explanation cannot be disregarded based on the evidence provided.

The groups of Franco *et al.* (1995) and McGhie and Posner (1980) demonstrated that increasing rates of water-repellent litter addition to soil increases the severity of induced soil water repellency symptoms. This may, however, have been due to an increased fraction of hydrophobic plant surface area in soil, and not to an increase in the hydrophobicity of soil particle surfaces. It is still not known whether natural soil water repellency is caused by particulate hydrophobic organic matter or by recalcitrant amorphous organic matter that cannot be separated from soil nondestructively. In either case, however, soil water repellency would be expected to be accentuated by addition of particulate hydrophobic organic matter. In most documented cases of naturally-occurring soil water repellency, there is no indication that particulate organic matter is the seat of water repellency symptoms. Particulate organic matter, however, often seems to be the most likely source of amorphous hydrophobic organic material in soil. Franco *et al.* (1995) postulated that particulate organic matter is a reservoir of waxy material in soil. They proposed that waxes move out of the inside of organic matter particles and spread onto their outer surface and on the surface of mineral soil particles when soil is heated under natural or artificial conditions.

The fact that addition of particulate or amorphous hydrophobic organic material to soil increases soil water repellency is consistent with theory. Increasing the ratio of hydrophobic:hydrophilic surface area in soil increases the severity of induced water repellency symptoms. The main problem with the postulated mechanism of accumulation of hydrophobic organic substances in soil is not with theoretical foundations, but with its practical application. Naturally-occurring soil water repellency is not normally caused by sudden large additions of organic material to soil or other unusual punctual events (e.g. fire). It typically becomes noticeable only several years or decades following disturbances, such as the clearing of native vegetation or contamination by petroleum hydrocarbons. The only exception to that rule is fire-induced water repellency, which normally appears soon following a fire. Fire-induced water repellency, however, is not usually attributed to addition of hydrophobic organic substances to soil, but rather, to heat-promoted, improved distribution of hydrophobic organic material within the soil (Savage 1974).

In naturally-occurring water repellency, accumulation of hydrophobic organic substances is usually suspected of giving rise to soil water repellency. This hypothesis entails that accumulation occurred predominantly in areas that would later develop water repellency. Proponents of this hypothesis, however, rarely offer explanations for why water-repellent and readily wettable adjacent soil should have received or accumulated different amounts of hydrophobic organic material over time. Yet, this is especially not evident where water-repellent and adjacent readily wettable soil occur in areas that were subjected to similar management practices and supported similar vegetation before the onset of soil water repellency.

There is little doubt that accumulation of hydrophobic organic matter in soil is a requirement for the development of soil water repellency. This contention is supported by the fact that destruction of organic matter eliminates soil water repellency. This criterion, however, remains too poorly documented in qualitative and quantitative terms to have use in making categorical distinctions between water-repellent, readily wettable soil, and soils at risk of developing water repellency. This is because the chemical structure of the target hydrophobic substances is not known and the process by which these gather to increase the fraction of hydrophobic surface area in soil has not been demonstrated. It is still not clear whether water-repellent and adjacent wettable soils differ only in fractional coverage or also in gravimetric content of causative agents of soil water repellency. Hydrophobic surface area in soil may be increased as a result of re-distribution or re-organisation of hydrophobic organic substances in soil and not necessarily as a result of enrichment on a gravimetric basis. The re-distribution mechanism is consistent with the delayed appearance of water repellency symptoms following disturbances such as the clearing of native vegetation or contamination of the soil by petroleum hydrocarbons. The following section discusses evidence that certain climatic conditions may provide the mechanism for the re-distribution or re-organisation of hydrophobic organic compounds in soil, thereby favouring the development of soil water repellency.

B. Re-distribution and re-organisation of hydrophobic organic material in soil

Accumulation of hydrophobic organic substances in soil seems to be a necessary, but not sufficient condition to give rise to soil water repellency. This is supported by two pieces of evidence: (1) fire often induces soil water repellency even though it likely removes more organic material than it adds to soil, (2) soils contaminated by petroleum hydrocarbons usually begin to display water repellency only several years or decades following the contamination event. Heating and drying are two abiotic processes that have often been attributed a role in the generation of water repellency in soil. Heating has been postulated to improve the spatial distribution of hydrophobic organic material in soil and to increase their fractional coverage of soil particle surfaces (Savage 1974; Franco *et al.* 1995). Drying, on the other hand, has been postulated to promote sorption of hydrophobic organic compounds onto soil in a conformation that maximises exposure of their hydrophobic moieties at the fluid/solid interface (Ma'Shum and Farmer 1985).

First, the established facts. A number of common observations regarding the role of heating and drying has been made by several researchers. One is that heating water-repellent soil at high temperatures (> 300 °C) under oxidising conditions can eliminate water repellency completely and irreversibly (Nakaya *et al.* 1977; Giovannini and Lucchesi 1984). This presumably occurs because most of the hydrophobic organic material in soil is thermally degraded. Another common one is that increasing the temperature at which soil is heated often intensifies the severity of soil water repellency symptoms (Doerr *et al.* 1998; Dekker *et al.* 1998). This trend has been observed within the heating temperature range of 25 to 105 °C and heating periods of up to 48 h. As a rule, the wetter the soil is before heating, the greater the magnitude of the heat-induced increase in water repellency. Gradual decreases in water repellency have been reported with exposure to higher temperatures depending on both the temperature used and the duration of the heating period (Scholl 1975; Giovannini and Lucchesi 1984; Nakaya *et al.* 1997). Thermal decomposition of hydrophobic organic material in soil does not seem to occur when soil is exposed to 105 °C or lower temperatures for less than 48 h, or if it does, its effect is to increase rather than to reduce soil water repellency. A third observation is that the severity of water repellency symptoms is usually greater when measured on air-dried or oven-dried soil than it is when measured on wetter soil.

Now, the unresolved issues. Reports indicate that heating or drying plays a role in the generation of water repellency in soils already containing hydrophobic organic material. What is not known is what mechanisms are responsible for the increases in soil water repellency that are observed in heating experiments. This is because the roles of heating and drying in the generation of soil water repellency are often difficult to separate based on evidence presented in literature reports. Before I discuss how heating and drying are thought to affect soil water repellency, I discuss how assessing soil water repellency without controlling soil moisture potential can produce apparent variations in soil water repellency that are independent of actual changes in soil surface properties.

How soil moisture variation interferes with water repellency assessment

There is a problem associated with the concept of potential and actual soil water repellency that was introduced by Dekker and Ritsema (1994). This concept states that field-moist soil displays actual water repellency, whereas air- or oven-dried soil displays potential (maximal) water repellency. The problem with this concept is that it does not take into account the fact that water in soil interferes with the assessment of soil water repellency and may cause variation in results that are independent of change in the wetting properties of the actual soil surface. The presence of water in soil nullifies the assumption that the model system whose wettability is studied consists of three separate phases, a dry solid phase and two immiscible fluids, the test liquid and air.

Although soil water repellency is manifested as whole-soil lack of affinity for water, it is really a manifestation of the lack of affinity of *solid particle surfaces* for water. The tests that are commonly used to assess soil water repellency are designed to produce a relative measure of the affinity of dry soil particles for water. More precisely, they are designed to produce a relative estimate of the average surface tension of soil solids.

Soil water repellency assessments obtained on wet soil measure the affinity of soil water and solid particle surfaces for the test liquid. Because water molecules have a strong affinity for other water molecules, interactions between water in moist soil and water in the test liquid causes underestimation of the water repellency of the solid phase. In other words, the presence in soil of a liquid phase that has affinity for the test liquid attracts test liquid into soil pores beyond the level that interactions between solid surfaces and the test liquid alone would allow.

As was mentioned earlier, the tests used to assess soil water repellency can only be validly interpreted when obtained on soil that is in equilibrium with ambient air. They measure the affinity of the solid phase for the test liquid with the underlying assumption that the solid phase is in a vacuum. Because there is usually little difference between a solid surface tension in a vacuum and one in air (Johnson and Dettre 1993), it is considered acceptable to measure water repellency on soil that is in equilibrium with air. Soil water repellency assessments made on soil that is wetter than air-dry, however, are invalid because a soil water-test liquid interaction variable has been introduced. The tests that are commonly used to measure soil water repellency are not designed to account for this extra variable. Water repellency assessments made on soils that are wetter than air-dry could be validly interpreted if the theory was modified to account for the variability introduced by liquid-liquid interactions.

The concept of actual soil water repellency that was introduced by Dekker and Ritsema (1994) is useful to describe the temporal variability of soil water repellency symptoms under natural field conditions. However, it remains that the results of water repellency assessments made on moist soil cannot be validly compared to results made on air- or oven-dried soil. In order to monitor the effect of different heating temperatures or other treatments on soil water repellency, soils subjected to the treatments should initially be in equilibrium with ambient air.

Mechanism 1: Heating causes re-distribution of hydrophobic organic compounds in soil, which in turn causes soil water repellency

Prolonged heating at 105 °C can be expected to drive a number of processes, such as removal of water, some liquefaction of nonvolatile hydrophobic organic compounds, and some evaporation of more volatile hydrophobic organic compounds. During a fire, re-distribution of vapours may occur with much loss to the aboveground atmosphere, but also some re-distribution within the soil profile. DeBano (1969) proposed that fire-induced soil water repellency is caused by the condensation in cooler (lower) soil horizons of vaporised hydrophobic plant material migrating from warmer (upper) soil horizons. Franco *et al.* (1995) postulated that smaller-scale re-distribution of melted, nonvolatile hydrophobic organic compounds may also occur and improve the uniformity of hydrophobic surface coverage when soil is heated to temperatures above 40 °C.

Much of the experimental evidence supporting the hypothesis that heating increases soil water repellency has been obtained with soil that was initially moist or organic matter-amended before heating. This complicates the process of mechanism identification because of the number of variables that are allowed to vary during heating experiments. For example, Dekker *et al.* (1998) observed that drying field-moist soil at 25 or 65 °C for 7 to 10 d consistently increased the severity of water repellency symptoms. They attributed this increase to heat-induced improved distribution of hydrophobic organic substances in the soil, even though soil moisture content likely varied between the two treatments. Most of the time, it is impossible to separate the contribution of heating time and temperature to the change in soil water repellency from that of moisture removal from soil based on evidence provided in literature reports. From my assessment of the content of many of these reports, there seems to be no indication that heating nonamended air-dried soil to temperatures ≤ 105 °C increases soil water repellency.

Franco *et al.* (1995) demonstrated that exposure to repeated wet-heating and cooling cycles increases the severity of water repellency symptoms that are induced by addition of particulate hydrophobic organic matter to soil. For the same rate of litter addition, they found that symptom severity was increased by increasing the number of heating and cooling cycles to which the amended soil was subjected. They also observed that wet-heating litter-amended soil at 70 or 105 °C for the same length of time produced more severe water repellency symptoms in the soil that had been heated at 105 °C. These results are interesting, but also difficult to interpret because several mechanisms might have concomitantly operated to produce the observed increases in water repellency. Franco *et al.* (1995) postulated that heating increases the severity of water repellency symptoms by promoting diffusion of nonvolatile waxy material from the inside of organic matter particles out onto their external surface and the surface of soil particles. They did not test if nonamended water-repellent soil and adjacent readily wettable soil also displayed more severe water repellency following similar wet-heating and drying cycles.

Heat-induced re-distribution of hydrophobic organic material in soil is usually the mechanism that is postulated to cause soil water repellency. It is a one-time event in fire-induced water repellency, but presumably an intermittent one in naturally-occurring soil water repellency. Heating may be required only once to impart water repellency to soil. Further heating may serve to replenish the supply of hydrophobic organic material in soil, as proposed by Franco *et al.* (1995), or to increase the stability of this material against physical, chemical and biological degradation. These hypotheses are consistent with the observation that fire-induced water repellency is typically shorter-lived than naturally-occurring water repellency. However, they require that explanations be provided for why soil adjacent to water-repellent soil has not also acquired water repellency over time. If heating hydrophobic organic material in the soil causes soil water repellency, it should be possible to demonstrate that there is spatial heterogeneity in soil heating patterns, in soil water regime, or in soil hydrophobic organic matter content.

Re-distribution of hydrophobic organic matter on soil particle surfaces was also postulated by McGhie and Posner (1980) to be the cause of chloroform-induced soil water repellency. These workers observed that soil water repellency can be eliminated by extraction with hot water and then restored by Soxhlet extraction with chloroform. They proposed that polar solvents (i.e. water in this case) cause the dispersion of clay aggregates and thereby increase the fraction of hydrophilic surface area in soil, whereas nonpolar, non-H-bonding solvents (i.e. chloroform in this case) cause the aggregation of clay particles and the deposition of hydrophobic organic matter onto the outer surface of these aggregates. This hypothesis, however, entails that Soxhlet refluxing in chloroform fails to remove the hydrophobic organic substances that it dissolves or brings into suspension.

The proposed re-distribution mechanism entails that the fractional surface coverage of hydrophobic organic substances in a soil layer be increased after cooling beyond what it was before heating. There is no direct experimental evidence indicating that this indeed happens, except perhaps for some micromorphological images that were obtained by SEM (Dekker *et al.* 1998). To confirm that heat-induced increases in soil water repellency are caused by improved surface distribution of hydrophobic organic material in soil, harder physical evidence should be sought. Ideally, the magnitude of the ratio of hydrophobic to hydrophilic surface area in soil before and after heating and the magnitude of that required to cause expression of soil water repellency (i.e. WDPT > 10 s) should be determined from direct measurement of soil surface properties. Saada *et al.* (1995) devised a method to measure the proportion of hydrophilic and hydrophobic surface area of clay minerals that could be modified for use in whole water-repellent soils.

Mechanism 2: Drying soil induces conformational changes in hydrophobic organic material, which in turn causes water repellency

As was discussed earlier, the fraction of the soil surface area that is covered with hydrophobic organic substances is likely to be an important factor in the development of soil water repellency. There is evidence, however, that soil wettability is determined not so much by the fractional coverage of hydrophobic organic molecules on soil as by the packing density of hydrophobic moieties at the outermost surface of soil particles.

Ma'Shum and Farmer (1985) were among the first to suggest that the conformation of hydrophobic organic substances in soil contributes to determining whether or not a soil will display water repellency. They provided evidence for this by comparing the water repellency of air-dried, oven-dried and freeze-dried soil. They found that soils that are severely water-repellent in the air-dried or oven-dried state are readily wettable in the freeze-dried state. Re-wetting and oven-drying the freeze-dried soil caused the soil to regain water repellency. Ma'Shum and Farmer (1985) attributed this reversible water repellency to changes in the molecular conformation of the hydrophobic organic material coating soil. According to them, hydrophobic organic compounds sorbed onto soil particle surfaces adopt a different conformation in the presence and absence of water. Evaporation of water causes more of the hydrophobic moieties of the organic material to become exposed at the fluid/solid interface because it allows for closer interactions of its polar functional groups away from that interface. In the presence of water, polar functional groups in the organic material interact with water as well as with one another and less segregation of hydrophobic moieties is needed to minimise free energy. According to Ma'Shum and Farmer (1985), freeze-drying soil preserves the conformation of wet organic matter, but air- or oven-drying does not.

Ordering of asymmetrical or amphiphilic organic molecules is known to take place upon condensation, precipitation, or physisorption onto solid surfaces (Muthukumar 1997). Further free energy-minimising changes are thought to occur in the conformation of organic molecules following their sorption onto soil. Wetting and drying, in particular, are suspected of inducing such changes because some peats, composts, and humic substances display reduced wettability following prolonged drying. The importance of the role of drying-induced conformational changes in the generation of soil water repellency has often been implied, but rarely demonstrated by researchers. This is because direct physical evidence of conformational changes at the outermost layer of soil particle surfaces is difficult to obtain. Literature reports suggest that removing moisture from soil increases the severity of soil water repellency symptoms (Dekker *et al.* 1998; Franco *et al.* 1995), but this cannot be confirmed experimentally with currently available techniques.

There is some evidence in the soil water repellency literature that exposure to solvents of differing polarity and H-bonding capacity can induce conformational changes in hydrophobic organic material that modify soil wettability. Although McGhie and Posner (1980) suggested another explanation for what they observed, the fact that chloroform extraction restored water repellency in hot water-extracted soil constitutes evidence in support of this hypothesis. Exposure to chloroform may have promoted closer interactions of polar functional groups and extension of hydrophobic moieties into the nonpolar liquid phase. Hudson *et al.* (1994) also observed increases in water repellency following extraction of water-wettable and water-repellent soil with nonpolar organic solvent, in this case, hexane. These authors attributed the observed increase in soil water repellency to re-distribution of hydrophobic organic substances in soil or retention of nonpolar solvent by the soil. They might also have added solvent-induced conformational changes to their list of alternative explanations. These reports at least suggest that exposure of soil to nonpolar, non-H-bonding solvents may cause conformational changes in the outermost layer of organic matter coatings that are analogous to those caused by removal of water from soil.

C. Stabilisation mechanisms that ensure persistence of induced water repellency symptoms

The cause of ephemeral or recurring water repellency, hereafter referred to as transient soil water repellency, is likely to differ from that of more persistent water repellency, hereafter referred to as chronic soil water repellency. Transient soil water repellency implies that water-repellent substances have a relatively short half-life as water-repellent substances in the soil, whereas chronic soil water repellency implies that they persist for several decades. Soils that display transient water repellency likely display this condition because they temporarily provide residence to particulate, suspended or dissolved hydrophobic organic material that is not irreversibly sorbed onto soil. In contrast, the causative agents of chronic soil water repellency appear to be irreversibly sorbed to soil and not susceptible to natural physical, chemical and biological removal processes. At the very least, a large enough fraction of them resists extraction by nondestructive extraction procedures and retains the ability to impart water repellency to soil.

The postulated mechanisms of accumulation of hydrophobic organic substances in soil, followed by heat-induced re-distribution or drying-induced re-organisation of hydrophobic organic substances in soil may explain the development of both transient and chronic soil water repellency. Another mechanism is required, however, to explain the unusual persistence of chronic soil water repellency. Persistence may be due to causative agents of chronic soil water repellency having a more complex chemical structure than that of causative agents of transient soil water repellency. Alternatively, it may be due to chronic low levels of microbial activity in the soil, strong association of causative agents with the soil, or perpetual replenishment of hydrophobic organic material in the soil. There is no evidence yet that causative agents of chronic and transient soil water repellency differ in chemical structure. Little is known about the level of microbial activity in soils that display either transient or chronic soil water repellency. The hypothesis of continual replenishment is inconsistent with the fact that chronically water-repellent soils typically support only sparse vegetation. The hypothesis of stronger association with the soil, on the other hand, is consistent with both circumstantial and experimental evidence. According to Alexander (1995), organic compounds typically become increasingly resistant to extraction with increasing residence time in the soil. The fact that chronic soil water repellency is generally more resistant to nondestructive extraction procedures than is transient soil water repellency also supports this hypothesis.

Ageing is commonly invoked to describe how organic compounds become increasingly resistant to extraction with lengthening time of residence in the soil. Reduced sorption reversibility is thought to result from multiplication of covalent and noncovalent cross-links within organic matter coatings and between these coatings and mineral soil surfaces. Soil heating and drying may promote ageing of water-repellent substances in soil as they do in a variety of manufactured organic polymers and protective coating materials. Soils displaying chronic water repellency may be characterised by more stable hydrophobic organic substances because they have experienced more numerous heating/cooling and wetting/drying cycles than soils displaying transient soil water repellency have.

CONCLUDING REMARKS

Soil water repellency is encountered in diverse ecosystems in many parts of the world. It is a condition that varies greatly in its degree of severity and persistence, as well as in the circumstances surrounding its occurrence. It is diagnosed as the inability of air-dry soil to absorb water droplets within 10 s or less. Soil water repellency is not a condition that can be defined in precise quantitative terms. This is because soil surfaces only approximate the ideal model surface from which wetting theories have been derived. Tests used to measure soil water repellency rely on sound theoretical principles, but at best provide only rough estimates of the average surface tension of soil solids.

The cause of soil water repellency is still not well understood. Several causative agents have been proposed in the past, but a mechanism by which proposed causative agents impart water repellency to soil has never been satisfactorily demonstrated. There are a number of limitations associated with the interpretation of results from past investigations into the nature of causative agents of soil water repellency. These should be better recognised and addressed in the future.

The question of the spatial scale at which wetting takes place in soil and at which the ratio of hydrophobic to hydrophilic surface area correlates with macroscale water repellency symptoms is a critical question confronting researchers studying the problem of soil water repellency. Theory predicts that water-repellent soils have a larger ratio of hydrophobic:hydrophilic surface area than do readily wettable soils. The value of this ratio and the scale at which it must be sought, however, remain to be identified. At the macroscale, available evidence suggests that two sequential processes are needed to give rise to soil water repellency: (1) accumulation of hydrophobic organic material in soil and (2) re-distribution and re-organisation of this material in soil. Most literature reports support this hypothesis. Plausible mechanisms have been proposed to explain how these processes come about, but none of them can explain why adjacent soil is spared from developing water-repellent character. A third process, stabilisation of the hydrophobic organic material, seems to be required to ensure persistence of induced water repellency symptoms. This being the least studied of the three proposed sequential processes, discussion provided on this topic is mostly conjectural.

The objective of my doctoral research was to extend the study of soil water repellency to its occurrence at old crude oil spill sites. The province of Alberta has several examples of formerly productive soils that have become severely water-repellent several years or decades following crude oil contamination. These soils strongly resist wetting and consequently support only sparse plant growth. Because of their high susceptibility to erosion, there are concerns that these soils pose a threat to the productivity of adjacent land.

My doctoral research was divided into four phases: (1) selection and characterisation of three water-repellent and corresponding control soils (Chapter 2), (2) isolation and characterisation of causative agents of soil water repellency (Chapter 3), (3) investigation into the cause of reversible soil water repellency (Chapter 4), (4) identification of processes that led to the development of soil water repellency at old crude oil spill sites (Chapter 5). My specific objectives were to identify the causative agents and the mechanism by which this material imparts water repellency to soil. To my knowledge, this is the first study focussing on the occurrence and cause of soil water repellency at old crude oil spill sites.

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CHAPTER 2

Characterisation of disaggregated nonwettable surface soils found at old crude oil spill sites[1]

INTRODUCTION

Hydrophobic mineral soils have been described from many parts of the world over the past 50 years. Such a condition has been encountered in various environments, including burned forest soils (DeBano and Rice 1973; Scott and Van Wyk 1990), citrus groves (Jamison 1947), subalpine tundra of various soil types (Barrett and Slaymaker 1989), golf sand greens (Miller and Wilkinson 1977; Hudson *et al.* 1994), sandy soils of Australia (Ma'Shum *et al.* 1988), New Zealand (Wallis *et al.* 1991), and the Netherlands (Bisdom *et al.* 1993), urban soils (Craul 1985), cultivated soils (Chan 1992) and soils contaminated with petroleum hydrocarbons from natural gas (Ellis and Adams 1961). The literature on nonwettable soils suggests that soil water repellency is most frequently encountered in sandy soils characterised by a relatively small specific surface area and low organic matter content. However, the phenomenon is not restricted to coarse-textured soils; finer-textured arable soils can also display severe water repellency (Chan 1992; Adams and Ellis 1960; McGhie and Posner 1980). Further details about water-repellent soils in general are available in the comprehensive review by Wallis and Horne (1992).

Soil water repellency is typically attributed to the presence of hydrophobic organic substances forming a coating over the surface of soil particles (Jamison 1947; Roberts and Carbon 1972; Tschapek 1984; Ma'Shum *et al.* 1988; Wallis and Horne 1992). This idea generates little debate because most mineral particle surfaces in soils are coated with organic substances, even in soils that absorb water normally (Tschapek 1984). A wide assortment of naturally-occurring organic substances have been postulated to give rise to soil water repellency. Because the majority of nonwettable soils that have been described in the literature have no history of exposure to industrial pollution, researchers have had no reason to suspect that substances other than naturally-occurring ones may cause soil water repellency. Why some naturally-occurring substances can generate water repellency in certain soils and not in others, however, remains to be elucidated. Until Tschapek (1984) and Ma'Shum and Farmer (1985) produced evidence suggesting that the molecular orientation of organic matter coatings on soil particles may be determining whether soils will repel or absorb water, most researchers thought that soil water repellency was

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attributable to the presence of natural organic matter of distinctive composition. Currently, the hypothesis that soil water repellency is caused by natural components of soil organic matter that possess both hydrophobic nonpolar moieties and hydrophilic polar or ionic functional groups is slowly gaining wider acceptance (Ma'Shum and Farmer 1985; Wershaw 1986; Ma'Shum *et al.* 1988; Anderson *et al.* 1995). According to this hypothesis, naturally-occurring amphiphilic or surface-active organic molecules, such as humic, fulvic, and fatty acids, can impart water repellency to a soil when their hydrophilic ends are oriented towards soil particle surfaces and their hydrophobic ends extend towards the open pore space (Voronin and Vityazev 1979; Tschapek 1984; Grelewicz and Plichta 1985; Ma'Shum and Farmer 1985; Ma'Shum *et al.* 1988; Wallis *et al.* 1990). The reverse arrangement is thought to prevail in soils that absorb water normally; that is, hydrophilic functional groups are expected to interact with the soil solution whereas hydrophobic functional groups are expected to interact with themselves and with the surface of organic coatings on mineral soil particles. Inversion of the orientation of amphiphilic organic molecules on the surface of soil particles has been postulated to occur during soil drying and following soil treatment with certain nonpolar organic solvents (Tschapek 1984; Ma'Shum and Farmer 1985; Ma'Shum *et al.* 1988).

I report here on a type of nonwettable soils that has been encountered with increasing frequency throughout the province of Alberta, Canada, over the past decade, and which, to my knowledge, has never been described in the literature before. The soils under study have become severely water-repellent and disaggregated several years or decades following crude oil contamination. As an introduction to these poorly known soils, I present information about the history of the development of structural degradation and water repellency in three typical nonwettable soils from Alberta, together with results of their physical, chemical and biological characterisation. Physical properties, including structure, texture, colour, moisture retention behaviour and response to heating treatment are described for both nonwettable and adjacent normal soils. Information on their chemical properties includes total C and mineral N content, cation exchange capacity (CEC), exchangeable cations and soil pH. In addition, results from preliminary biological characterisation work focussed on bacterial plate counts, some metabolic capabilities, and morphological features are also presented. This paper documents the apparent link between crude oil contamination and the development of soil water repellency and structural degradation and provides some basic soil characterisation necessary for the formulation of hypotheses about the mechanisms leading to soil disaggregation and hydrophobicity and the elaboration of effective remediation strategies.

MATERIALS AND METHODS

General description of the sites

The disaggregated nonwettable soils under study occupy areas 2 ha or less and display hydrophobicity to a depth of ≈15 cm. They occur in cultivated lands, forested areas, and industrial sites known to have been contaminated with crude oil two to five decades earlier. Because they support sparse plant growth, resist wetting during rainfall, and are structurally disaggregated, these soils are highly susceptible to erosion and thereby threaten to damage adjacent land and disperse contaminants to nearby environments. According to a number of private landowners, areas of disaggregated nonwettable soil have gradually expanded over the years, most markedly so in arable lands subjected to seasonal tillage. This soil no longer presents any sign of oil contamination; that is, it does not have the feel, appearance or odour of oil-contaminated soil. Most of the components of crude oil in the layer of nonwettable soil thus appear to have either escaped by volatilisation or undergone oxidative degradation. Some sites still present evidence of oil contamination, but the latter is confined to shallow subsoil horizons underneath the water-repellent soil.

Site selection and soil preparation

Soil samples were obtained from three old crude oil spill sites located within a 60 km-radius of the city of Edmonton, Alberta, Canada. The three soils were selected on the basis of their contrasting physicochemical properties and management history. Each site contains at least one large patch of barren, disaggregated water-repellent soil.

Ellerslie experimental site (ELL)

This study site is located at the Ellerslie research station of The University of Alberta, ≈18 km south of Edmonton. Its legal location is NE 24-51-25-W4 (53°25'N, 113°33'W). The soil is classified as a well-drained, Eluviated Black Chernozem of the Malmo Silty Clay Loam series. This soil developed on fine-textured, slightly saline glaciolacustrine sediments. The site has a level topography, and is surrounded by vegetation characteristic of the Aspen Grove section (Crown and Greenlee 1978). The native vegetation consisted mostly of tall grasses, shrubs, and deciduous trees.

The ELL site was experimentally contaminated with crude oil in 1973 as part of a study on reclamation practices for soils damaged by crude oil spills (Toogood 1977). Following oil contamination, the site was divided into plots to be reclaimed and plots to be left untreated. The study was terminated 5 years later when soil in the reclaimed plots had recovered most of its original productive capability (Toogood

1977). The reclamation treatments tested in the study consisted of different tillage practices and fertilisation rates. In subsequent years, repeated attempts to return the site to agricultural production yielded patchy crop growth and resulted in considerable mixing of nonreclaimed with reclaimed soil. A decision was then made to maintain the site as a fallow field for future research. The ELL site now contains three patches of nonwettable soil where the oiled but nonreclaimed plots used to be located. Only the nonreclaimed soil has become water-repellent and disaggregated; the reclaimed soil in adjacent plots absorbs water normally and shows some residual macroaggregation. The site was fallowed from 1984 to 1994, during which time the soil did not receive any organic or inorganic fertiliser additions. In August 1994, the site was seeded to fall rye under-seeded to alfalfa. Growth was heavy on all portions of the plots except the nonwettable sections. The rye was clipped to obtain dry matter yields using 1 m^2 samples in early July 1995. The average dry matter yield recorded for nonwettable plots was 1.6 ± 0.4 t ha^{-1} compared to 9.6 ± 0.5 t ha^{-1} for the oiled plots that were successfully reclaimed in the 1970s and never developed water repellency. The residual oil content of the nonwettable and control wettable adjacent soil at this site is respectively 9.8 ± 0.4 and 1.0 ± 0.0 g oil per kg soil (oven-dry soil basis), as determined by 24-h Soxhlet extraction using dichloromethane as the extractant.

Devon site (DEV)

This site is located on agricultural land near Devon, ≈15 km south-west of Edmonton. Its legal location is NW 23-50-26-W4 (53°20'N, 113°42'W). The original soil is classified as a weakly Eluviated Black Chernozem of the Ponoka Loam series developed on alluvial lacustrine, medium-textured materials. In the native state, the area was covered with a mixture of poplar groves and shrub patches. The present vegetation is characteristic of the Aspen Grove section. The topography is level to undulating, with long and smooth slopes and the soil is naturally well drained.

This site was contaminated with crude oil following the blow-out of the Atlantic No. 3 oil well in 1947. Although much of the spilled oil was probably removed or burned in the subsequent fire, substantial amounts of oil percolated into the subsoil where it can still be found. According to a report by Kerr (1986), most of the contaminated soil at this site was successfully returned to cereal production within a few years after the spill. If so, then the soil condition must have slowly deteriorated over time because the current landowner claims that large patches of disaggregated nonwettable soil already scarred the site over 30 years ago (J.A. Rebus, pers. commun.). Although some tillage and seeding has been practised, this nonwettable soil was not tilled, seeded or fertilised regularly for most of the last 30 years and probably longer. The DEV site today contains four large patches of nonwettable soil covering a total area in excess of 2 ha. These patches spread away from the relic well head, following a gentle slope declining in both north-ward and west-ward directions. The residual oil content of the nonwettable and control wettable adjacent soil at this site is 6.5 ± 0.3 and 1.5 ± 0.1 g oil per kg soil (oven-dry soil basis), respectively, as determined by 24-h Soxhlet extraction using dichloromethane (DCM) as the extractant.

Bruderheim site (BRU)

This third study site is located ≈6 km north of the town of Bruderheim, or ≈50 km north-east of Edmonton. Its legal location is NW 19-56-20-W4 (53°51'N, 112°58'W). The soil, which consists of dune sand, is classified at the subgroup level as an Orthic Regosol. It was developed on aeolian parent material and is characterised by highly quartzitic sand. Under native conditions, the dune sand area supported grass and shrub growth. The present vegetation is characteristic of the Aspen Grove section with trembling aspen as the dominant tree species. The topography of the site is undulating to hilly, or dune-like.

This site was contaminated with crude oil in the mid-1970s when it used to support an oil-producing facility (oil battery site). The nonwettable soil at this site occurs in a small relief depression ≈ 100 m^2 large. The adjacent sloping terrain supports sparse shrub and grass vegetation and absorbs water normally. The water-repellent soil is virtually bare and contains consolidated asphaltic material ("tar balls") between 10 cm to < 2 mm in diameter. The residual oil content of the nonwettable and control wettable adjacent soil at this site is 2.3 ± 0.2 and less than 0.1 ± 0.0 g oil per kg soil (oven-dry soil basis), respectively, as determined by 24-h Soxhlet extraction using DCM as the extractant.

Even though information about the quantity and quality of the oil spilled at two of the three study sites is not readily available, the approximate timing of those spills and the time since the contaminated soils began to display severe water repellency and structural deterioration are generally better known (Table 2.1). Oil-contaminated soil at these sites only began to manifest severe water repellency and structural degradation a decade or more following oil contamination.

Sampling

Samples of nonwettable (NW) and control wettable (CW) surface soil (top ≈15 cm) were collected in plastic bags in August 1994 after scraping off the first centimetre to remove litter and occasional thin surface crusts. CW soil was collected immediately outside the NW soil boundaries. The DEV-CW soil samples were obtained from underneath a healthy wheat crop. The ELL-CW and BRU-CW soil samples were obtained from areas that were only sparsely covered with weeds, predominantly Canada thistle. CW soil was taken as that which supported some plant growth and readily absorbed water droplets placed on its surface. The collected field-moist soil was sieved to pass a 2-mm-sieve and thoroughly mixed to produce uniform composite samples of CW and NW soil for each of the three study sites. The composite samples were stored in glass jars in the dark at 4 °C prior to analysis. There is no true replication at the site level.

Assessment of soil water repellency

The molarity of ethanol droplet (MED) test, first proposed by Watson and Letey (1970) and later developed by King (1981), was used to measure soil water repellency. This simple and rapid method has been widely tested and is considered reliable when used on air-dried or oven-dried soil (King 1981; Karnok *et al.* 1993). 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 the liquid and thereby enables infiltration regardless of the soil contact angle (Wallis *et al.* 1991). According to the interpretation guidelines provided by King (1981), soils with a MED index ≤ 1 *M* are not significantly water-repellent, whereas soils with a MED index ≥ 2.2 *M* are considered to be severely water-repellent. I assessed soil water repellency using ethanol concentrations of 0.2-*M* intervals in the range of 0-6.0 *M*. MED indices were routinely measured on both air- and oven-dried (105 °C, 24 h) soil, but I report only the MED values obtained on oven-dried soil because they were more consistent and essentially the same as those measured on air-dried soil. At higher soil moisture contents than air-dry, MED indices become unreliable because the water present in the soil attracts the added water through cohesive forces.

Characterisation of microbiological properties

Viable plate count procedure

The spread plate technique was used to test the hypothesis that communities of viable and culturable microorganisms are less abundant and diversified in NW soil than they are in CW soil. After ≈7 d in cold storage, three subsamples of ELL-CW and ELL-NW soil were taken out of the cold room to perform viable plate count enumerations. A 10^{-1} dilution was prepared by adding 20 g of field-moist soil to 180 mL of the following sterile mineral salts solution (g L^{-1}): Na_2HPO_4, 6; KH_2PO_4, 3; NaCl, 0.5; and NH_4Cl, 1, (pH 7). Decimal dilutions through 10^{-8} were prepared from the 10^{-1} dilution. Plates containing Plate Count Agar (Difco Laboratories, Detroit, Michigan, U.S.A.) were streaked with 0.1-mL aliquots of each dilution and each dilution was plated in triplicate. Colony-forming units (CFU) were counted after 3 d of incubation at ≈21 °C under normal daylight. The plates carrying the highest dilutions (10^{-6} to 10^{-8}) were incubated at ≈21 °C for a total of 12 d to allow for the collection and purification of several bacterial isolates.

Microscopic observation of microbial isolates

To obtain additional qualitative information about microbial communities in ELL-CW and ELL-NW soil, a total of 34 bacterial isolates from the Plate Count Agar plates were selected and examined under phase-contrast microscopy. Cell shape, size, and motility, the presence of spores and/or inclusion bodies, and general colony appearance was recorded for each isolate. Comparisons were made between microbial numbers and community characteristics in ELL-CW and ELL-NW soil.

Characterisation of chemical properties

Total C was determined by dry combustion using a LECO induction furnace (CR-12). No attempt was made to remove carbonates prior to analysis for fear of losing labile organic compounds in the process of removing the carbonates. Exchangeable NH_4^+ and NO_3^- were determined by automated colourimetric analysis of 2 *M* KCl extracts from air-dried soil samples (Keeney and Nelson 1982). Soil pH was determined in distilled deionised water and 0.01 *M* $CaCl_2$ at a soil:water ratio of 1:2 with separate glass and calomel electrodes using a Fisher Accumet® pH Meter Model 630. CEC and exchangeable base-forming cations were determined following the method of Lavkulich (1981). Briefly, exchangeable cations were determined by saturating cation exchange sites with NH_4^+ using 1 *M* ammonium acetate (NH_4OAc) (pH 7) and analysing the leachate for Ca^{2+}, Mg^{2+}, K^+, and Na^+ using atomic absorption spectroscopy (Atomic Absorption Spectrophotometer Perkin-Elmer 503). CEC was determined on the NH_4^+-saturated samples following repeated washings with IPA to remove residual 1 *M* NH_4OAc (pH 7). The IPA-washed samples of NH_4^+-saturated soil were then leached several times with 1 *M* KCl to displace exchangeable NH_4^+ and the resulting extracts analysed for NH_4^+ using a Technicon auto-analyser unit to determine CEC. Most of the above analyses were performed in duplicate and thus were not subjected to statistical analyses. Total C and mineral N analyses were performed in triplicate and the mean values compared using Student t-tests.

Characterisation of physical properties

Soil colour

Soil colour was determined on air-dried soil samples using Munsell soil colour charts (Munsell Color Company, Inc., Maryland, U.S.A.).

Particle size analysis and determination of soil texture

Particle-size analysis was performed by the Bouyoucos hydrometer method, without pretreatment to remove organic matter or soluble salts, following the procedure described by Kalra and Maynard (1991). Textural class names were assigned using the criteria of the Canadian System of Soil Classification.

Soil-moisture characteristic curves

The moisture desorption behaviour of the three NW and corresponding CW soils was determined using a pressure plate apparatus. The CW soil samples were placed on a porous plate in a pressure tank and saturated by allowing distilled water to infiltrate through the bottom of the samples overnight. The NW soil samples had to be force-wetted (shaken with water) before they were placed on the porous plate next to the CW soil samples because they would not absorb water by capillarity. The gravimetric water content of the soils was determined at six suction values (i.e. 0.01, 0.033, 0.1, 0.2, 0.4, and 1.5 MPa), each of which was held for 48 h.

Dry aggregate size distribution

Dry aggregate size distribution was determined to obtain a semiquantitative assessment of the extent of structural degradation in the three NW soils. It was determined by dry sieving CW and NW soil using a modified Yoder sieving apparatus equipped with six nested sieves of aperture sizes 1.0, 0.50, 0.25, 0.125, 0.063 and 0.045 mm. I used 500 g of soil that had previously been air-dried and sieved to pass a 2-mm sieve. It is unlikely that air drying and sieving affected aggregation in the NW soils because the latter are found only in the air-dry state and flow like water through a 2-mm sieve. The rotary sieve machine was allowed to run at 150 vibrations$\cdot$min^{-1} for 10 min. Material passing through each of the sieves was collected and weighed without attempting to distinguish between aggregates and individual soil particles. Unadjusted and adjusted mean weight diameter (MWD) values were computed using the regression equation proposed by Kemper and Roseneau (1986).

Microstructure observation using scanning electron microscopy

The NW soils were also examined under SEM to complement the dry aggregate distribution data and possibly detect the presence of an organic coating on NW soil particle surfaces. The apparatus used was a Jeol JSM-630FXV Scanning Electron Microscope attached to an Energy Dispersive X-Ray Analyzer Kevex 5500. Magnification of 50× to 20 000× was used to produce digital images of the six soils.

Oven-heating treatment

This test was performed to determine what combination of temperature and time would provide the mildest thermal treatment leading to the complete elimination of soil water repellency. I subjected triplicate samples of NW soil (≈15 g) from each site to forced-air oven temperatures of 105, 150 and 200 °C and measured their MED index after 1 and 14 d of continuous heating. The oven-heating experiments were repeated three times for each test temperature to ensure triplication of soil × duration × temperature combinations for the three NW soils. I selected the lowest oven temperature to completely remove water repellency in 24 h and conducted another oven-heating experiment similar to the one already described to determine the number of hours required to completely eliminate soil water repellency at the selected temperature. At the start of this 24-h oven-heating experiment, 12 samples of air-dried ELL-NW, BRU-NW and DEV-NW soil were placed in the pre-heated oven. A new soil sample from each site was taken out of the oven every 2 h over the 24-h period, cooled in a desiccator, and assessed for soil water repellency. This 24-h oven-heating experiment was repeated three times within the same week to ensure that each soil × temperature × duration treatment combination was triplicated. The MED values reported are the arithmetic means of triplicate values.

Differential thermal analysis

Differential thermal analyses (DTA) were performed on ELL-CW and ELL-NW soil samples. The purpose was to determine if the two soils would respond to controlled heating with different net enthalpy changes, thereby reflecting differences in the type and/or magnitude of thermal reactions and organo-mineral interactions taking place in each soil. The soil samples were ground to a fine powder with a mortar and pestle, placed into a sample holder and analysed with respect to Al_2O_3 reference material. The DTA apparatus was run at a linear heating rate of 30 °C min^{-1} under static air until the temperature of 525 °C was reached. The system used was a Perkin-Elmer System 7/4 Thermal Analysis Controller connected to a Perkin-Elmer DTA 1700 Differential Thermal Analyzer and a Hewlett Packard 7035B X-Y Recorder.

RESULTS AND DISCUSSION

Characterisation of microbiological properties

Viable plate count and microscopic observation

The numbers of viable and culturable CFU per gram of oven dried soil were in the same order of magnitude in ELL-NW and ELL-CW soil. I enumerated 4×10^5 CFU·g^{-1} in ELL-NW soil and 9×10^5

CFU·g^{-1} in ELL-CW soil. The values reported here were obtained by averaging counts from two replicates.

Among the ELL-NW soil bacterial isolates that were examined under microscope, I found representatives of the genera *Pseudomonas* and *Cytophaga*, which are not known to produce spores or cysts, and numerous *Bacillus* and actinomycete species, which are known to produce resistant spores in soil.

Based on these observations, I concluded that ELL-NW soil still harbours viable vegetative bacterial cells, as well as resistant microbial spores and cysts. The numbers obtained in this study are low compared to the numbers that were obtained in 1973 for the same soil using the same method, but only 4 months after oil addition. For example, the number of microorganisms enumerated 21 years ago was 400 ± 110 × 10^5 CFU·g^{-1} in ELL-CW soil and 870 ± 400 × 10^5 CFU·g^{-1} in ELL-NW soil (Toogood 1977). My estimates of microbial numbers in ELL soil are at least 100-fold lower than these earlier estimates. Several factors could account for the observed reduction in the size of the viable and culturable microbial community in ELL soil. For instance, the past several years of fallowing at the ELL site may have contributed to a reduction in microbial numbers due to gradual depletion by soil microorganisms of readily available energy sources and mineral nutrients. The gradual development of soil water repellency and concomitant establishment of chronic low levels of available water in soil may also have contributed to the elimination of drought-intolerant soil microorganisms.

To obtain additional qualitative information about the microbial component of ELL-NW and ELL-CW soil, 34 bacterial isolates were examined under phase-contrast microscopy over a 12-d period following the original plating. Cell shape, size, and motility, the presence of spores or inclusion bodies, and general colony appearance was recorded for each isolate. Fourteen of the isolates examined were from ELL-CW soil. The other 20 were from the ELL-NW soil. One third (11/34) of all microbial isolates examined consisted of representatives of the *Bacillus* genus. These appeared to be represented in equal proportions in ELL-CW and ELL-NW culture plates (5/14 + 6/20). Two out of the 14 isolates obtained from ELL-CW soil and five of the 20 isolates obtained from ELL-NW soil were actinomycetes. Three different brightly coloured colonies of coccoid bacteria that had a very unique elastic consistence were found only in the ELL-NW soil plates. Attempts to sample these colonies with a sterile loop would always result in the whole colony springing off the solid medium and clumping onto the loop. These colonies were also impossible to disperse in saline solution (0.85% NaCl, w/w), even when prolonged vortexing was used.

Of the 34 isolates examined, two isolates obtained from ELL-NW soil were characterised by dense packing of both large translucent and small opaque inclusion bodies. These inclusion bodies may have contained storage polymers, such as polyhydroxyalkanoates or glycogen (Lageveen *et al.* 1988; Stuart *et al.* 1995), although some more closely resembled the intracellular sulphur granules found in purple sulphur bacteria. None of the bacterial isolates obtained from ELL-CW soil were cocci-shaped cells, whereas four were found among the 20 isolates obtained from ELL-NW soil. I tried to select different organisms for microscopic observation, but it is possible that, in some instances, I looked at different isolates of the same bacterial species. This is because I selected isolates based on colony morphology, which is an attribute that may vary considerably over a matter of days. I concluded from this preliminary microbiological work that ELL-NW soil contains as many diverse bacteria as adjacent ELL-CW soil does. Quantitative and qualitative differences in the fungal communities of ELL-CW and ELL-NW soil were not detected using the enumeration and microscopic observation techniques employed in this study.

Characterisation of chemical properties

Total C and exchangeable NH_4^+ and NO_3^-

Characterisation of some of the physicochemical properties of the soil at the three selected sites was needed to provide a background set of information to guide my research. A summary of the information obtained is presented in Tables 2.2 and 2.3. I found total C to be slightly higher in NW soil than in CW soil, except in soil from the DEV site. Higher total C in ELL-NW and BRU-NW soil was attributed to the presence of residual petroleum hydrocarbons rather than to differences in native organic matter or carbonate content between corresponding CW and NW soil samples. The native physicochemical properties of CW and NW soil are not likely to differ substantially because CW and NW soil samples were collected < 25 m apart at each study site. At the ELL and BRU sites, an additional precaution was taken to sample CW soil from areas that were as sparsely vegetated as the areas sampled for NW soil. In contrast, DEV-CW soil was obtained from underneath a growing crop of wheat because CW soil surrounding water-repellent areas was under cultivation at the time of sampling. The total C content in the six test soils was taken as an estimate of their organic C content because the surface layer of Eluviated Black Chernozems and quartzitic sand dunes generally contains negligible amounts of carbonates.

The mineral N data presented in Table 2.3 revealed no consistent trend in the relative or absolute distribution of NH_4^+-N and NO_3^--N forms in CW and NW soil. Mineral N was determined mostly to gain information about the availability of this nutrient to microorganisms subsisting in NW soil. I found relatively large amounts of available N in ELL-CW and ELL-NW soil and DEV-CW and DEV-NW soil, but comparatively little in BRU-CW and BRU-NW soil.

Mineral N levels in ELL-CW soil were also determined by Toogood (1977) and colleagues prior to oil contamination in 1973. Using a similar procedure (Bremner 1965), they determined it contained 0.49 mg·kg^{-1} NH_4^+-N and 9.25 mg·kg^{-1} NO_3^--N. Comparing these earlier results with mineral N results obtained in this study suggests that concentrations of available N in ELL-CW and ELL-NW soil increased more than 10-fold over the past 25 years. Such an increase in mineral N could only have resulted from a combination of biological N_2 fixation, organic matter mineralisation, and atmospheric deposition. The ELL site had not received organic or inorganic amendment in at least a decade before I collected ELL-CW and ELL-NW soil samples for this study.

I found no consistent trend in the total concentration of mineral N of corresponding CW and NW soils. As a rule, NO_3^--N was the predominant form in CW and NW soil from the three sites. NO_3^--N was neither consistently higher nor lower in NW soil than in CW soil. On the other hand, NH_4^+-N was consistently higher in NW soil than in CW soil at each of the three study sites. The relatively higher NH_4^+-N content of NW soil may have arisen as a consequence of its chronic dry state under natural field conditions. The gradual and irreversible air-drying of NW soil under field conditions may have enhanced NH_4^+ adsorption to soil particles. Although I do not have experimental evidence to substantiate this statement, other researchers have reported small but significant increases in exchangeable NH_4^+-N and even NO_3^--N following air-drying of soil (Nelson and Bremner 1972).

Alternatively, the NW soils may have accumulated comparatively more NH_4^+-N than the corresponding CW soils did because of lower nitrification rates. According to Paul and Clark (1989), NH_4^+-N often accumulates in water-stressed and cool soils because mineralisation reactions producing NH_4^+-N are generally less sensitive to both water stress and low temperature than are nitrification reactions. Given the severe deterioration of the NW soils and the low tolerance of nitrifying bacteria to poor microhabitat conditions, conversion of NH_4^+-N to NO_3^--N probably occurs more slowly, if at all, in NW soil than in CW soil.

Another factor that may have accounted for higher NH_4^+-N levels in NW soil is the activity of N_2-fixing cyanobacteria (also known as blue-green algae). These are thought to experience bursts of activity when rainwater accumulates at the surface of NW soil. The formation of green mats in water ponds sitting on the surface of NW soil was observed at the ELL site following a heavy rainfall during warm summer days. This activity may result in the release and accumulation of NH_4^+ ions that precipitate or become adsorbed onto soil particle surfaces upon evaporation of the rainwater. Biological transformations leading to alterations in the amounts and forms of inorganic N during storage were likely negligible given the 4 °C storage temperature that was used and the virtually air-dried state of the field-moist soil that was stored (Table 2.2).

Soil pH

I found no remarkable pH differences between CW and NW soil from ELL and BRU sites. The three NW soils were characterised by fairly similar, slightly acidic soil reactions. The pH measured in DEV-CW soil exceeded the pH that would normally be expected for a soil belonging to the Ponoka Loam series (pH 6.5 in saturated soil paste). I cannot explain why such a large difference in pH was found between DEV-CW and DEV-NW soil. Differences in native properties of CW and NW soil samples collected less than 25 m apart could not possibly account for such a large difference in reaction. I am confident that the large pH difference is not due to experimental error because I repeated the measurements several times with different electrodes and obtained the same results every time. The most likely explanation is that the cropped DEV-CW soil sampled in this study still contained residual calcium carbonate from amendments made in previous years.

CEC and exchangeable base-forming cations

I performed these analyses to determine if CEC and the concentration of major exchangeable cations could be used to distinguish between NW and CW soil. I determined the concentration of the exchangeable base-forming cations Ca^{2+}, Mg^{2+}, K^+, and Na^+ in both types of soils also to find out if NW soils were characterised by severe chemical imbalance problems, such as high concentration of exchangeable Na^+ ions.

The CEC was substantially lower in ELL-NW and DEV-NW soil than in ELL-CW and DEV-NW soil, but equivalent in BRU-NW and BRU-CW soil. The statistical significance of differences observed between the CEC values measured in CW and NW soil was not tested because the CEC and exchangeable cation determinations were performed on duplicate samples. The difference noted between the CEC values of CW and NW soil from the DEV and ELL sites, however, is substantial enough to suggest that NW soil at these sites differs considerably from CW soil in the density of its negative surface charge. I attributed differences in CEC between CW and NW soils to differences in organic matter content, organic matter composition, and fractional content of clay-size particles (Table 2.2). The higher pH and exchangeable Ca^{2+} in DEV-CW soil may have been due to previous addition of free lime to soil.

Because the filtrates obtained from NW soil during the alcohol extraction step were much darker in colour than those obtained from CW soil, I conducted a simple experiment to determine if soil water repellency decreased part way through the CEC extraction procedure. I repeated the sequence of extractions used for the determination of exchangeable cations and CEC and measured the MED index of the soils after each extraction step performed in the prescribed sequence. The MED index of the three NW soils was measured after triplicate samples of NW soil had been leached thoroughly with (1) 1 *M* NH_4OAc (pH 7), (2) 1 *M* NH_4OAc (pH 7) followed by IPA, and (3) 1 *M* NH_4OAc (pH 7), followed by IPA and 1 *M* KCl. The soil samples were not allowed to dry between additions of leaching solution. The three different extraction sequences were performed on three consecutive days. The extracted soil samples were transferred from their Buchner funnels into clean tin cans, allowed to air-dry for 7 d, and then oven dried for 24 h at 105 °C in a forced air oven. MED indices were measured on oven dried soil samples (Table 2.4).

Soil water repellency was substantially reduced after the IPA washing step (Table 2.5), but virtually unaffected by extraction with either of the two aqueous solutions (1 *M* NH_4OAc and 1 *M* KCl). Extraction with NH_4OAc alone did not lower the MED index of the soils considerably, except in the case of the sandy BRU-NW soil. The fact that IPA was much more effective at reducing water repellency in all of the three NW soils than were the two aqueous solutions suggests that water-repellent substances in NW soil consist predominantly of organic compounds having some polar or amphiphilic character. IPA is a weak amphiphilic solvent that would be expected to extract organic compounds having similar chemical and structural properties. IPA is used to wash the soil free of excess soluble salts (residual 1 *M* NH_4OAc) after cation exchange sites have been saturated with NH_4^+, before the adsorbed NH_4^+ can be replaced by K^+ in a subsequent saturation step (Lavkulich 1981). This alcohol is considered to be an adequate washing solution because NH_4OAc is highly soluble in it and because it keeps the sample flocculated and prevents loss of NH_4^+ by hydrolysis (Bohn *et al.* 1985).

These last tests were performed to determine if soil water repellency was reduced by the procedures used to determine CEC. This information was needed to determine whether the NW soils on which CEC measurements were made were rendered wettable part way through the CEC determination through loss of some organic matter. I do not know how or even if this might alter CEC, but it is important to be clear about whether the analytical procedure not only determines the analyte of concern, but also changes the key variable of interest - wettability. Based on the results presented in Table 2.5, it is evident that the method I used for CEC determination markedly reduced soil water repellency.

The concentrations of exchangeable Ca^{2+}, Mg^{2+}, K^+ and Na^+ measured in NW soil were similar to those found in CW soil from the three sites (Table 2.4). These data suggest that the composition of exchangeable cations is not a property that is remarkably affected by the development of soil water repellency and structural degradation in soils that have been contaminated with crude oil. I also found low concentrations of exchangeable Na^+ ions (< 0.5 cmol(+) kg^{-1}) and low SAR (< 0.22) values in all three NW soils. Unless the standard methods used in the chemical analyses were inappropriate for use with water-repellent soil, the above findings suggest that the inorganic chemistry of NW soils does not differ appreciably from that of CW soils.

Soil colour

I determined soil colour on air-dried soil samples to provide readers with a means of comparing the appearance of the CW and NW soils described in this paper. ELL-CW soil corresponds to the Munsell colour Very Dark Grey (10YR 3/1 dry), whereas ELL-NW soil matches more closely a Very Dark Brown (10YR 2/2 dry). DEV-CW soil is Black (10YR 2/1 dry), whereas DEV-NW soil is closer to Very Dark Brown (10YR 2/2 dry). BRU-CW soil is Brown (10YR 5/3 dry), whereas BRU-NW soil is Light Olive Brown (2.5YR 5/4 dry). As a rule, air-dried NW soil has a slightly paler colour than air-dried CW soil. This may be due to differences in the type of organic matter CW and NW soils contain, or to differences in the amount of moisture these soils retain in the air-dried condition. Structural degradation also imparts a dusty appearance to the NW soils, which probably contributes additional dullness to their colour.

Particle size analysis

The results of particle size analysis revealed that DEV-NW and ELL-NW soil contains less clay-size particles than corresponding DEV-CW and ELL-CW soil (Table 2.2). I attributed this difference to erosion and translocation or settling of clay-size particles out of the NW soil layer. Erosion because NW soil is dry and bare for most of the year, and clay translocation or settling because a 1-3 cm thick layer of cemented soil is often found below NW soil at old crude oil spill sites. It is also possible that the water-repellent coating of NW soils prevented clay dispersion and adequate clay-size fraction estimation. The textural class names that were assigned were Very coarse sand for BRU soil, Coarse sandy loam for DEV soil, and Fine silt loam for ELL soil. The difference in textural composition (particle size analysis) between CW and NW soils were not sufficient to justify separating them into different textural classes according to the Canadian System of Soil Classification.

Soil-moisture characteristic curves

I measured the gravimetric water content of the test soils at six different tensions to determine if there were consistent differences in the moisture-holding behaviour of CW and NW soil that were independent of sampling site and native soil physicochemical properties. I found the water-holding capacity of the CW soils to be generally higher than that of the NW soils at the six tensions tested, except for ELL-CW and ELL-NW soil at -0.01 MPa. Water retention curves for soil from the three sites are presented in Fig. 2.1. The water retention values reported are the arithmetic means of two replicates with the standard deviation represented as error bars. The fact that DEV-CW soil retained more water than DEV-NW soil throughout the range of suction values tested is probably a consequence of higher fresh organic matter content in DEV-CW soil and strong intermolecular attraction forces between this organic matter and water.

The water desorption results I obtained do not agree with the findings of Ellis and Adams (1960). Those workers found more water held in water-repellent gas-saturated soil than in normal adjacent soil under suction values in the range of 0.033 to 1.5 MPa. They concluded that higher water-holding capacity made force-wetted water-repellent soils a more suitable microclimate for microorganisms and plant roots. This statement, however, cannot be extended to the NW soils that I studied.

Dry sieving analysis

The results of the dry sieving analysis are presented in Table 2.6. Both the unadjusted and adjusted MWD values are reported for the three NW and corresponding CW soils. These data were used to compare the aggregate size distribution of NW and adjacent CW soil. According to both unadjusted and adjusted MWD values, particles or aggregates remaining in ELL-NW and DEV-NW soil are generally smaller than those found in ELL-CW and DEV-CW soil. No such difference was found between BRU-CW and BRU-NW soil samples because the native soil at that location consists of single-grained dune sand exhibiting limited natural aggregation. The results presented in Table 2.6 clearly demonstrate that NW soils are more structurally disaggregated than corresponding CW soils.

Microstructure using scanning electron microscopy

SEM was used to examine the structure of NW soils and possibly detect the presence of an organic coating on soil particle surfaces. Although aggregates of diameter ≈100 µm were notably scarce in the samples under observation, I found enough microaggregates in NW soil to conclude that their structure is not completely destroyed. An organic coating around soil particles could not be detected (e.g. by rounded edges, film connecting single particles, etc.), even under high magnification (15 000 ×), presumably because of uniform thin surface coverage, or alternatively, irregular or patchy coverage.

SEM micrographs of the three NW soils and three CW soils are included to provide readers with an opportunity to examine the microstructure of these unusual soils. Fig. 2.2 contains SEM micrographs of air-dry CW and NW soil samples from the ELL, BRU, and DEV sites. Features to notice in these micrographs include the more disaggregated and relatively 'dirtier' appearance of NW soil compared to CW soil. The 'dirtier' appearance of the BRU-NW soil may be an indication of the presence of water-repellent organic substances on soil particle surfaces. Structural degradation, while much less striking under SEM than under simpler visual examination, is still discernible in the SEM micrographs of ELL-NW and DEV-NW soil.

Oven-heating treatment

Even though oven-drying at 105 °C for 24 h often slightly raises the MED index of air-dried NW soil (data not shown), higher oven temperatures and longer exposure times were expected to contribute to the removal or destruction, by desorption, oxidation or pyrolysis, of some or all of the water-repellent substances coating NW soil particle surfaces. Preliminary tests were conducted to determine what was the lowest oven temperature needed to eliminate soil water repellency completely within 24 h. I found that oven-heating at 105 or 150 °C for 21 d only slightly reduced soil water repellency, whereas oven-heating at 200 °C completely eliminated it within less than 24 h (Table 2.7). I then proceeded to determine exactly how many hours of thermal treatment at 200 °C were needed to eliminate soil water repellency completely.

Soil water repellency in all soils decreased with time in the oven at 200 °C (Fig. 2.3). The MED index of BRU-NW soil slightly increased during the first 2 h, but then started to decrease gradually afterwards, reaching a value of 0 after a total of 18 h. In contrast, the water repellency index of ELL-NW soil did not change or changed only slightly during the first 2 h of thermal treatment before it too started to decrease gradually. It took a total of 20 h at 200°C to eliminate soil water repellency completely in ELL-NW soil. It also took 20 h to eliminate soil water repellency in DEV-NW soil, but this soil began to lose water repellency immediately upon exposure to the high oven temperature. Other researchers have removed soil water repellency using temperatures higher than 200°C (Scholl 1975; Nakaya *et al.* 1977; John 1978; Giovannini and Lucchesi 1984). There is little doubt that the use of temperatures >200°C would have resulted in faster elimination of soil water repellency in the studied ELL-NW, BRU-NW and DEV-NW soil too.

Differential thermal analysis

DTA determines energy changes between a sample and reference material as the two are heated side by side at a controlled rate. When the sample undergoes a transformation, the heat of reaction (net enthalpy change) causes a difference in temperature between the sample and reference material and this difference is recorded as a function of temperature (Tan *et al.* 1986). No detectable thermal reactions took place in the reference material Al_2O_3 when it was heated from room temperature to 525 °C. The flat line produced by Al_2O_3 is the abscissa in Fig. 2.4. This line is used to determine the temperature at which net endothermic reactions exactly counterbalance net exothermic reactions in the heated soil samples. The DTA curves of ELL-CW and ELL-NW soil were both characterised by a broad endothermic peak with a minimum at 140 °C, probably due to the dehydration of the sample and desorption of some lower-molecular-weight organic compounds, and a broad exothermic peak with a maximum at ≈330 °C, probably due to the oxidation of organic matter (Fig. 2.4). These endothermic and exothermic peaks were of higher intensity in ELL-CW soil than in ELL-NW soil. The break-even point between endothermic and exothermic peaks occurred at 260 °C in ELL-CW soil and 243 °C in ELL-NW soil. Unlike Giovannini and Lucchesi (1984), I did not find a unique peak in the DTA curve of the NW soil that could be described as diagnostic for soil water repellency. The diagnostic peak reported by those authors was a well-defined exothermic peak at 490 °C present in the DTA curves of NW soil and organic material extracted from this soil using acetylacetone-benzene, but absent in the DTA curve of the extracted soil. This peak was attributed to the combustion of organic matter that is uniquely present in NW soil. In this study, I found a relatively small exothermic peak at 490 °C in the DTA curve of the CW soil only. The fact that the 490 °C peak was absent in ELL-NW soil may simply be an indication that the organic substances causing water repellency in the pine forest soil studied by Giovannini and Lucchesi (1984) differ from those causing water repellency in ELL-NW soil. Mallik and Rahman (1985) also failed to find a peak at 490 °C in the DTA curve of burned water-repellent soil from Scotland.

Given the similarity of their DTA curves, similar types of reactions probably took place in ELL-CW and ELL-NW soil as temperature was increased to 525 °C. I noted a difference in the intensity of the peaks, however, which made it possible to distinguish between ELL-CW and ELL-NW soil. The intensity of the broad endothermic peak was ≈30% less in ELL-NW soil than in ELL-CW soil, and the intensity of the broad exothermic peak was ≈17% less in ELL-NW soil than in ELL-CW soil. The two soil samples analysed by DTA were of similar size (≈20 mg), packing density, and native physicochemical properties. Based on these considerations, I concluded that differences in the net enthalpy of their thermal reactions could only be attributed to differences in the nature of the organic matter they contain or in the sorption mechanism by which the latter is associated with the soil. Although ELL-NW soil contains slightly more total C, ELL-CW soil reacted more vigorously to thermal treatment. This could be an indication that organic compounds in ELL-NW soil are more strongly sorbed to mineral particles, and therefore more thermally stable, than they are in ELL-CW soil.

CONCLUSION

Three soils that have become severely water-repellent and disaggregated several years or decades following contamination with crude oil were described in this paper. Although these soils occupy relatively small areas (< 10 ha), some appear to be continually expanding over time. Soil water repellency and structural degradation typically affect only the top 10-15 cm of the soil profile and the properties described throughout this paper refer only to this layer. The results of my preliminary characterisation work can be summarised as follows: (i) NW soil contains more smaller-sized dry aggregates than CW soil does, (ii) the presence of an organic coating on NW soil particles was not detected by SEM, (iii) the three studied NW soils are severely water-repellent with MED > 3, (iv) CW and force-wetted NW soils display similar water-holding capacity, (v) ELL-NW soil contains a sizeable community of viable and culturable bacteria, including spore-formers and vegetative, presumably resting, cells, (vi) the three studied NW soils lost water-repellent character following heating in a forced air oven for 18-20 h at 200 °C, and (vii) NW soil is generally characterised by: a lower CEC than CW soil, a relatively high content of mineral N and total C, and a ratio of exchangeable base-forming cations and pH value comparable to that found in CW soil.

Standard chemical, physical and microbiological techniques that require the preparation of soil suspensions in aqueous solutions present numerous disadvantages for the characterisation of severely water-repellent soils. The use of widely accepted analytical techniques that do not adequately simulate *in situ* conditions in NW soils might also lead to the production of irrelevant information, which should be interpreted with caution. The characterisation information described in this paper provides a useful basis for the comparison of NW and normal adjacent soils with soils that have not been exposed to crude oil contamination. In addition, it provides the background information necessary for the formulation of better-focussed hypotheses dealing directly with questions about the nature and origin of soil water repellency at old crude oil spill sites. Data presented in this report suggest that water-repellent soils found at old crude oil spill sites do not differ appreciably from normal adjacent soils in terms of their inorganic chemistry. More remarkable differences between water-repellent and normal adjacent soils, however, are likely to be found through analyses of their organic and physical chemistry.

Disaggregated water-repellent soil found at old crude oil spill sites throughout the province of Alberta provides a unique opportunity to study the long-term impact of crude oil contamination in soil and the interactions that take place over time between mixtures of petroleum hydrocarbons, microorganisms, and mineral and organic soil constituents. These sites are vivid examples of the fact that crude oil contamination in soil can sometimes cause persistent and severe damage to healthy and productive soil ecosystems.

Table 2.1. Characteristics of the three selected study sites

Site	Land use	Texture	MED[z]	Date of spill
ELL	Agricultural	Clay loam	3.9 ± 0.1[y]	1973
BRU	Industrial	Loamy sand	3.5 ± 0.1	≈1975
DEV	Agricultural	Loam	4.2 ± 0.0	1947

[z] Molarity of Ethanol Droplet test performed on oven-dried soil (105 °C, 24 h)
Interpretation guidelines: MED < 1.0, slight water repellency; 1.0 < MED < 2.2, moderate; MED > 2.2, severe (King 1981)

[y] Standard deviation

Table 2.2. Physicochemical properties of the three NW and corresponding CW test soils (0-15 cm)[z]

	ELL		BRU		DEV	
Property	CW	NW	CW	NW	CW	NW
pH (in water, 2:1)	5.8	5.8	6.5	6.3	7.8	6.3
pH (in 0.01 M $CaCl_2$)	5.3	5.4	5.5	5.4	7.3	5.8
CEC (cmol (+)·kg^{-1})	42	34	3	3	43	28
Water at 33 kPa (g·kg^{-1})	360	360	50	40	340	250
Field moisture content (g·kg^{-1})	220	70	20	10	280	40
Sand (g·kg^{-1})	290	300	860	860	380	400
Silt (g·kg^{-1})	350	370	20	20	320	350
Clay (g·kg^{-1})	360	330	120	120	300	250

[z] Not tested for statistical significance

Table 2.3. Total C and mineral N content of the three NW and corresponding CW test soils

	ELL		BRU		DEV	
Property	CW	NW	CW	NW	CW	NW
Total C ($g{\cdot}kg^{-1}$)	61.0	67.8**	2.0	5.3**	38.9	40.9*
NO_3^--N ($mg{\cdot}kg^{-1}$)	93.6	63.3**	2.5	2.8ns	5.7	48.0**
NH_4^+-N ($mg{\cdot}kg^{-1}$)	7.1	19.3**	2.4	9.5**	2.9	70.8**

** CW and NW means are significantly different at the 1 % level of significance

* CW and NW means are significantly different at the 2 % level of significance

ns CW and NW means are not significantly different ($0.5<p<1.0$)

Table 2.4. Concentration of exchangeable Ca^{2+}, Mg^{2+}, K^+, and Na^+ (cmol (+)·kg^{-1}) in CW and NW soils as determined in 1 *M* NH_4OAc (pH 7)

	cmol (+) kg^{-1}					
Soil	Ca^{2+}	Mg^{2+}	Na^+	K^+	Sum	SAR[‡]
ELL-CW	29.2	5.3	0.4	0.8	35.7	0.11
ELL-NW	25.7	4.3	0.4	0.8	31.2	0.10
BRU-CW	2.1	0.4	<0.1	0.2	<2.8	0.14
BRU-NW	2.2	0.4	<0.1	0.1	<2.8	0.18
DEV-CW	35.8	8.4	1.1	0.4	45.7	0.25
DEV-NW	20.8	4.2	0.5	0.4	25.9	0.22

[‡] SAR: Sodium adsorption ratio, calculated as $[Na^+]/SQRT\ \{([Ca^{2+}]+[Mg^{2+}])/2\}$, all values reported in $meq{\cdot}L^{-1}$

Table 2.5. Change in water repellency of three NW soils during extraction for CEC determination by the method of Lavkulich (1981)

Soil	MED[z] (*M*) before extraction	MED[z] (*M*) after extraction with A[y]	A+B[y]	A+B+C[y]
ELL-NW	3.8 ± 0.0[x]	4.0 ± 0.0	0.5 ± 0.1	0.3 ± 0.1
DEV-NW	4.2 ± 0.1	4.2 ± 0.0	0.0 ± 0.0	0.7 ± 0.2
BRU-NW	3.4 ± 0.0	2.3 ± 0.1	0.0 ± 0.0	0.0 ± 0.0

[z] MED = Molarity of Ethanol Droplet test performed on oven-dried soil

[y] A = 1 *M* NH_4OAc (pH 7), B = *iso*propanol, and C = 1 *M* KCl

[x] Standard deviation

Table 2.6. Unadjusted and adjusted MWD values computed for the three NW and corresponding CW soils

Soil	Unadjusted MWD	Adjusted[z] MWD
ELL-CW	0.403	0.274
ELL-NW	0.303	0.186
BRU-CW	0.207	0.102
BRU-NW	0.208	0.104
DEV-CW	0.577	0.426
DEV-NW	0.243	0.134

[z] Adjusted MWD = 0.876 (unadjusted MWD) - 0.079 (Kemper and Roseneau 1986)

Table 2.7. Water repellency of NW soils after heating in a forced-air oven for 24 h or 14 d

	MED[z] (*M*)					
	ELL		BRU		DEV	
Temperature (°C)	24 h	14 d	24 h	14 d	24 h	14 d
21	3.8	3.8	3.2	3.2	5.0	5.0
105	3.8	3.8	3.2	3.2	4.0	3.8
150	3.8	1.6	3.6	0.4	3.8	1.6
200	0.0	0.0	0.0	0.0	0.0	0.0

[z] MED = Molarity of Ethanol Droplet test performed on oven-dried soil

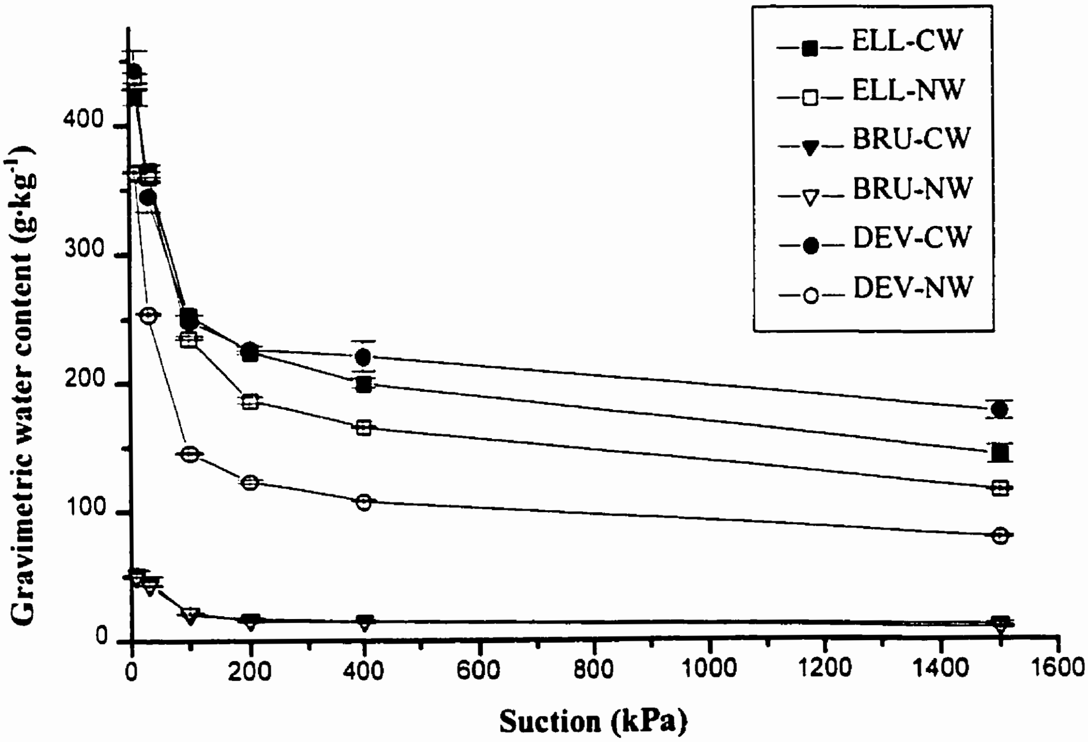

Figure 2.1. Water retention curves of three NW soils and corresponding CW soils.

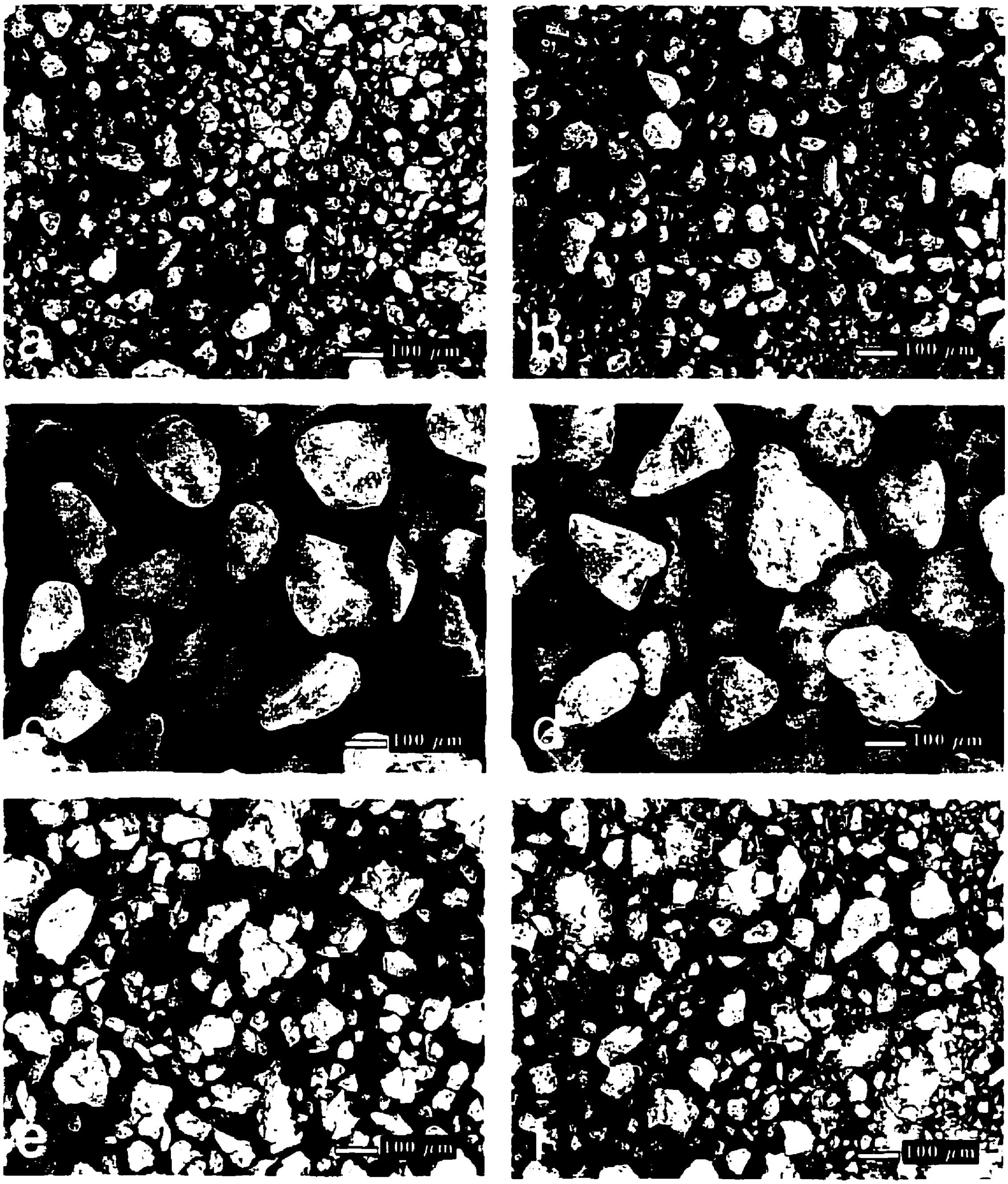

Figure 2.2. Scanning electron micrographs of CW (left) and NW (right) soil from three old crude oil spill sites. ELL = a, b, BRU = c, d, and DEV = e, f.

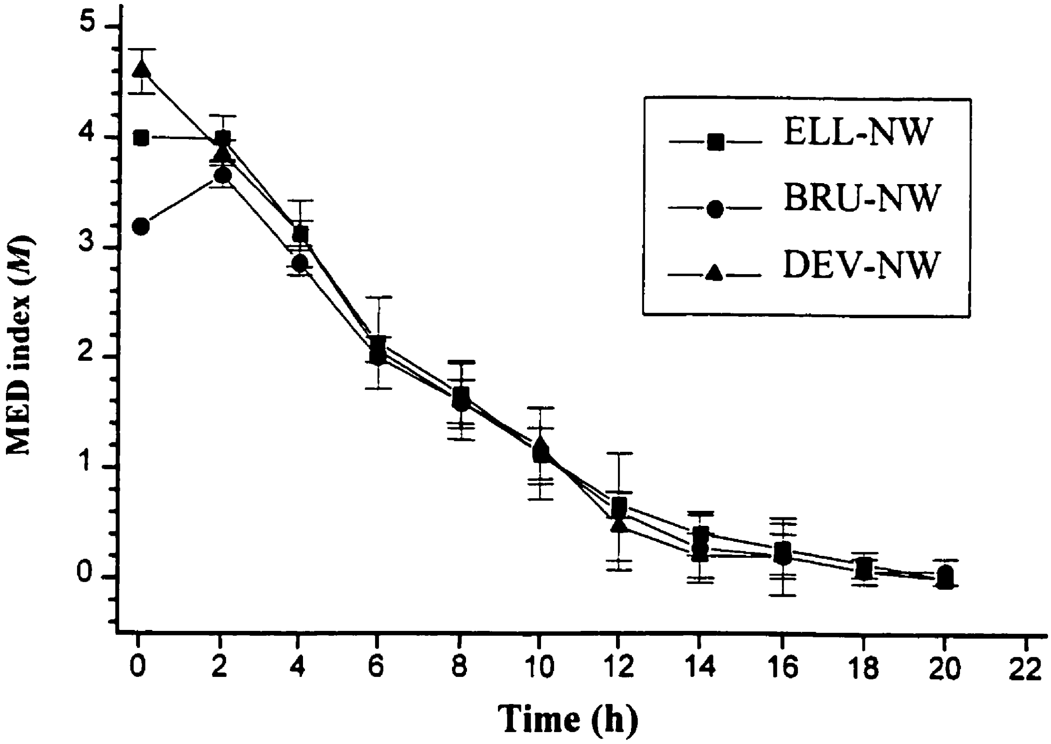

Figure 2.3. Oven-heating experiment performed to determine the time required at 200 °C for complete elimination of water repellency in ELL-NW, BRU-NW and DEV-NW soil.

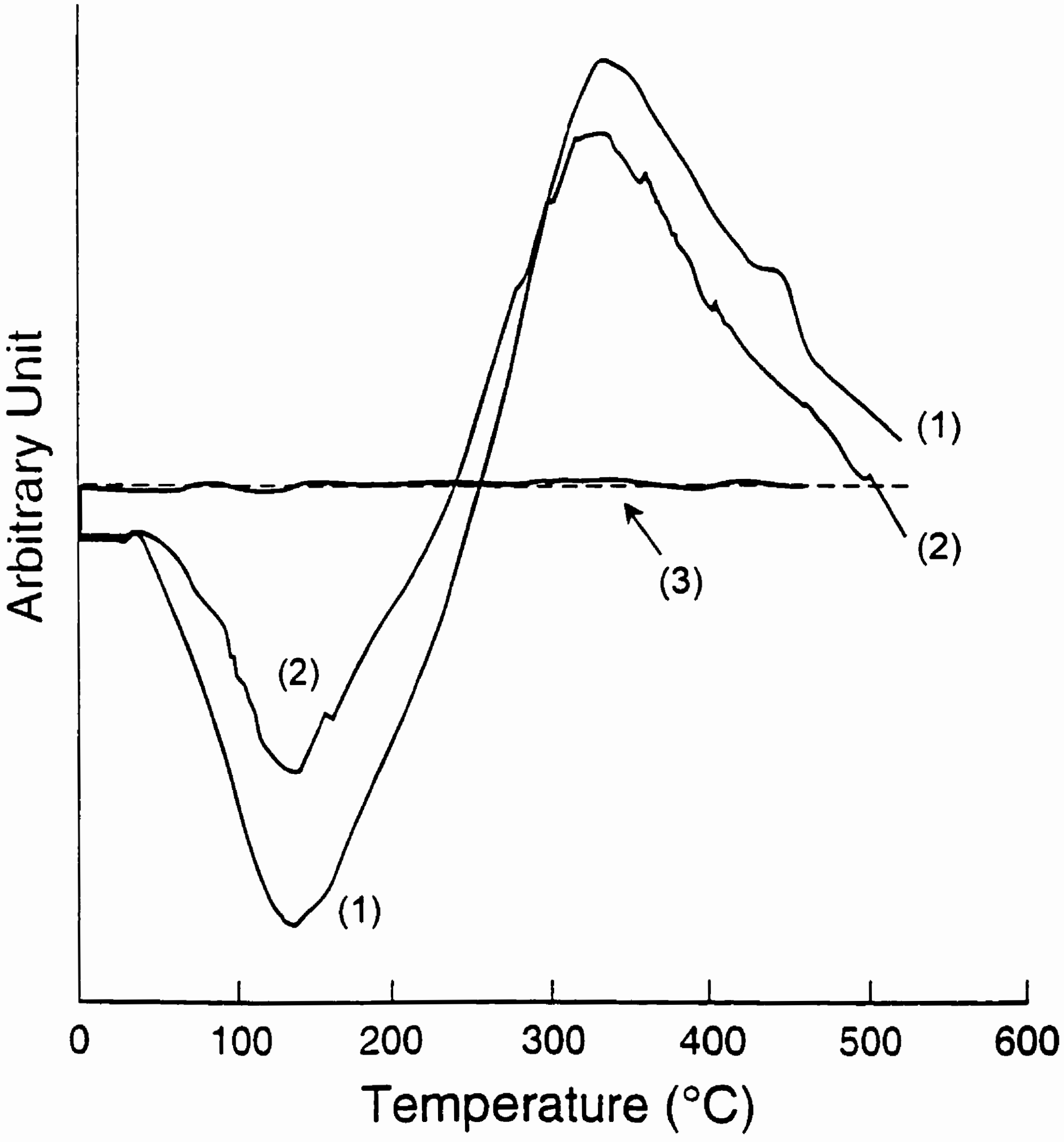

Figure 2.4. Differential thermal analysis curves of intact ELL-CW and ELL-NW soil samples. (1) ELL-NW, (2) ELL-CW, (3) Al_2O_3 reference material.

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CHAPTER 3

Petroleum residues as water-repellent substances in weathered nonwettable oil-contaminated soils[1]

INTRODUCTION

Soil water repellency is encountered in diverse ecosystems in many parts of the world. Most literature reports are of naturally-occurring or fire-induced soil water repellency, but there have also been reports of *pollution-induced* soil water repellency (Ellis and Adams 1961; Craul 1985). The soils described in this report are an example of the latter. They are soils that became water-repellent several years or decades following oil contamination. The severity of their water repellency is such that they resist wetting even under heavy rainfalls. This condition has prevailed unabated for over 20 years and there is no indication that it is waning.

Despite the fact that soil water repellency has been studied since early this century, progress has been slow toward identifying its causes. A wide variety of potential causative agents have been proposed, but a mechanism responsible for the generation of soil water repellency has never been identified. Most researchers attribute soil water repellency to the presence of hydrophobic organic material coating soil particle surfaces (Wallis and Horne 1992). Inorganic materials are not usually suspected as causative agents because the few known hydrophobic minerals in soils (e.g. graphite, sulphide, and elemental sulphur) are typically present in low to trace quantities only (Tschapek 1984). Mineral surfaces coated with amorphous silica containing siloxane groups are probably the most widely occurring hydrophobic mineral surfaces in soils, but their surface density is generally too low to give rise to soil water repellency.

The characterisation of causative agents of soil water repellency confronts researchers with several analytical difficulties. Firstly, most nondestructive extraction procedures fail to eliminate soil water repellency completely. Secondly, organic extracts obtained from water-repellent soil usually consist largely of naturally-occurring compounds that are commonly encountered in readily wettable soils. Thirdly, soil water repellency can be eliminated without removal of any compounds from soil

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(Ma'Shum and Farmer 1985). Fourthly, organics that can impart water repellency to soil occur naturally in most soils. Furthermore, based on evidence that has been gathered so far, soil water repellency seems to depend not only on the presence and surface density of water-repellent substances in soil, but also, on their ability to display conformational flexibility at fluid-solid interfaces in soil.

Compounds imparting persistent water-repellent character to soil must be recalcitrant, water-insoluble, hydrophobic organic compounds. They may be strictly nonpolar molecules or molecules that have segregated polar and nonpolar regions (i.e. surface-active or amphiphilic compounds). Their recalcitrance may be due to a large molecular size or to strong interaction with soil surfaces. Surface-active compounds, such as humic substances and certain biogenic lipids, are commonly encountered in soils (Tschapek 1984; Anderson *et al.* 1995). Strictly nonpolar organic compounds, on the other hand, are much less prevalent. This is because nonpolar character is usually readily lost in soil as a result of chemical or biological oxidation reactions (Dinel *et al.* 1990).

Humic acids (Tschapek 1984; Ma'Shum and Farmer 1985) and decomposing plant residues (McGhie and Posner 1980; Barrett and Slaymaker 1989) have often been proposed as causative agents of naturally-occurring soil water repellency. It is not known how exactly these might impart water repellency to soil, but indirect evidence suggests that they are implicated in the process. In soils that become severely water-repellent several years or decades following oil contamination, alternative sources of causative agents are also being considered. These are recalcitrant petroleum residues and metabolic products of hydrocarbon-degrading soil microorganisms.

Virtually all constituents of crude oil mixtures are hydrophobic organic compounds that could impart water repellency to soil. Polar compounds of the resin and asphaltene fractions, however, are more likely culprits because of their relatively high microbial recalcitrance *and* high sorption affinity to soil (Atlas 1981; McGill *et al.* 1981). These compounds are suspected of causing reduced water-wettability of rock surfaces in petroleum reservoirs (Denekas *et al.* 1959; Crocker and Marchin 1988). Despite the above theoretical considerations, I am not excluding low-molecular-weight petroleum hydrocarbons as potential causative agents. I cannot exclude them because some soils develop water repellency following contamination with natural gas (Ellis and Adams 1961). Oil-degrading microorganisms are known to produce high-molecular-weight alkanes, wax esters, and fatty acids. Several groups (Jobson et al. 1972; Walker and Colwell 1976) have reported the synthesis of complex high-molecular-weight hydrocarbons by microorganisms during utilisation of petroleum hydrocarbons. Such compounds must also be considered as an additional potential source of water-repellent substances in the studied soils.

Ma'Shum *et al.* (1988) were the first to report on the successful extraction of water-repellent substances from nonwettable soils under relatively mild conditions. They found that Soxhlet extraction with a mixture of IPA/NH_4OH completely eliminated water repellency in nonwettable sandy soils. Extraction with NaOH (Roberts and C 1972; Miller and Wilkinson 1977; Karnok *et al.* 1993) and H_2O_2 (Tucker *et al.* 1990; Bisdom *et al.* 1993) is also effective at eliminating soil water repellency. However, these harsher extractants were deemed inappropriate for use in analytical work because they extract organic matter nonselectively or destroy the extracted material.

In this report, I describe how I isolated, characterised, and identified putative water-repellent substances in three soils that developed severe water repellency several years or decades following oil contamination. My objective was to test the hypothesis that water-repellent substances in these soils consist predominantly of recalcitrant petroleum residues (e.g. resins or asphaltenes) or of products of microbial metabolism (e.g. biogenic lipids). Several extraction solvents were tested, including the one used by Ma'Shum *et al.* (1988), to find one that would completely eliminate water repellency in the three selected nonwettable soils. Extracted putative water-repellent substances were then characterised by solid-state ^{13}C-NMR spectroscopy, ThermEx-GC/EI/MS and ThermEx-GC/CI/MS, and their origin tentatively described. I present here compounds that I identified by molecular weight information and extracted ion current profiles and that resemble more closely compounds of petroleum origin than compounds of microbial or plant origin.

MATERIALS AND METHODS

General description of the sites

Three nonwettable soils from different weathered oil-contaminated sites were selected for this study (Table 3.1). Two are located in formerly productive agricultural fields and one is from an industrial site that supported an oil-producing facility until the mid-1980s. All are located within a 60-km radius of the city of Edmonton, Alberta, Canada. The three sites were described in detail in Chapter 2. Briefly, soil from the agricultural Ellerslie (ELL) site (53°25'N, 113°33'W) consists of Malmo silty clay loam (Eluviated Black Chernozemic) that was contaminated with crude oil in 1973; soil from the industrial Bruderheim (BRU) site (53°51'N, 112°58'W) consists of dune sand (Orthic Regosolic), which was contaminated with crude oil in 1982; and soil from the agricultural Devon (DEV) site (53°20'N, 113°42'W) consists of Ponoka loam (Eluviated Black Chernozemic), which was contaminated with crude oil in 1947. The three sites each contain at least one patch of barren nonwettable soil that is between 0.1 and 10 ha in size. The dry and powdery nonwettable soil that was sampled for this study is confined to the top 10-15 cm of the soil column. It does not smell, look, or feel like it contains any oil, but underlying subsoil layers typically release a distinct petroleum odour and, at the DEV site, present evidence of low redox conditions (greyish green colour).

Soil sampling and sample preparation

Nonwettable and adjacent control wettable soil

Samples of wettable and nonwettable soil (0-15 cm) from the three old crude oil spill sites were collected and processed as described in Chapter 2. I identified nonwettable (NW) soil as field-moist soil that does not absorb water droplets in 10 s or less. Readily wettable soil to be used as control wettable (CW) soil was sampled within a 25 m-perimeter surrounding the NW soil sampling area. I identified CW soil as field-moist soil that absorbs water droplets in 10 s or less. CW soil at the DEV site (DEV-CW) was sampled from underneath a growing wheat crop, whereas that obtained from the ELL (ELL-CW) and BRU (BRU-CW) sites was sampled in fallow areas that were only sparsely covered with weeds. Although field-moist ELL-CW soil was readily wettable at the time of sampling, air drying indoors caused this soil to acquire slight water repellency. It was nevertheless kept as the ELL-CW soil. ELL-CW soil was contaminated with crude oil at the same time as ELL-NW soil was. I know this because I sampled ELL-CW soil within the documented perimeter of the oil-contaminated area of this site. In the absence of such documentation for the DEV and BRU sites, I cannot confirm the pristine or contaminated state of BRU-CW and DEV-CW soil. According to anecdotal reports, however, the area sampled for DEV-CW soil was also contaminated by crude oil, whereas that sampled for BRU-CW soil was not. The sampled field-moist soil was air-dried, sieved to pass through a 2 mm-sieve, and then stored in glass jars in the dark at 4 °C prior to analysis (up to one year). Selected chemical and physical properties of the three NW and corresponding CW soils are presented in Table 3.2. Fig. 3.1 depicts how PW, CW and NW soil were sampled in the field.

Pristine wettable soil used for comparison

Two pristine soil materials were used. One was an acid-washed (AW) sand (0.004% total C) prepared by soaking white quartz sand (Aldrich) (0.2-0.3 mm) overnight in 6 *M* HCl and rinsing several times with tap water followed by deionised water. The other one was a pristine wettable (ELL-PW) soil (0-10 cm) that was sampled well outside the oil-contaminated area at the ELL site. The ELL-PW soil is a silty clay loam with 5.2% total C and 0.5% total N, which belongs to the same soil series as the ELL-CW and ELL-NW soils.

Assessment of soil water repellency

The molarity of ethanol droplet (MED) test was used to measure soil water repellency (Watson and Letey 1970; King 1981). The MED test records the molarity of ethanol in a droplet of water required for soil infiltration within 10 s. Ethanol solution concentrations of 0.2 *M* intervals in the range of 0-6 *M* were used to assess soil water repellency. At soil moisture contents higher than air-dry, the MED test no longer provides a reliable assessment of soil water repellency (King 1981). MED values decrease as soil moisture content increases. This is because the attraction of water molecules for one another becomes progressively more predominant as water content increases, such that the measurement is eventually dominated by water-water interactions and not soil-water interactions. In my work, MED values measured on oven-dried (105 °C, 24 h) soil were more consistent, but otherwise essentially the same as MED values measured on air-dried soil. Consequently, I chose to report only MED values obtained on oven-dried soil.

Solvent extraction of putative water-repellent substances prior to the assessment of soil water repellency

Air-dried samples of wettable and nonwettable soil (25 g oven-dry basis) from the DEV, ELL and BRU sites were Soxhlet-extracted with 175 mL glass-distilled solvent for 24 h. A blank consisting of a clean, empty cellulose thimble was also extracted to provide a correction factor for the presence of residual organics in the glass-distilled solvent and/or Soxhlet glassware. The concentration of solvent-extractable material was determined gravimetrically as described by McGill and Rowell (1980). Briefly, the extracted material dissolved in solvent were concentrated on a rotary evaporator, transferred into preweighed aluminium dishes, and allowed to dry in a fume hood to constant mass. The mass of the air-dried extracted material was then recorded and the concentration of solvent-extractable material calculated. The extracted soil samples were allowed to air-dry for 7 d, then oven-dried in a forced-air oven at 105 °C for 24 h, cooled in a desiccator over silica gel, and assessed for soil water repellency using the MED test. Analyses were performed in triplicate on corresponding CW and NW soil and on the blank for each test solvent. The MED values that are reported in this paper are thus the arithmetic means of triplicate values followed by their associated standard deviation. These procedures were repeated with a total of eight solvents of varying polarity: cyclohexane (CCH) and dichloromethane (DCM) ("nonpolar"), methanol ("polar"), *n*-propanol and *iso*propanol (IPA) ("amphiphilic"), and three different IPA/aqueous phase mixtures (7:3, v/v) ("amphiphilic"). The three amphiphilic IPA/aqueous phase mixtures were: (i) IPA/14.8 *M* ammonium hydroxide (IPA/NH_4OH), (ii) IPA/5.2 *M* acetic acid (IPA/CH_3COOH), and (iii) IPA/deionised water (IPA/H_2O). Complete removal of soil water repellency, as determined by the MED test, was the criterion used to evaluate extraction efficiency.

Supercritical fluid extraction (SFE) with and without polar modifier

Supercritical fluid extractions (SFE) of the ELL-CW and ELL-NW soils only were carried out by the Department of Public Health Sciences at The University of Alberta using a Dionex SFE-703 system. Approximately 25 g of air-dried soil were placed in 32-cm^3 high-pressure extraction cells (Suprex Inc.)

and extracted with CO_2. The nozzle temperature was maintained at 45 °C to prevent plugging. The cells were pressurised to 100 atm for 1 min, then quickly ramped at a rate of 50 atm·min^{-1} to the final test pressure (350 or 400 atm) and allowed to remain at this pressure for 40 or 60 min, depending on the treatment. IPA (10%, v/v) was added to the supercritical CO_2 via an auxiliary pump as a modifier fluid in three of the four runs. The extracted soil samples were air-dried for 7 d, oven-dried at 105 °C for 24 h, cooled in a desiccator, and assessed for soil water repellency using the MED test. Because SFE failed to remove water repellency from the ELL-NW soil, the extractions were not replicated or performed on the remaining soils, nor was the extract analysed further.

Solid-state CPMAS ^{13}C nuclear magnetic resonance spectroscopy

Solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy with cross-polarisation and magic-angle spinning (CPMAS) was used to characterise the organic C contained in three samples of DEV-NW soil, which had been treated as follows: (i) extracted with IPA/NH_4OH (MED = 0 *M*), (ii) extracted with IPA/CH_3COOH (MED=0), and (iii) not previously extracted (MED = 4.2 *M*). The soil samples were oven-dried at 105 °C for 24 h and ground to a fine powder (< 150 μm) prior to analysis. Grinding was necessary to provide a homogeneous mixture with a particle size that could easily be packed into a rotor. Oven-drying was necessary for assuring consistency in my standardised MED assessment procedures. The solid-state CPMAS ^{13}C NMR analyses were performed by the Department of Chemistry of The University of Alberta on a Bruker AM-R-300 spectrometer operated at a frequency of 75.47 MHz with a magic angle spinning rate of 5 kHz. Cross-polarisation contact time was 1 ms, pulse repetition time 2 s, and proton decoupling field 50 kHz. Spectra were accumulated for between 15 000 and 30 000 scans until acceptable signal to noise ratios were obtained. Chemical shifts are reported relative to adamantane at 0 ppm (external standard).

Extract-loaded sample of acid-washed sand for ThermEx-GC/CI/MS analysis

Approximately 9 g·kg^{-1} IPA/NH_4OH-extractable material obtained from the DEV-NW soil was added to acid-washed (AW) sand for analysis using ThermEx-GC/CI/MS. Ten grams of oven-dried AW sand was added to a concentrated solution of IPA/NH_4OH-extractable material (50 ml, ≈1.8 g·L^{-1}) and solvent was allowed to evaporate. When only about one pore volume of solvent was left in the sand, the sample was held on a vortex mixer to homogenise the distribution of material in the sand during evaporation of the remaining solvent. The sample was further air-dried in a fume hood to constant mass and then oven-dried (24 h, 105 °C) and stored in a glass scintillation vial at 4 °C prior to analysis.

Thermal desorption followed by GC/EI/MS and GC/CI/MS analyses

Thermal desorption-GC/EI/MS analyses were performed on the sample of AW sand that was treated with ≈9 g·kg^{-1} IPA/NH_4OH-extractable material obtained from the DEV-NW soil. The sample was oven-dried at 105 °C for 24 h prior to thermal desorption-GC/EI/MS to maintain consistency in my MED assessment procedures. Thermal desorption was performed at the Alberta Research Council using a Ruska™ Laboratories ThermEx pyrocell interfaced to a gas chromatograph (Carlo Erba HRGC 5160) and a mass spectrometer (Finnigan™ 4500). Approximately 10 mg of soil was placed in the pyrocell and thermally desorbed under a flow of helium at a linear heating rate of 30 °C·min^{-1} from 50 to 280 °C, then 4 °C·min^{-1} to 300 °C. The GC oven temperature was kept at 35 °C until thermal desorption was complete. Chromatography of the thermally extracted material was performed using a high-resolution DBHT-1 fused-silica capillary column (0.25 mm I.D. x 30 m, 0.25 µm film thickness) with heating from 35 °C to 320 °C at a linear temperature gradient of 10 °C·min^{-1} followed by a 5-min hold at 320 °C. The mass spectrometer was operated in a multiple ion detection mode, scanning from 29 to 470 a.m.u. in 0.95 s. The ion source temperature was 150 °C and the electron multiplier operated at 1150 V. The corresponding electron impact was 70 eV.

The same mass spectrometer (Finnigan™ 4500) was operated in the positive chemical ionisation mode to identify organic compounds that could not be characterised by high-resolution GC/MS with electron impact ionisation (GC/EI/MS). The technique of Townsend discharge (1800 V) chemical ionisation GC/MS with nitrous oxide as the reagent gas, a source pressure 0.45 Torr, and a 120 °C source temperature was used. This method has been described in detail by Dzidic *et al.* (1992). Again, only the extract-loaded AW sand was analysed by ThermEx-GC/CI/MS.

Mass spectra, chromatography and extracted ion current profiles were used to characterise the desorbed material. Some of the characteristic fragment ions that were used in the identification of extract components are presented in Fig. 3.2.

RESULTS

Solvent extraction of nonwettable and wettable control soil using various polar, nonpolar and amphiphilic solvents

Based on reduction of MED and the mass of material extracted, the nonpolar solvents CCH and DCM consistently had the lowest extraction efficiency (Tables 3.3 and 3.4), whereas the amphiphilic solvent mixtures IPA/NH_4OH, IPA/CH_3COOH and IPA/H_2O (7:3, v/v) consistently had the highest. The polar solvent methanol markedly reduced soil water repellency, but not to the same extent as did the amphiphilic solvents *n*-propanol and IPA (Table 3.3). Soils extracted with the amphiphilic mixture IPA/NH_4OH were completely wettable following extraction, whereas those extracted with the IPA/H_2O and IPA/CH_3COOH mixtures were nearly so. Extraction with CCH slightly increased, rather than decreased, the water repellency of some nonwettable soil samples (Table 3.3). ELL-CW and DEV-CW soil even acquired slight water repellency following extraction with the two nonpolar solvents CCH and DCM. A subsequent test revealed that, unlike ELL-CW soil which came from the oil-contaminated area, pristine soil coming from outside of it (ELL-PW soil) did not acquire water repellency following extraction with nonpolar solvents (data not shown). I also found that addition of IPA/NH_4OH-extractable material to acid-washed sand rendered the sand hydrophobic (MED>6.0 *M*), whether the source soil was CW or NW soil (data not shown).

Supercritical fluid extraction (SFE) with and without polar modifier

None of the four sets of operating conditions tested (A to D) extracted enough water-repellent substances to render ELL-NW soil completely wettable (Table 3.5). Extraction protocols A (400 atm, 100 °C, dynamic mode, 40 min) and C (400 atm, 100 °C, static mode with polar modifier 10% IPA, 40 min) left the soil more water-repellent than it was prior to SFE. Extraction protocol D (350 atm, 55 °C, dynamic mode with 10% IPA, 60 min) reduced soil water repellency more than extraction B (400 atm, 100 °C, dynamic mode with 10% IPA, 40 min). The MED index of the ELL-CW soil was 0 *M* after the four extraction tests (data not shown).

Solid-state ^{13}C nuclear magnetic resonance spectroscopy

The CPMAS ^{13}C-NMR spectra were subdivided into seven chemical shift regions and the associated areas expressed as percentages of the total integrated area (relative intensity) (Table 3.6). The spectra were divided as follows: 0-50 ppm for alkyl C; 50-60 ppm for methoxyl C (OCH_3); 60-96 ppm for *O*-alkyl C; 96-141 ppm for di-*O*-alkyl and nonoxygenated aromatic C; 141-159 ppm for phenolic C; 159-185 ppm for carboxyl C; and 185-210 ppm for aldehyde and ketone C (deMontigny *et al.* 1993). In the context of this work, C resonating within the chemical shift region of 0 to 96 ppm was therefore designated as aliphatic C, whereas C resonating within the chemical shift regions of 96-141 ppm, 141 to 159 ppm, and 159 to 210 ppm was designated as aromatic C, phenolic C and carbonyl + carboxyl C, respectively (Fig. 3.3).

Data in Table 3.7 for C distribution before and after extraction, together with data from Tables 3.2 and 3.4 for original C content and for mass of extractables removed, were used to estimate the amount of C in each fraction that might be expected to have been removed by the amphiphilic extractants (Table 3.8). Over 70% of the extracted material appears to be aliphatic (0-96 ppm) and 14-20% aromatic based on this estimation protocol. Most of the aliphatic C that was removed by either amphiphilic solvent was C resonating in the 0-50 ppm region, which is usually assigned to the paraffinic C found in branched and straight-chain alkanes, cycloalkanes, and alkanoic acids (Hatcher *et al.* 1983).

Thermal desorption followed by GC/EI/MS and GC/CI/MS analysis

Using GC/MS with electron impact (EI) ionisation

All compounds thermally desorbed from the extract-loaded sample of AW sand were considered putative water-repellent substances. They were subjected to GC/EI/MS analysis without derivatisation or other pretreatments. Extract component identification was made using mass spectral library searches, extracted ion current profiles of characteristic ion fragments, and detection of homologous series (Fig. 3.4). The identified compounds included a homologous series of C_{21} (mol. wt. 296) to C_{31} (mol. wt. 436) even- and odd-C-numbered *n*-alkanes (Fig. 3.4) and another of C_{11} (mol. wt. 186) to C_{28} (mol. wt. 424) even- and odd-C-numbered *n*-fatty acids. Only minute amounts (roughly 1/10 of the amount of their straight-chain constitutional isomers) of the branched odd-C-numbered fatty acids C_{15}, C_{17} and C_{19} (Fig. 3.6). Finally, a homologous series of C_{30} to C_{34} (mol wt. 412 to 468) hopanes (i.e. pentacyclic terpanes) was detected based on molecular weight and the presence of the characteristic *m/z* 191 molecular ion fragment (Volkman *et al.* 1992) (Fig. 3.7). Some steranes were also detected based on molecular weight information and the presence of the characteristic *m/z* 217 molecular ion fragment (Volkman *et al.* 1992; Wang *et al.* 1994) (Fig. 3.7).

There was no predominance of odd- or even-C numbers in the distribution of the *n*-alkanes (Fig. 3.5), but the *n*-fatty acid distribution was clearly dominated by even-C numbered species, with C_{16}, C_{18}, and C_{20} representing the most abundant ones (Fig. 3.8). Some of the identified *n*-fatty acids are labelled in the chromatogram presented in Fig. 3.8A. A similar distribution of mostly even-numbered long-chain *n*-fatty acids with 16 to 32 C atoms was identified by Ma'Shum *et al.* (1988) in material extracted from nonwettable sand using IPA/NH_4OH. A series of fatty acid methyl esters from C_{23} to C_{29} (mol. wt. 342 to 426) characterised by the unique ion fragments *m/z* 74 and *m/z* 87 were also detected (data not shown).

Characteristic crude oil asphaltene and resin residues, such as N- or S-heterocyclics, polyhydric phenols and polycyclic aromatic hydrocarbons, were not detected. This could mean that they are not extracted from DEV-NW soil by IPA/NH_4OH, and therefore are not present in the analysed extract, or that they are extracted and are indeed present in the extract, but escape detection by thermal desorption-GC/EI/MS because they are not volatile. Minute amounts of oxygenated compounds other than carboxylic acids were also identified (e.g. C_9 ketone, C_7 aldehyde). No trace of the extraction solvent

IPA was detected even when the GC inlet temperature was lowered to -10 °C to condense the thermally desorbed compounds before chromatographic separation. Some phthalates (benzene dicarboxylic acids) were detected most likely due to contamination from the plastic bags that were used for soil sampling. The largest molecular weight that could be detected using the chosen GC/EI/MS protocol was ≈470 a.m.u.

Using GC/MS with chemical ionisation (CI)

Because compounds thermally desorbed from the extract-loaded AW sand could not all be identified by GC/EI/MS, a sample of extract-loaded AW sand was also subjected to thermal desorption followed by GC/MS with chemical ionisation (GC/CI/MS). Analysis and identification of the thermally desorbed compounds was made using molecular weight information, extracted ion current profiles, and chromatography. This enabled me to determine the composition of the unresolved complex mixture giving rise to the large hump in the chromatogram presented in Fig. 3.4. It consists mostly of C_{24} to C_{32} aliphatic hydrocarbons with a predominance of 3- to 5-ring cycloalkanes (e.g. terpanes and steranes) and some 1- to 2-ring cycloalkanes and long-chain *n*-alkanes. Branched and *n*-fatty acids were also found, but *n*-fatty acids largely predominated over branched ones. Branched fatty acids were distinguished from *n*-fatty acids on the basis of their differing boiling points, and therefore time of elution from the chromatographic column. Polycyclic aromatic compounds or phenolic compounds were again not detected among the desorbed compounds. The mass spectrum of the "hump" that was characterised by GC/CI/MS is shown in Fig. 3.9.

DISCUSSION

Soil water repellency assessment on oven-dried soil

According to King (1981), MED measurements are essentially unchanged as the soil moisture content is increased from oven-dry to air-dry, but become less reliable when made at soil moisture contents greater than air-dry. More recently, Franco *et al.* (1995) observed that MED values recorded on soil heated at 105 °C for 48 h were generally higher and more consistent than values recorded on air-dried samples or samples heated at 70 °C for 48 h. I chose to standardise my MED assessment procedure by measuring soil water repellency on oven-dried soil (105 °C, 24 h). Tests conducted with the three selected nonwettable soils confirmed that MED values obtained on oven-dried soil were more consistent and not statistically different from those obtained on air-dried soil (data not shown).

Heating soil in a forced air oven at 105 °C for 24 h is not recommended before soil organic matter studies because it exposes the sample to potentially extensive thermal degradation. Lower temperatures and shorter drying periods under an O_2-free environment are usually prescribed for such purposes. In the context of my work, however, thermal degradation was not considered a serious limitation. This is because oven-drying did not measurably alter the degree of water repellency displayed by soil and because the material I was interested in characterising was only that which imparts water repellency to soil.

Extraction of soil water repellency

Supercritical CO_2 and eight organic solvents varying in polarity and boiling point temperature were used to extract nonwettable and control wettable soils and isolate water-repellent substances for subsequent characterisation. Variety in the set of selected test extractants was necessary to determine what solvent properties contribute most effectively to the removal of soil water repellency. The amphiphilic solvent mixture IPA/NH_4OH (7:3, v/v) was chosen because Ma'Shum *et al.* (1988) reported that it completely eliminated water repellency in several nonwettable Australian sandy soils. The acidic amphiphilic mixture IPA/CH_3COOH (7:3, v/v) was chosen to determine if the alkalinity of IPA/NH_4OH contributed more to its extraction efficiency than did its amphiphilic properties. The more neutral amphiphilic solvent IPA/H_2O was included to determine if strong acid-base properties enhanced the extraction efficiency of the IPA/CH_3COOH and IPA/NH_4OH solvent mixtures. The high-boiling amphiphilic and nonpolar organic solvents *n*-propanol (97 °C) and CCH (78 °C) were chosen to test the hypothesis that the higher reflux temperature of the amphiphilic solvents IPA/NH_4OH (b.p. ≈80 °C), IPA/CH_3COOH (b.p. ≈95 °C) and IPA/H_2O (b.p. ≈90 °C) improved their extraction efficiency. Even though solvent condenses before it comes into contact with soil in the extraction chamber of a Soxhlet apparatus, high-boiling solvents maintain a distinctly higher temperature after condensation than lower-boiling solvents. This is due in part to the heat source (sand bath, in this case) being set at a higher temperature to achieve similar refluxing rates for low- and high-boiling solvents, and in part to the limited amount of time allowed for solvent cooling after condensation at the relatively rapid refluxing rate of 10 $\text{cycles}\cdot h^{-1}$. The effectiveness of supercritical CO_2 was tested to determine if SFE could be used to replace the more time- and solvent-consuming Soxhlet extraction as my routine method of extraction.

The extraction of water-repellent substances and elimination of soil water repellency appear to be independent of extractant reflux temperature, but strongly dependent on extractant polarity. For example, even though the two organic solvents CCH and *n*-propanol have boiling points approaching that of the amphiphilic solvents IPA/NH_4OH, IPA/H_2O, and IPA/CH_3COOH, they had comparatively low extraction efficiencies according to my criterion of evaluation (Tables 3.3 and 3.4). In contrast, solvent polarity appeared to have a considerable influence on extraction efficiency. In agreement with observations made by Ma'Shum *et al.* (1988), a marked decrease in extraction efficiency was noted in the order going from amphiphilic to polar, and then to nonpolar solvents. The performance of polar and monophasic amphiphilic solvents clearly surpassed that of nonpolar solvents, including supercritical CO_2, even though they did not completely eliminate soil water repellency. Supercritical CO_2 extraction, on the other hand, was about as ineffective as Soxhlet extraction with nonpolar organic solvent in eliminating water repellency in the NW soil tested (Tables 3.3 and 3.5). Theoretically, after extraction with nonpolar solvents, soils should contain less nonpolar organic matter (e.g. fats and waxes) than nonextracted soils. Accordingly, those extracted with amphiphilic solvents should contain less amphiphilic organic matter (e.g. humic acids and polar crude oil residues) than nonextracted soils. The fact that extraction with nonpolar solvent removes large amounts of organic compounds from nonwettable soils (Table 3.4), but yet leaves the extracted soil severely nonwettable (Table 3.3), suggests that nonpolar organic matter does not alone contribute measurably to soil water repellency.

The IPA/NH_4OH solvent mixture was the most effective extractant for the removal of water-repellent substances from soil. It completely eliminated water repellency in the three nonwettable soils. The mixtures IPA/H_2O and IPA/CH_3COOH were only slightly less effective than the IPA/NH_4OH mixture (Table 3.3). The small difference in the MED index of nonwettable soils extracted with IPA/NH_4OH (pH $\approx$11.9) and with IPA/H_2O (pH $\approx$9.1) or IPA/CH_3COOH (pH $\approx$2.7) suggests that amphiphilicity is the single most important solvent property contributing to the removal of soil water repellency, and that a strongly alkaline reaction only slightly improves extraction efficiency.

I postulated that the complete elimination of soil water repellency following extraction with IPA/NH_4OH was due either to: (1) removal of water-repellent substances from nonwettable soil, (2) retention of solvent molecules by water-repellent substances, or (3) partial solvation and re-organisation of water-repellent substances on soil particle surfaces. The second and third alternative hypotheses had to be included to account for the fact that ELL-CW and DEV-CW soil became water-repellent following extraction with nonpolar solvents (Table 3.3).

Hudson *et al.* (1994) proposed that retention of nonpolar solvent molecules by soil may explain why extraction with hexane increased the water repellency of control wettable and nonwettable soil samples taken from golf sand greens. I considered this alternative hypothesis to explain why ELL-CW and DEV-CW soil acquired water repellency following extraction with DCM and CCH, but I find more evidence against it than in favour of it. This evidence can be summarised into three arguments: (1) in my work, exposure to nonpolar solvent increases the water repellency of oil-contaminated ELL-CW and DEV-CW soil, but did not affect the wettability of pristine ELL-PW soil, BRU-CW soil, and AW sand; (2) nonpolar solvent molecules retained by soil surfaces should have volatilised during the prolonged air- and oven-drying treatments that always preceded the assessment of soil water repellency; and (3) IPA and DCM solvent peaks were never detected in the gas chromatograms of solvent-extracted soil samples that were subjected to thermal desorption-GC/MS analyses (DCM data not shown). Even though these observations may not justify ruling out the hypothesis that retention of nonpolar solvent molecules can generate water repellency in some soils (cf. Hudson *et al.* 1994), they at least suggest that organic matter coatings in hydrocarbon-contaminated soil differ in surface chemistry from those found in pristine soils.

It is impossible to confirm beyond a doubt that extraction with IPA/NH_4OH removes water-repellent substances exhaustively, partially, or at all from soils that it renders wettable. Ma'Shum and Farmer (1985) have observed that considerable variation in soil water repellency can occur without removal of compounds from soil. According to McGhie and Posner (1980), changes in soil water repellency may have to be ascribed to changes in the molecular conformation of organic matter rather than to the removal of water-repellent substances. I nevertheless proceeded with the characterisation of IPA/NH_4OH-soluble material extracted from nonwettable soil on the basis that these probably contained at least some of the target water-repellent substances.

Chemical characterisation of extracted putative water-repellent substances

The primary objective of this work was to characterise organic substances imparting water-repellency to nonwettable soils. From the fact that polar and amphiphilic solvents reduce soil water repellency to a greater extent than nonpolar solvents, I infer that substances associated with soil water repellency are more soluble in more polar solvents and therefore probably consist of amphiphilic rather than strictly nonpolar hydrophobic compounds. I did not perform gas chromatographic and mass spectroscopic analyses directly on the dissolved IPA/NH_4OH-extracted material because I was unable to find a GC-compatible solvent that could completely re-dissolve the air-dried IPA/NH_4OH-extracts. Ma'Shum *et al.* (1988) characterised only the chloroform-soluble fraction (≈70%, on a mass basis) of their IPA/NH_4OH-extracted material obtained from water-repellent sands. I chose instead to characterise the extracted substances using methods that did not require the sample to be in a liquid phase.

GC/EI/MS analytical techniques provide sensitivity and specificity only for volatile compounds that are soluble in GC-compatible solvents. Because the substances associated with soil water repellency are not soluble in GC-compatible solvents, an alternative extraction or analytical method was needed. Thermal extraction is a safe and fast alternative to classical extraction procedures for a wide range of semivolatile organic compounds. The technique of thermal extraction-GC/EI/MS requires only drying and milling of soil samples prior to analysis. A soil sample is heated at a controlled rate and semivolatile organic compounds within the soil matrix are desorbed under conditions that minimise the risk of oxidative degradation (as opposed to pyrolysis). The analytes are volatilised into the helium carrier gas flow at a controlled preprogrammable temperature profile and subsequently cryocondensed onto a gas chromatographic column, which can in turn be connected to a mass spectrometer. The method has been demonstrated by Junk *et al.* (1991).

CI is a soft ionisation mass spectrometric technique that employs a chemical ionisation reagent gas to ionise organic compounds so that molecular weight information can be obtained. In thermal desorption-GC/CI/MS analysis, compounds are thermally extracted under controlled conditions and the desorbed products are identified by their unique mass spectra. The use of high-resolution GC/EI/MS in combination with GC/CI/MS provides a valuable tool in environmental organic analysis as all of the volatile and semivolatile organic material present in a sample can be accounted for and tentatively identified.

Thermal extraction-GC/EI/MS and GC/CI/MS analyses were performed on the sample of AW sand treated with ≈9 $g \cdot kg^{-1}$ IPA/NH_4OH-extractable material obtained from DEV-NW soil (Fig. 3.4). I postulated that thermal extraction would desorb all organic material susceptible of being volatilised upon exposure to temperatures increasing linearly from 50 to 280 °C over a 20-min period, and that this would include at least some of the putative water-repellent substances. The temperature maximum of ≈280 °C was selected to minimise thermal degradation (cracking by pyrolysis) of higher-molecular-weight organic molecules (Schnitzer and Hoffman 1964).

The compounds coating the surface of AW sand particles are compounds that were extracted from DEV-NW soil using IPA/NH_4OH and then added to the sand. They are referred to as putative water-repellent substances because their removal from DEV-NW soil leaves this soil wettable and their addition to the sand leaves the sand water-repellent. The results of my thermal desorption-GC/EI/MS and GC/CI/MS analyses indicate that the amphiphilic solvent mixture IPA/NH_4OH removes mostly long-chain *n*-fatty acids, *n*-alkanes, and cycloalkanes from DEV-NW soil. These compounds are widespread in soils and could be either of petroleum, plant, or microbial origin (Dinel *et al.* 1990; Volkman *et al.* 1992). However, petroleum biomarker compounds, such as steranes and hopanes, were also detected, which do not commonly occur in pristine soil environments (Volkman *et al.* 1992). Furthermore, the identified long-chain and polycyclic aliphatic compounds occurring in extensive homologous series suggest a composition resembling that of weathered crude oil mixtures. From this, I conclude that the identified putative water-repellent substances are most likely of petroleum origin. My results partly agree with those of Ma'Shum *et al.* (1988) who arrived at the conclusion that soil hydrophobicity is caused by organic molecules with extensive polymethylene chains. The major difference between water-repellent substances in nonwettable Australian sandy soils that were never exposed to petroleum contamination and those in soils that develop water repellency following oil contamination seems to lie in their origin, and not so much in their chemical structure.

The presence of an unresolved complex mixture of aliphatic hydrocarbons is a common feature in GC chromatograms of crude oils that have undergone partial weathering. Unresolved complex mixtures, however, have been shown to succumb slowly to microbial degradation both in vitro and in the environment (Atlas 1981). The fact that appreciable amounts of *n*-alkanes and *n*-fatty acids remain in DEV-NW soil more than four decades after oil contamination suggests that crude oil weathering is interrupted or at least retarded at an early stage in the recovery process at some crude oil spill sites. Long-chain aliphatic compounds naturally occur in most soils and soil microorganisms following oil contamination may have produced more. Nevertheless, I infer from their presence in relatively large amounts and extensive homologous series in weathered oil-contaminated soil that they are predominantly of petroleum origin.

CPMAS ^{13}C-NMR spectroscopy can be a useful analytical tool for the structural characterisation of insoluble macromolecular substances such as soil humic substances (Hatcher *et al.* 1983). Even though the quantitative reliability of the CPMAS ^{13}C NMR technique for soil organic matter characterisation has long been of concern, much valid information can still be obtained from CPMAS spectra. In many studies, it is sufficient to compare relative intensities of peaks across a series of similar samples (Preston 1996). The poorer resolution of solid-state ^{13}C NMR spectra, compared to that which can be achieved in liquid state, is partially overcome when spectral comparisons are made for similar soil samples analysed under identical NMR protocols. Since ^{13}C NMR spectra of whole soils usually exhibit many overlapping signals throughout the spectrum, it has become customary to divide a spectrum into suitable regions corresponding to the main functional groups that are present. I divided the spectra according to the protocol of deMontigny *et al.* (1993). Although other protocols could have been used, there is general agreement between most sets of limits that are commonly used to separate aliphatic from aromatic compounds, which was my main concern. The intensity of each region was then obtained by measuring the area enclosed by the spectrum and vertical lines were dropped at the boundaries of each region. The method is not entirely satisfactory, however, since the wings of signals in one region can overlap into neighbouring regions and is an obvious source of error (Kinchesh *et al.* 1995).

The CPMAS ^{13}C-NMR spectra provide a further test of the GC/EI/MS and GC/CI/MS data. These spectra confirm that IPA/NH_4OH removes mostly long-chain aliphatic organic compounds from DEV-NW soil and that, although it extracts some aromatic compounds, it leaves most of the aromatic fraction behind (Table 3.8). The results presented in Tables 3.7 and 3.8 also indicate that IPA/CH_3COOH and IPA/NH_4OH remove very similar compounds from DEV-NW soil. The CPMAS ^{13}C-NMR spectra confirmed the presence of a substantial aromatic fraction in both the nonextracted and solvent-extracted DEV-NW soil ($\approx$30-35% of total organic C in soil). Considering that phthalates were the only aromatic compounds detected in the extract-loaded AW sand analysed by GC/EI/MS and GC/CI/MS, I infer that the aromatic fraction in DEV-NW soil is highly resistant to extraction with IPA/NH_4OH. The results of my CPMAS ^{13}C-NMR studies support the conclusions that were drawn from the results of thermal desorption-GC/EI/MS and GC/CI/MS analyses.

CONCLUSION

The extraction of substances involved with soil water repellency from the range of soils used here appears to be independent of extractant reflux temperature, but strongly dependent on extractant polarity. Amphiphilicity is the single most important solvent property contributing to the removal of substances involved with soil water repellency. Extraction with amphiphilic solvents also consistently removed more organic matter from soil than did extraction with nonpolar solvents. Strongly alkaline reaction only slightly improves extraction efficiency. The IPA/NH_4OH solvent mixture was the most effective extractant among the eight tested. Supercritical fluid extraction under the conditions used was not effective at removing soil water repellency.

Exposure to nonpolar solvent (e.g. DCM, CCH) generates water repellency in wettable fine-textured soils that were once contaminated by petroleum. Such solvents do not generate water-repellency in similar wettable fine-textured soils that were never exposed to petroleum hydrocarbons. I cannot confirm with certainty that water-repellent substances need to be removed partially, completely, or at all in order to remove water repellency. I can state, however, that extraction with IPA/NH_4OH eliminates water repellency. I can also state that extraction of nonwettable soil with IPA/NH_4OH removes some aromatic C (only phthalates identified), but predominantly aliphatic C, comprising homologous series of long-chain and polycyclic aliphatic compounds; namely, *n*-fatty acids, *n*-alkanes, and cycloalkanes. I infer from their presence in nonwettable soils in such large amounts, uniform distribution, and extensive homologous series that they are predominantly of petroleum origin in the studied soils.

Table 3.1. Characteristics of the three selected study sites[z]

Site	Land use	Texture	MED[y]	Date of spill
ELL	Agricultural	Clay loam	3.9 ±0.1[x]	1973
BRU	Industrial	Loamy sand	3.5 ±0.1	≈1975
DEV	Agricultural	Loam	4.2 ±0.0	1947

[z] Adapted from Table 2.1

[y] Molarity of Ethanol Droplet test performed on oven-dried soil (105 °C, 24 h)
Interpretation guidelines: MED < 1.0, slight water repellency; 1.0 < MED < 2.2, moderate; MED > 2.2, severe (King 1981)

[x] Standard deviation

Table 3.2. Physicochemical properties of the three NW and corresponding CW soils (0-15 cm)[z]

	ELL		BRU		DEV	
Property	CW[y]	NW	CW	NW	CW	NW
Sand (g·kg^{-1})[x]	290	300	860	860	380	400
Silt (g·kg^{-1})[x]	350	370	20	20	320	350
Clay (g·kg^{-1})[x]	360	330	120	120	300	250
CEC (cmol (+)·kg^{-1})[w]	42	34	3	3	43	28
Water at -33 kPa (g·kg^{-1})[v]	360	360	50	40	340	250
Total C (g·kg^{-1})[u]	61	68	2	5	39	41
Mineral N (mg·kg^{-1})[t]	101	83	5	12	9	119
pH (in 0.01 M $CaCl_2$, 2:1)[s]	5.3	5.4	5.5	5.4	7.3	5.8

[z] Adapted from Tables 2.2 and 2.3

[y] CW = control wettable; NW = nonwettable

[x] Kalra and Maynard (1991)

[w] Lavkulich (1981)

[v] Gravimetric determination using a pressure plate apparatus

[u] Determined by dry combustion using a Leco induction furnace (CR-12)

[t] Determined by automated colourimetric analysis using the method of Keeney and Nelson (1982)

[s] Determined using a Fisher Accumet™ pH Meter Model 630 (separate glass and calomel electrodes)

Table 3.3. Water repellency index of the three NW and corresponding CW soils following Soxhlet extraction with different solvents and oven-drying at 105 °C for 24 h

	MED index (*M*) of extracted soil					
Solvents	ELL-CW	ELL-NW	BRU-CW	BRU-NW	DEV-CW	DEV-NW
None	1.2 ±0.0[z]	3.9 ±0.1	0.0 ±0.0	3.5 ±0.1	0.0 ±0.0	4.2 ±0.0
CCH	2.1 ±0.1	3.7 ±0.0	0.0 ±0.0	3.7 ±0.1	1.7 ±0.2	4.0 ±0.0
DCM	0.9 ±0.1	3.2 ±0.1	0.0 ±0.0	3.3 ±0.1	2.1 ±0.1	3.6 ±0.1
Methanol	0.0 ±0.0	2.2 ±0.6	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	1.6 ±0.0
IPA	0.0 ±0.0	1.6 ±0.2	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	1.2 ±0.5
n-propanol	0.0 ±0.0	0.9 ±0.1	0.0 ±0.0	0.4 ±0.3	0.0 ±0.0	1.4 ±0.4
IPA/H_2O	0.0 ±0.0	1.4 ±0.9	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.4 ±0.4
IPA/CH_3COOH	0.0 ±0.0	0.6 ±0.2	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
IPA/NH_4OH	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0

[z] Standard deviation

Table 3.4. Mass of organic material collected following Soxhlet extraction of the three NW and corresponding CW soils with solvents of varying polarity

	Mass of extractables ($g \cdot kg^{-1}$)					
Solvents	ELL-CW	ELL-NW	BRU-CW	BRU-NW	DEV-CW	DEV-NW
CCH	0.6 ±0.1[z]	7.8 ±0.2	0.0 ±0.0	1.4 ±0.1	0.4 ±0.0	4.4 ±0.2
DCM	1.0 ±0.0	9.8 ±0.4	<0.1 ±0.0	2.3 ±0.2	1.5 ±0.1	6.5 ±0.3
Methanol	1.8 ±0.0	4.6 ±0.5	0.1 ±0.1	1.9 ±0.2	2.2 ±0.1	4.4 ±0.2
IPA	2.1 ±0.1	7.4 ±1.4	0.1 ±0.1	2.4 ±0.0	1.8 ±0.2	7.1 ±0.2
n-propanol	2.1 ±0.3	10.2 ±0.2	0.0 ±0.1	2.5 ±0.1	1.8 ±0.2	8.0 ±0.4
IPA/H_2O	2.9 ±0.2	10.1 ±0.1	0.1 ±0.0	2.9 ±0.1	2.8 ±0.1	8.7 ±0.5
IPA/CH_3COOH	2.9 ±0.3	11.1 ±0.4	0.2 ±0.1	3.7 ±0.6	3.5 ±0.8	10.7 ±0.6
IPA/NH_4OH	4.3 ±0.0	12.4 ±0.6	0.2 ±0.1	3.1 ±0.2	4.7 ±0.2	9.3 ±0.8

[z] Standard deviation

Table 3.5. Supercritical fluid extraction parameters and MED index of ELL-NW soil after four different extraction runs (initial MED = 3.8 *M*)

Parameters	A	B	C	D
Pressure (atm)	400	400	400	350
Extraction time (min)	40	40	40	60
Temperature (°C)	100	100	100	55
Fluid density (g·mL^{-1})	0.7	0.7	0.7	0.9
Modifier fluid	none	10% IPA	10% IPA	10% IPA
Extraction mode	dynamic	dynamic	static	dynamic
MED after extraction	4.6	3.6	4.4	2.4

Table 3.6. ^{13}C-NMR characteristics of nontreated and solvent-extracted DEV-NW soil

Chemical shift	Percent of total organic C content		
region (ppm)	Nontreated[x]	Extracted[y]	Extracted[z]
0 - 50	18.5	14.2	12.7
50 - 60	5.7	5.4	5.0
60 - 96	23.6	21.2	21.9
96 - 141	31.2	34.2	34.9
141- 159	9.2	10.3	12.1
159 - 185	8.6	10.3	10.0
185 - 210	3.2	4.2	3.2

[x] MED = 4.2 *M*

[y] Extracted with IPA/NH_4OH for 24 h, final MED = 0 *M*

[z] Extracted with IPA/CH_3COOH for 24 h, final MED = 0 *M*

Table 3.7. Distribution of organic C in nontreated and solvent-extracted DEV-NW soil as determined by ^{13}C-NMR spectroscopy

Chemical shift region (ppm)	Percent of total organic C content		
	Nontreated[z]	Extracted[y]	Extracted[x]
Aliphatic C (0 - 96 ppm)	47.8	40.9	39.6
Aromatic C (96 - 141 ppm)	31.2	34.2	34.9
Phenolic C (141 - 159 ppm)	9.2	10.3	12.1
Carbonyl & carboxyl C (159 - 210 ppm)	11.8	14.5	13.3

[z] MED value = 4.2 *M*

[y] Extracted with IPA/NH_4OH for 24 h, final MED value = 0 *M*

[x] Extracted with IPA/CH_3COOH for 24 h, final MED value = 0 *M*

Table 3.8. Distribution of organic C extracted from the DEV-NW soil by IPA/NH_4OH or IPA/CH_3COOH

Extraction treatment	Aliphatic	Aromatic	Phenolic	Carbonyl & Carboxyl	Total
			C^z ($g \cdot kg^{-1}$)		
None	20	13	3.8	4.8	42
IPA/NH_4OH					
Soil residue	13	11	3.3	4.7	32
Extract	6.3	1.7	0.43	0.13	8.6
IPA/CH_3COOH					
Soil residue	13	12	4.1	4.5	34
Extract	6.3	1.1	-0.29	0.37	7.5
			Extract composition		
IPA/NH_4OH	0.73	0.20	0.05	0.02	1.00
IPA/CH_3COOH	0.84	0.15	-0.04	0.05	1.00

[z] Calculated using a C content of 80% for the extracted material and data from Tables 3.2, 3.4 and 3.7.

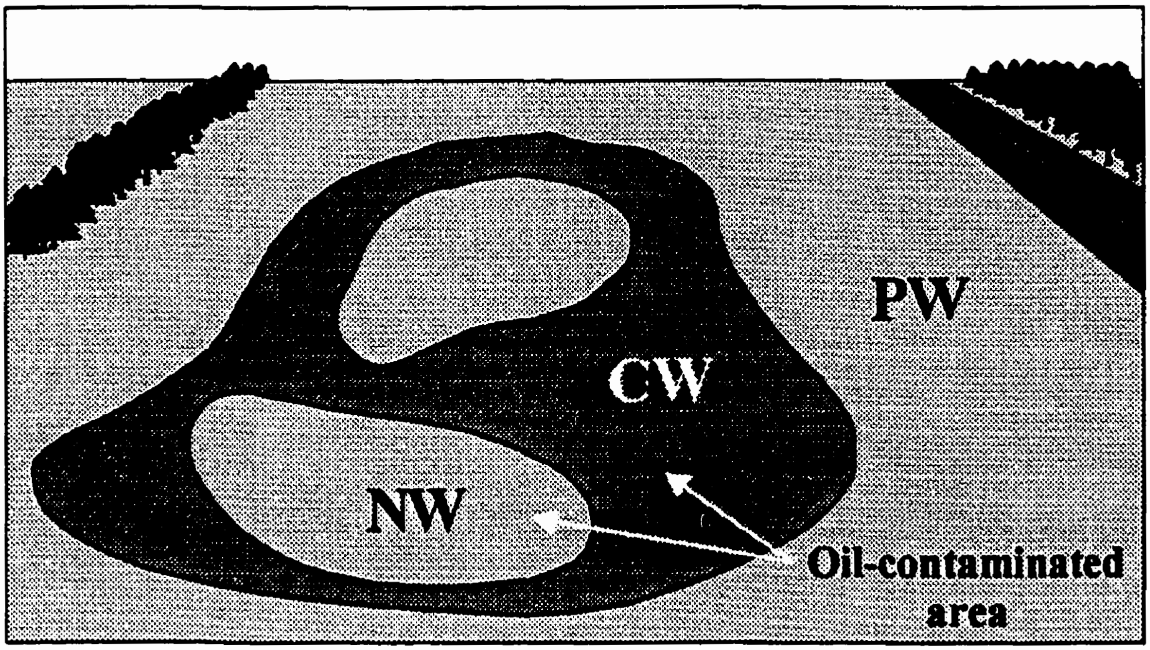
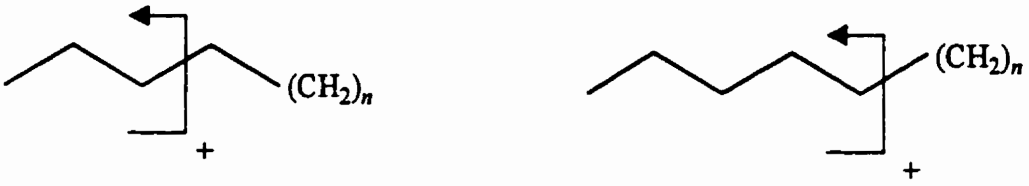


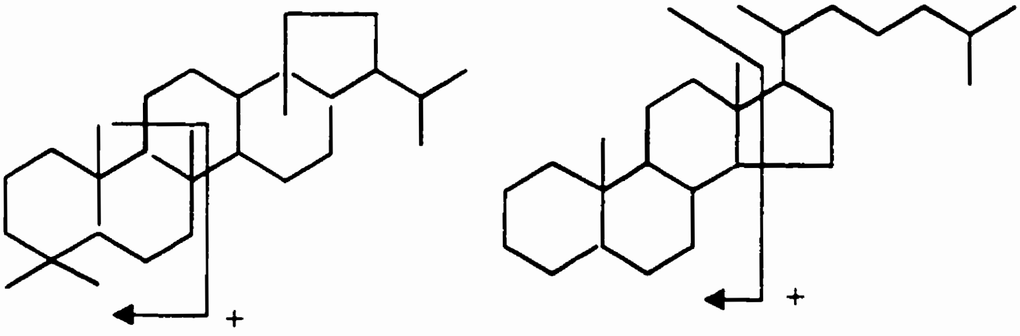
Figure 3.1. Illustration of the rationale for labelling soil PW, CW and NW.



m/z 43　　*m/z* 71

m/z 60
(rearrangement)

m/z 73



m/z 191　　*m/z* 217

Figure 3.2. Characteristic molecular ion fragments detected in mass spectroscopic analyses. Identification of extract components was achieved using extracted current profiles of characteristic ion fragments, molecular weight information, and chromatography.

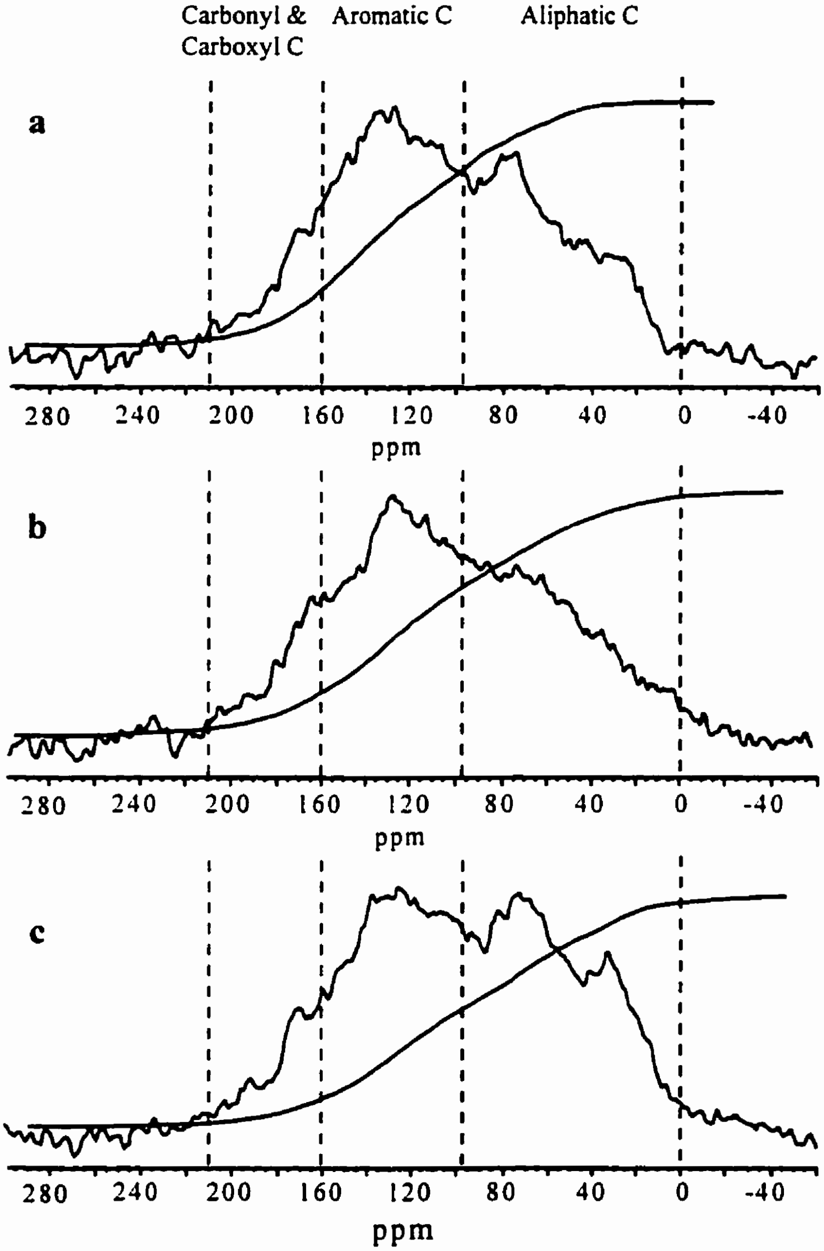


Figure 3.3. ^{13}C-NMR spectra of DEV-NW soil samples (a = IPA/CH_3COOH-extracted, b = IPA/NH_4OH-extracted, and c = nonextracted). Dividing vertical dotted lines represent areas of the spectrum where resonances characteristic of indicated types of organic C are typically found.

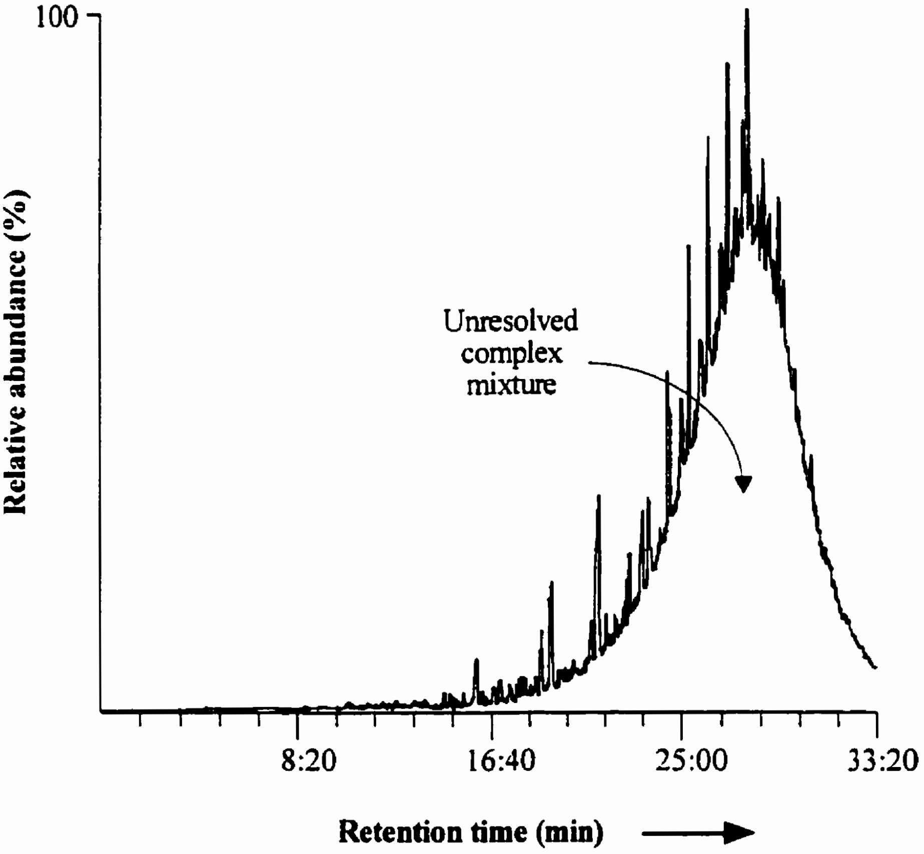


Figure 3.4. Gas chromatogram of thermally desorbed putative water-repellent substances obtaine from DEV-NW soil by extraction with IPA/NH_4OH and then added to AW sand at the concentratio of ≈9 g·kg^{-1}. The labelled unresolved complex mixture ("hump") is typical of weathered aliphatic petroleum hydrocarbons.

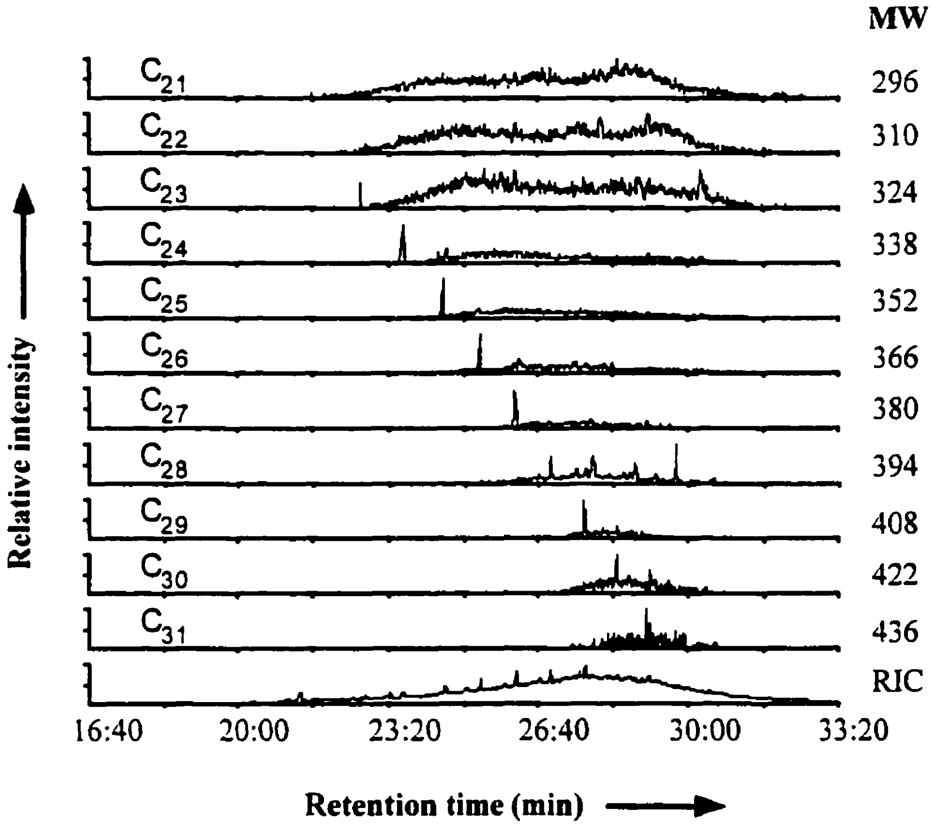


Figure 3.5. Homologous series of *n*-alkanes identified using GC/EI/MS information among the compounds that were thermally desorbed from the sample of extract-loaded AW sand. There is no predominance of even- or odd-C numbered species. Extracted ion current profiles were obtained by monitoring the characteristic fragment ions *m/z* 43, 57, 71 and 85 (not shown) and molecular weight (MW). RIC = relative ion count.

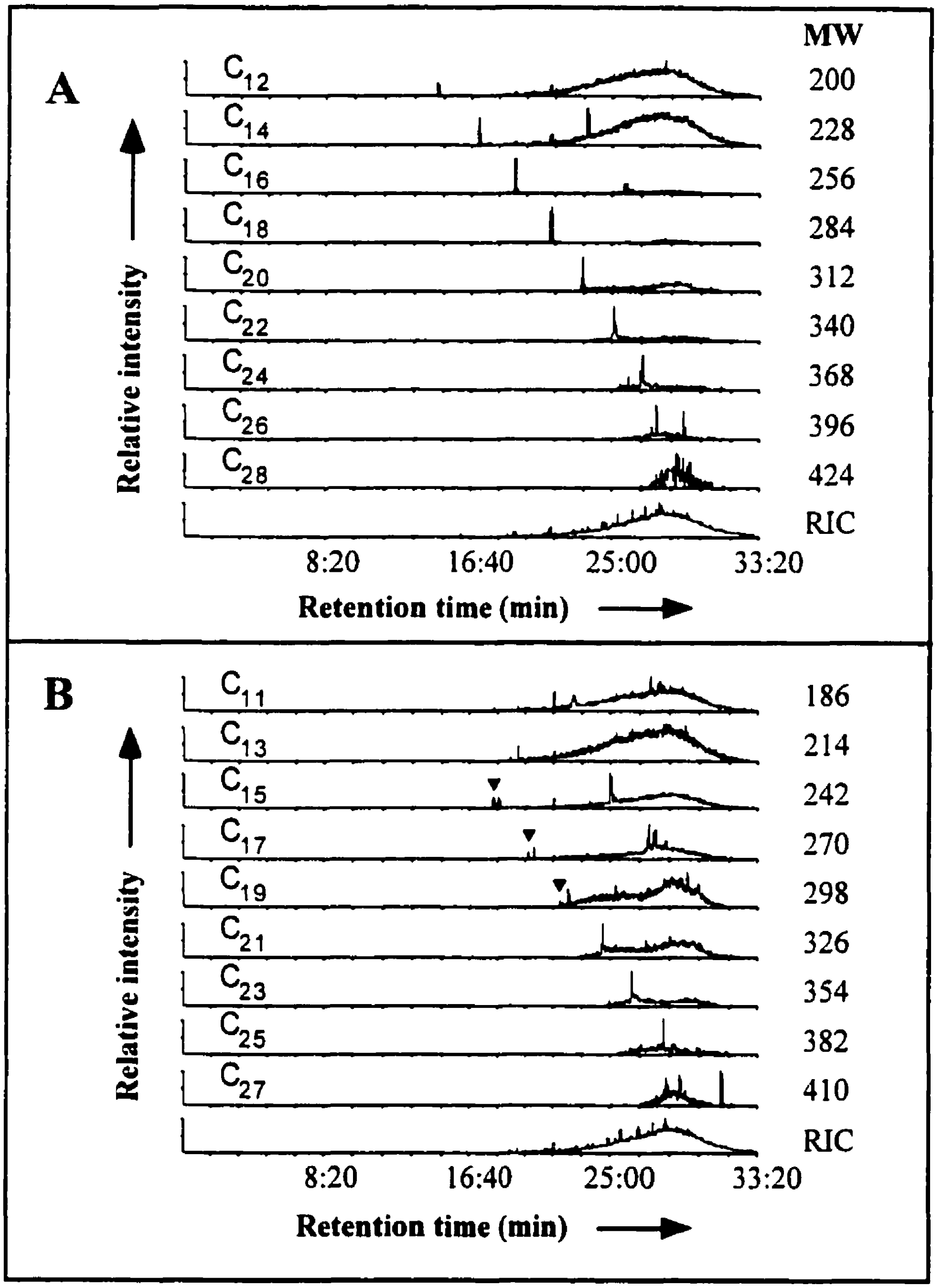


Figure 3.6. Homologous series of nonesterified *n*-fatty acids identified using GC/EI/MS information among the compounds that were thermally desorbed from the extract-loaded AW sand. ▼ indicate branched fatty acid isomers. A = even-C numbered species, B = odd-C numbered species. Extracted ion current profiles were obtained by monitoring the characteristic fragment ions *m/z* 60, 73, and 129 (not shown) and molecular weight (MW). RIC = relative ion count.

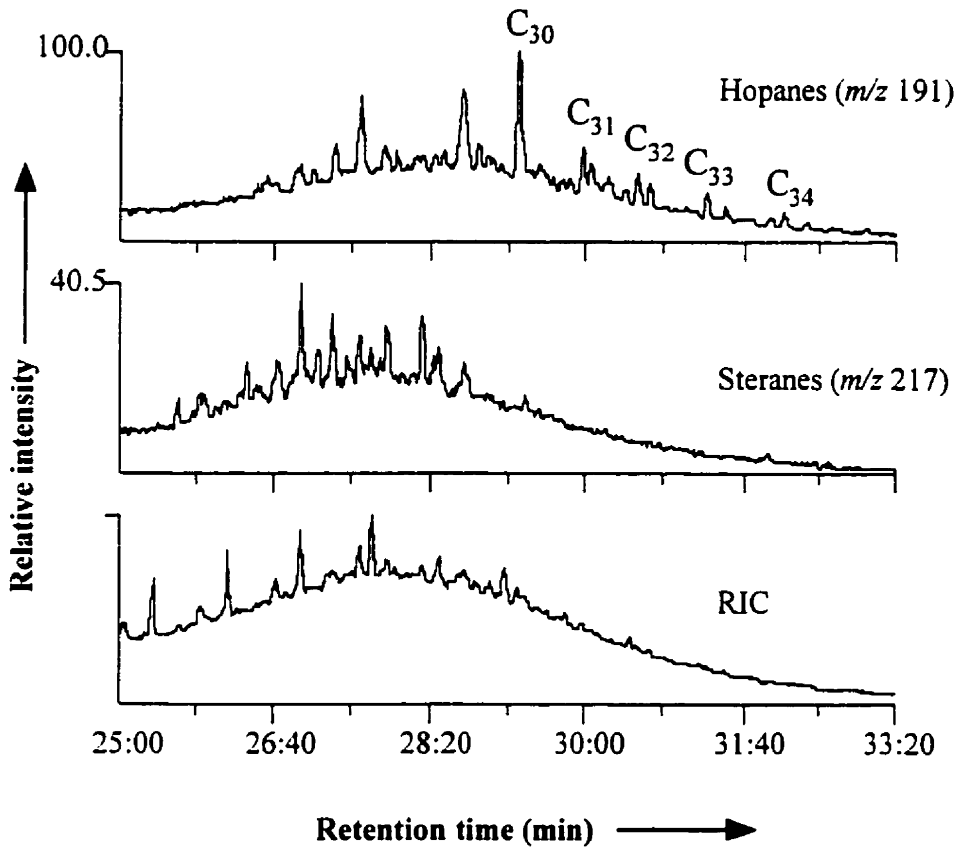


Figure 3.7. Homologous series of hopanes and steranes identified using GC/EI/MS information among the compounds that were thermally desorbed from the extract-loaded AW sand. Extracted ion current profiles were obtained by monitoring the characteristic fragment ions *m/z* 191 for hopanes and *m/z* 217 for steranes. RIC = relative ion count.

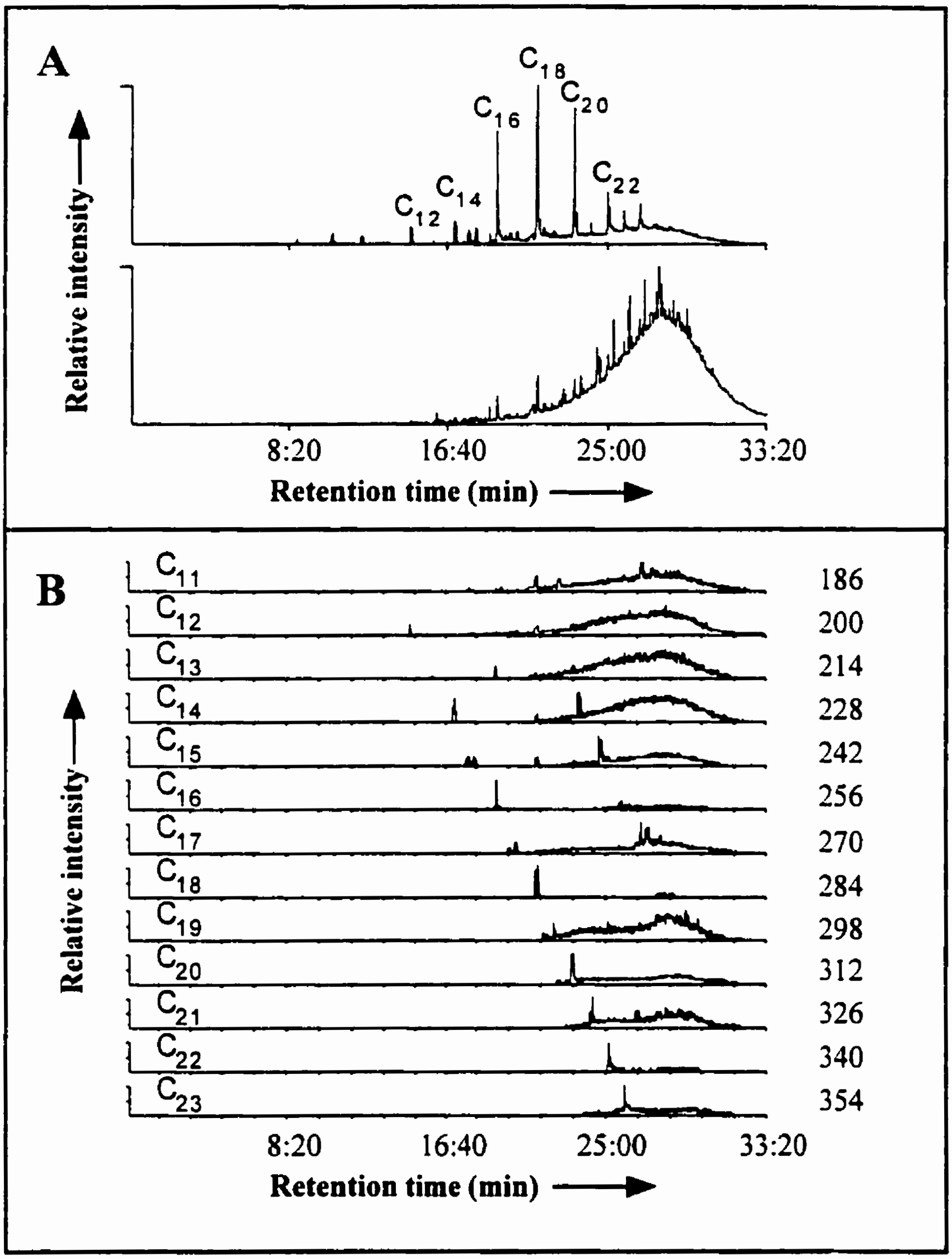


Figure 3.8. Predominance of even-C numbered *n*-fatty acids over odd-C numbered ones in the distribution of fatty acids that were thermally desorbed from the extract-loaded AW sand and identified using GC/EI/MS information (B). The more abundant *n*-fatty acids are labelled in the top chromatogram (A).

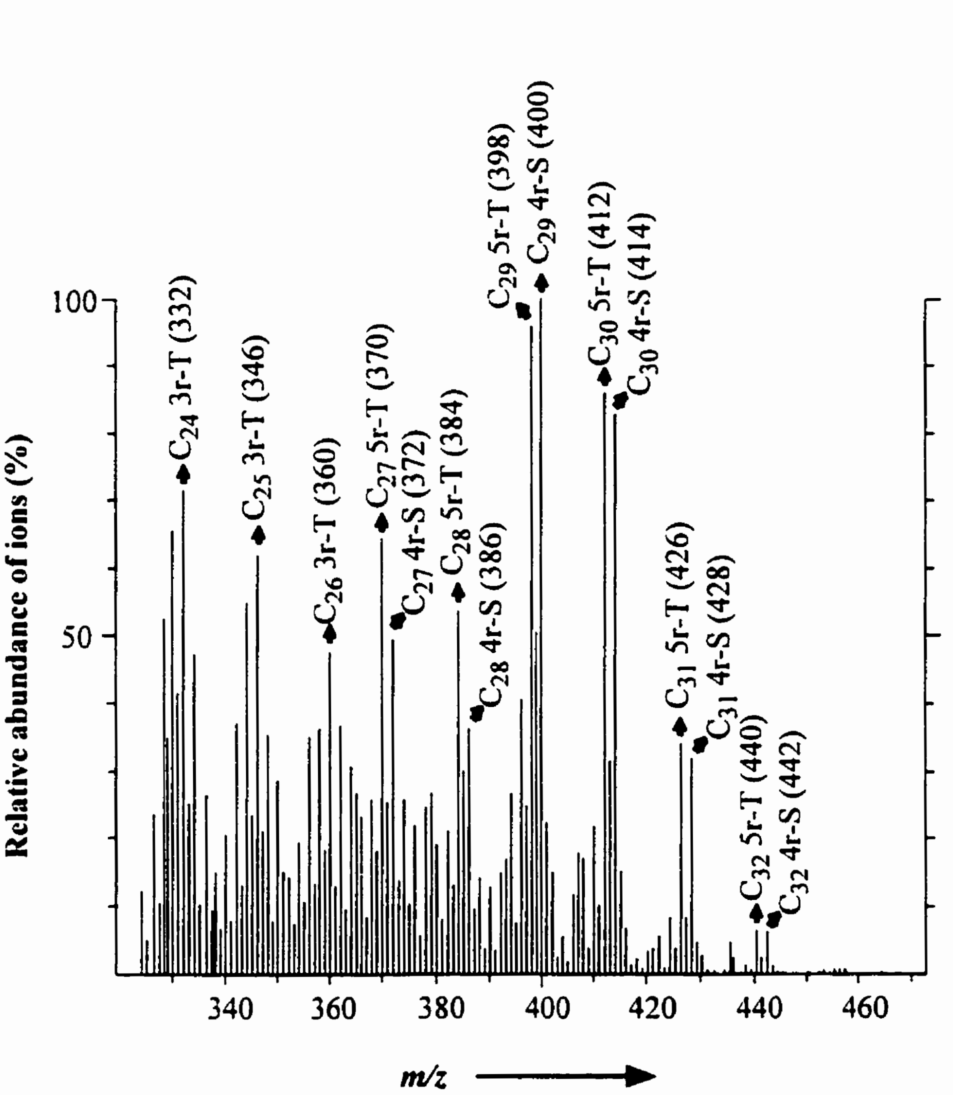


Figure 3.9. Chemical ionization mass spectrum of the extract-loaded sample of AW sand adding all the scans in the chromatogram. It shows the molecular weight information that was used in conjunction with information obtained from GC/EI/MS analysis to identify compounds forming the hump in the GC chromatogram of the extract-loaded sample of AW sand. Compounds identified are labelled as follows: T for terpane, S for sterane, and 3-, 4- and 5-r for number of rings. Molecular weights are in brackets. These assignments were confirmed by electron impact mass spectroscopy, which showed typical fragment ions for saturated aliphatic hydrocarbons (e.g. *m/z* 191 for hopanes and *m/z* 217 for steranes).

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CHAPTER 4

Flexible conformation in organic matter coatings: A hypothesis about soil water repellency[1]

INTRODUCTION

A number of difficulties are associated with characterising substances that impart water-repellent character to soil. One is that considerable variation in soil water repellency can occur without removal of any compounds from soil. Ma'Shum and Farmer (1985), for example, found that freeze-drying converts force-wetted water-repellent soil into readily wettable soil. However, subsequent re-wetting and oven-drying regenerated water repellency. Another difficulty is that soil water repellency that is completely eliminated by one extractive treatment often returns following exposure to clean nonpolar organic solvents. McGhie and Posner (1980) reported that a severely water-repellent clay-rich soil extracted with hot water or 0.1 *M* NaOH followed by chloroform was always wettable after the aqueous solvent extraction, but water-repellent after the chloroform extraction.

Repeated observations of reversible water repellency suggest that mechanisms other than removal of causative agents can also contribute to reductions in soil water repellency. Ma'Shum and Farmer (1985) proposed that the interfacial conformation of sorbed water-repellent substances changes in response to changes in the composition of interstitial pore fluids. According to them, hydrophilic functional groups in organic matter, such as -OH, -COOH, and $-NH_2$, interact with water molecules when the soil is wet, but with each other when the soil is dry. In freeze-dried soil, they contend that the molecular conformation of wet organic matter is preserved, that polar functional groups previously associated with water molecules are left exposed at the surface, and that this is why soil is readily re-wetted. On the other hand, air-drying is thought to increase soil water repellency because removal of water promotes interactions between polar functional groups, which in turn increases the exposure of nonpolar alkyl chains at the interface between organic matter coatings and interstitial pore fluids. Others have proposed a similar reasoning to explain why humic acids and some peats shrink and resist wetting following air-drying (Hayes 1985; Valat *et al.* 1991).

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[1] A version of this chapter has been accepted for publication in the Canadian Journal of Soil Science. Roy, J.L. and W.B. McGill. Flexible conformation in organic matter coatings: A hypothesis about soil water repellency.

In Chapter 3, I described how single exhaustive solvent extractions could increase or decrease soil water repellency depending on characteristics of the solvents used. For example, extraction with the amphiphilic solvents IPA/NH_4OH and IPA/CH_3COOH (IPA = *iso*propanol) virtually eliminated soil water repellency, whereas extraction with the nonpolar, non-H-bonding solvents dichloromethane (DCM) or cyclohexane (CCH) only slightly reduced or increased soil water repellency. Extraction with DCM or CCH also imparted water repellency to readily wettable oil-contaminated soils. In the present study, sequences of solvent extraction were performed to test hypotheses about reversible soil water repellency and characterise further the interactions of water-repellent coating constituents with selected solvents. An additional amphiphilic solvent, sodium dodecyl sulphate (SDS), was included to test further the hypothesis that amphiphilic character is required for removal of soil water repellency. Soil samples that were extracted with SDS were subsequently saturated with chloroform ($CHCl_3$) to test for reversible water repellency, such as was reported by McGhie and Posner (1980) and Ma'Shum and Farmer (1985).

The specific objectives of the work reported here were to: (i) test the extraction efficiency of the anionic surfactant SDS and (ii) test for reversible soil water repellency following extraction with solvents of varying polarity, interfacial activity, and H-bonding capacity. The main findings can be summarised as follows: (i) all H-bonding amphiphilic solvents tested completely eliminated soil water repellency, (ii) all non-H-bonding, nonpolar solvents tested generated, partially restored, or failed to eliminate water repellency in oil-contaminated soils, (iii) prior exposure to DCM increased the extractability of soil water repellency in H-bonding amphiphilic solvent. From data presented here and recent literature on the structural flexibility of organic macromolecules, I infer that water-repellent substances in previously oil-contaminated soils display solvent-induced conformational flexibility. Solvent-induced conformational changes alter the fractional coverage of surface-exposed alkyl chains and thereby alter the severity of macroscale water repellency symptoms.

THEORY

Significance of MED indices

Energy relations at surfaces determine the wetting of solids. The necessary condition for spreading to be possible is simply that the process shall involve a reduction in free energy (Burdon 1949). In soils, this condition is met when the average surface tension of soil solids exceeds the surface tension of water and the soil/water interfacial tension. Ideally, soil water repellency should be assessed by measuring the average surface tension of soil solids. This measurement, however, cannot be obtained directly (Johnson and Dettre 1993). The average surface tension of soil solids can only be estimated indirectly using methods such as the Molarity of Ethanol Droplet (MED) test.

The theoretical basis of the MED test is sound. Spontaneous wetting is defined as that occurring within a maximum of 10 s. A standard-size droplet of liquid is placed on the levelled, dry soil surface and allowed 10 s to be completely absorbed. Small droplets (2-3 mm diameter) are typically used to minimise hydrostatic pressure contributions to the wetting process. Complete droplet entry is observed when the contact angle at the soil/liquid/air interface has decreased to 0° (i.e. when the droplet is no longer visible). The test is initially performed using water droplets (0 *M* or 72 $mN \cdot m^{-1}$). If complete water droplet entry within 10 s is not observed, the test is pursued using droplets of aqueous ethanol solution. The aqueous ethanol solution concentrations tested usually differ by 0.2-*M* increments and span the range of 0.2 to 5.0-6.0 *M*.

Increasing the ethanol solution concentration causes the liquid surface tension to decrease. Lowering the liquid surface tension alters the thermodynamics of the system towards spontaneous soil wetting. Eventually, complete droplet absorption within 10 s is observed. This indicates that liquid surface tension has been lowered sufficiently that the sum of the liquid surface tension and soil/liquid interfacial tension now totals less than the average soil surface tension. The MED index of the soil is recorded as the molarity of the least concentrated aqueous ethanol solution to be absorbed in 10 s or less. This concentration has theoretical meaning when it is converted to its equivalent liquid surface tension.

An MED value is not a direct estimate of average soil surface tension because it does not account for the wetting barrier that is the soil/liquid interfacial tension. It is, however, a good *indicator* of average soil surface tension and a reliable, relative index of soil water repellency. In this report, I provide the mathematical relationship linking liquid surface tension to molarity of ethanol solution for concentrations ranging from 0 to 6 *M*.

MATERIALS AND METHODS

Study sites

Nonwettable and corresponding control wettable soil samples were collected at three old crude oil spill sites: Ellerslie (ELL), Bruderheim (BRU), and Devon (DEV). The three sites are located within a 100-km radius of the city of Edmonton, Alberta, Canada. The ELL site (53°25'N, 113°33'W) is a fallowed agricultural field that was contaminated in 1973. The DEV site (53°20'N, 113°42'W) is a fallowed agricultural field that was contaminated in 1947. The BRU site (53°51'N, 112°58'W) is an industrial site that was contaminated in the mid-1970s. Soil from the ELL site consists of Malmo silty clay loam (Eluviated Black Chernozemic); from the BRU site, of dune sand (Orthic Regosolic); and from the DEV site, of Ponoka loam (Eluviated Black Chernozemic). More detailed information about site characteristics can be found in Chapter 2

Soil sampling and sample preparation

Nonwettable and adjacent control wettable soil

Samples of control wettable (CW) and nonwettable (NW) soil (0-15 cm) from the three selected sites were collected and processed as described in). Readily wettable soil to be used as CW soil was sampled within a 25-m perimeter outside the boundaries of the NW soil at each site. CW soil was taken as that which supported some plant growth and which, at field moisture content, readily absorbed water droplets placed on its surface. DEV-CW soil was sampled from underneath a growing wheat (*Triticum aestivum* L.) crop, whereas ELL-CW and BRU-CW soils were sampled in areas that were only sparsely covered with weeds.

Field-moist ELL-CW soil was readily wettable at the time of sampling, but subsequent air drying indoors left this soil slightly water-repellent. It was nevertheless kept as the ELL-CW soil. Slight water repellency in air-dried ELL-CW soil may be due to contamination by adjacent ELL-NW soil. It is known that ELL-CW soil was contaminated with crude oil at the same time as ELL-NW soil was. Such information is not available in the case of the DEV-CW and BRU-CW soils. According to anecdotal reports, however, the area sampled for DEV-CW soil was also contaminated by crude oil in 1947, but that sampled for BRU-CW soil never was.

Air-dried soil was passed through a 1-mm sieve and thoroughly mixed to produce uniform composite samples of CW and NW soil for each site. These samples were then stored in glass jars in the dark at 4 °C prior to analysis (i.e. up to a year). Selected chemical and physical properties of the three NW and corresponding CW soils, as reported in Chapter 2, are listed again in Table 4.1. The residual oil content of these soils was previously determined by measuring their concentration of DCM-extractable organics me *et al.* 1999). These results are also included in Table 4.1.

Pristine wettable soil used for comparison

Pristine wettable (PW) soil (0-10 cm) was sampled well outside the oil-contaminated area at the ELL site. This soil has 5.2% total C and 0.5% total N and it belongs to the Malmo soil series. Air-dried ELL-PW soil was passed through a 1-mm sieve and stored at room temperature before use (i.e. up to a year).

Assessment of soil water repellency

The MED test was used to assess soil water repellency (Watson and Letey 1970; King 1981). I sieved soils to < 1 mm instead of < 2 mm because this reduced variability in MED results. I report here only MED values assessed on oven-dried soil because they were essentially the same as those assessed on air-dried soil, although generally less variable (data not shown). Reported values are the arithmetic means of three replicate measurements and the associated standard deviation.

An arbitrary scale developed by King (1981) is sometimes used in this paper. This scale ranks soil water repellency as slight (MED ≤ 1.0 *M*), moderate (1.0 *M* < MED < 2.2 *M*), or severe (MED ≥ 2.2 *M*).

Measurement of liquid surface tension

Triplicate surface tension measurements were made using a Fisher Surface Tensiomat (Fisher Scientific, Model 21, Cat. No 14-814). Surface tension values ($mN \cdot m^{-1}$) were measured at 21 ±1 °C for 30 ethanol solution concentrations ranging from 0 to 6 *M*. Molarity was calculated without correcting for the 5% (v/v) impurities present in the ethanol used. The ethanol used was HPLC grade ethanol containing 95% (v/v) denatured ethanol 3A and 5% (v/v) IPA (Sigma-Aldrich, Cat. No. 27,074-1). Deionised water was used to bring the different solution concentrations to volume. Surface tension was plotted against molarity of ethanol solution. The relationship was analysed using Origin™ (Microcal™ Software, Inc., version 4.0) in the nonlinear least squares fitting mode.

Solvent classification

Three solvent characteristics appear to dictate what changes in soil water repellency take place upon solvent removal. These are solvent polarity, interfacial activity and H-bonding capacity. There is no generally accepted method of classifying solvents according to these scales. The set of criteria that I developed and used to classify solvents is described below. Solvent mixtures were classified by accounting for all of their components, including water. My classification scheme thus takes into account the volume fraction of all solutes in the mixtures.

Polarity

Solvents are usually loosely classified as polar or nonpolar based on their dielectric constant value. Different authors, however, tend to choose different values to separate between the two classes. King (1973) used the arbitrary value of 30. I chose to define polar solvents as solvents that have a dielectric constant (ε_r) value > 10, and nonpolar solvents as solvents that have a ε_r value ≤ 10. This arbitrary value was chosen to facilitate discussion. It places solvents that are most effective at eliminating soil water repellency into the polar class and solvents that are least effective at it into the nonpolar class.

Dielectric constant (relative permittivity) values were measured at 20 °C using a microwave dielectrometer operated at the average frequency of 915 MHz. These dielectric constant values represent the ratio of the strength of the Coulomb field in the test liquid to that in air. The system used was set with the dielectric constant of water as its upper limit. Measured values for mixtures consisting mostly of water thus approached the measurement limits of the system used.

Amphiphilic character

I define amphiphilic solvents as those solvents that display interfacial activity. This condition is met by solvents that contain molecules having a polar or ionic functional group at one end and a nonpolar alkyl chain two or more C atoms long at the other.

H-bonding capacity

The H-bonding capacity of solvent mixtures was classified according to a solvent scale developed by Burrell (1955). It was inferred for those solvent mixtures not listed in Barton (1989) based on knowledge of the H-bonding capacity and volume fraction of their separate constituents.

Extraction with SDS followed by treatment with $CHCl_3$

I subjected samples of nonextracted, IPA/NH_4OH-extracted, and DCM-extracted BRU-CW, DEV-CW, BRU-NW and DEV-NW soil to extraction at room temperature with two different solution concentrations of the anionic surfactant SDS [$CH_3(CH_2)_{11}SO_4^-Na^+$] (0.05 and 0.5 *M* SDS). Fifty-millilitre aliquots of SDS solution were added to 100-mL plastic centrifuge tubes containing 10 g of soil (oven-dried basis). These tubes were capped and shaken overnight on a reciprocal shaker. The SDS-extracted soil samples were transferred into 250-mL plastic centrifuge bottles and rinsed by centrifugation a minimum of four times with ≈300 mL of deionised water. Each rinse consisted in 30-min centrifugation at 12 100 × g with fresh deionised water. After rinsing, the soil samples were transferred into aluminium dishes, air-dried for 7 d, oven-dried at 105 °C for 24 h, and cooled in a desiccator prior to assessment of soil water repellency. $CHCl_3$ treatment entailed adding enough of this solvent to saturate the oven-dried SDS-extracted soil. The mixture was then vortexed in a fume hood until complete solvent evaporation. The $CHCl_3$ treatment is basically a wetting and drying treatment. No material is removed from, or added to, soil other than $CHCl_3$. The air-dried solid samples were then oven-dried at 105 °C for 24 h, cooled in a desiccator, and assessed for soil water repellency.

Water repellency following sequential Soxhlet extractions with selected polar amphiphilic and nonpolar solvents

Air-dried CW, NW and PW soil samples (≈25 to 75 g, oven-dried) were subjected to different sequential Soxhlet extractions. Two two-step sequential extractions were performed using IPA/14.8 *M* NH_4OH (7:3, v/v) (IPA/NH_4OH) followed by DCM and IPA/5.2 *M* CH_3COOH (7:3, v/v) (IPA/CH_3COOH) followed by CCH. One six-step sequential extraction was also tested, which entailed subjecting soil to three successive IPA/NH_4OH followed by DCM two-step extractions. Solvent-extracted soil was allowed to air-dry inside the cellulose thimbles for 2 to 4 d between extraction steps. The six-step extraction sequence was performed twice, once to assess the water repellency of the extracted soil, and once to measure the mass of material extracted at each step of the sequence. In the first run, subsamples (≈10 g) of air-dried extracted soil were taken from the thimbles after every extraction step. These subsamples were oven-dried in a forced-air oven at 105 °C for 24 h, cooled in a desiccator and assessed for soil water repellency. During the second run, precautions were taken not to disturb the soil mass during and between extraction steps. Extractable material obtained after each extraction step was determined gravimetrically, as described by McGill and Rowell (1980).

All sequential extraction steps were performed in triplicate with 175-200 mL solvent for 24 h at the refluxing rate of 10 cycles·h^{-1}. Polytetrafluoroethylene boiling chips (Teflon*, Fisher Scientific) were used for all Soxhlet extractions. This minimised extract losses due to irreversible sorption of dissolved organics onto the boiling chips.

RESULTS

Solvent classification

Throughout this paper, I refer to test solvents according to the classification scheme depicted in Table 4.2. Only the dielectric constant values were determined experimentally.

Relationship between surface tension and molarity of ethanol solution

The best fit ($\chi^2 = 0.10$, $r^2 = 0.99$) was obtained with the following logarithmic function:

$$y = 61.05 - 14.75 \ln (x + 0.5) \qquad (1)$$

where x = molarity of ethanol solution in *M*, and y = surface tension in mN·m^{-1} (Chapter 4). Surface tension values corresponding to MED values ranging from 0 to 6 *M* can thus be computed by using this equation. It must be stressed that these surface tension values represent the surface tension of ethanol solution before contact with soil. They may not represent the surface tension of droplets that were in contact with soil for up to 10 s. It is likely that the surface tension of droplets placed on the soil surface varied during MED assessment due, among other factors, to dissolution of surface-active soil constituents and to selective sorption of ethanol by the soil.

Soil water repellency following extraction with SDS and subsequent treatment with $CHCl_3$

All soil samples were completely wettable (MED = 0 *M*) following extraction with either solution concentration of SDS (Table 4.3). Subsequent treatment with $CHCl_3$ partially restored water repellency in nontreated and IPA/NH_4OH-extracted NW soil samples. The $CHCl_3$ treatment did not restore water repellency in the DCM-extracted soil samples, which all displayed water repellency before SDS extraction. It also did not generate water repellency in any of the CW soil samples. Data presented in Table 4.3 indicate that: (i) IPA/NH_4OH and SDS used alone or in sequence do not remove all water-repellent substances from NW soil, (ii) prior exposure to DCM increases the extractability of water-repellent substances in SDS, and (iii) IPA/NH_4OH or SDS used alone or in sequence remove the potential for solvent-induced water repellency in DEV-CW soil.

Soil water repellency following sequential Soxhlet extractions with selected amphiphilic and nonpolar solvents

Two-step extraction. All three NW soils were completely wettable, or nearly so, following a 24-h extraction with IPA/NH_4OH or IPA/CH_3COOH (MED = 0 *M*), but moderately to severely water-repellent following a subsequent 24-h extraction with DCM or CCH (Table 4.4). Only the NW soils displayed reversible water repellency. The three CW soils and the ELL-PW soil were readily wettable (MED = 0 *M*) after each extraction step. These results contrast with those observed following a single extraction with DCM or CCH, which imparts moderate to severe water repellency to ELL-CW and DEV-CW soils (Chapter 3). They suggest that IPA/NH_4OH- or IPA/CH_3COOH-extracted ELL-CW and DEV-CW soils no longer contain sufficient water-repellent substances to display DCM- or CCH-induced water repellency.

Six-step extraction. Water repellency in NW soils was virtually eliminated following each IPA/NH_4OH extraction step and partially restored following each DCM extraction step (Fig. 4.2). The severity of restored water repellency, however, diminished with each DCM extraction. Again, only the NW soil samples displayed reversible water repellency. The mass of extracted material diminished during the sequential extraction, but some was available for quantification after each successive, and presumably exhaustive, extraction step (Fig. 4.3). This suggests that extraction with alternating solvents increased the extractability of soil material over time. IPA/NH_4OH consistently removed more material from all seven soils than DCM did.

DISCUSSION

My observations on reversible water repellency can be summarised as follows:

1. Oil-contaminated NW soil is made wettable by extraction with amphiphilic solvent (IPA/NH_4OH, IPA/CH_3COOH and SDS),
2. Amphiphilic solvent-extracted NW soil regains some water repellency by exposure to nonpolar solvent (DCM, CCH and $CHCl_3$),
3. Oil-contaminated CW soil is made water-repellent by exposure to nonpolar solvent (DCM and CCH, from Chapter 3),
4. Oil-contaminated CW soil, if previously extracted with amphiphilic solvent, no longer gains water-repellent character by exposure to nonpolar solvent (DCM and CCH from Table 4.4),
5. Nonextracted and amphiphilic solvent-extracted pristine soil (i.e. ELL-PW and BRU-CW soil) does not acquire water repellency following exposure to nonpolar solvent,
6. Prior exposure of NW soil to DCM increases extractability of water-repellent substances in amphiphilic solvent (SDS and IPA/NH_4OH).

The synthesis of these observations point to three main findings. These are discussed below.

Amphiphilic solvents completely eliminate soil water repellency, but do not remove all water-repellent substances from NW soil

IPA/NH_4OH, IPA/CH_3COOH and 0.5 and 0.05 M SDS are all amphiphilic solvents and similarly effective at eliminating water repellency (Tables 4.3 and 4.4 and Fig. 4.3). NW soils made wettable by extraction with these amphiphilic solvents, however, partially regain water repellency by subsequent exposure to nonpolar, non-H-bonding solvents, such as DCM, CCH, or $CHCl_3$. Reversibility of water repellency in NW soil suggests that even apparently effective amphiphilic solvents do not remove all water-repellent substances from soil.

Removal of at least some water-repellent substances by amphiphilic solvent is confirmed by: (i) a net reduction in the water repellency of NW soil that can be restored by subsequent exposure to nonpolar solvents, (ii) removal of the potential of CW soil to acquire water repellency by exposure to nonpolar solvents, and (iii) ability of IPA/NH_4OH-extracted material obtained from CW and NW soils to impart water repellency to AW sand (data not shown).

Nonpolar solvents generate, partially restore, or fail to eliminate water repellency in oil-contaminated soil

Single extraction with the nonpolar solvents DCM and CCH leaves NW soil nonwettable (Chapter 3). Sequential extraction with IPA/NH_4OH or IPA/CH_3COOH followed by DCM or CCH leaves NW soil wettable following the amphiphilic solvent extraction step, but nonwettable following the nonpolar one (Table 4.4). The alternate IPA/NH_4OH-DCM extraction sequence performed three times successively also leaves NW soil nonwettable following each DCM extraction step (Fig. 4.2).

One exception to that rule was noted with NW soil that is extracted with DCM followed by SDS, and then exposed to nonpolar, non-H-bonding $CHCl_3$ (Table 4.3). From concurring data presented in Fig. 4.2 and 4.3, I infer that prior exposure to DCM similarly increases the extractability of water-repellent substances in the two amphiphilic solvents IPA/NH_4OH and SDS. By doing so, it allows amphiphilic solvent to remove more water-repellent substances from oil-contaminated soils and thereby reduce their potential for solvent-induced water repellency.

Oil-contaminated soils display reversible water repellency, whereas pristine soils do not

I previously reported that single extraction with DCM and CCH generates water repellency in ELL-CW and DEV-CW soils, but fails to do so in BRU-CW and ELL-PW soils and in an AW sand (Chapter 3). These earlier data confirmed that nonextracted ELL-CW and DEV-CW soils contain sufficient water-repellent substances to display moderate water repellency.

Data presented in Table 4.4 indicate that extraction with DCM or CCH *following* extraction with IPA/NH_4OH or IPA/CH_3COOH no longer generates water repellency in ELL-CW and DEV-CW soils. These data confirm that amphiphilic solvent extraction reduces the content of water-repellent substances of both oil-contaminated CW and NW soils. Substances extracted from DEV-NW soil using IPA/NH_4OH were characterised in Chapter 3. These were identified as consisting predominantly of long-chain and polycyclic aliphatic organic compounds of petroleum origin.

Soils reported on here that have the potential to display reversible water repellency appear to have in common prior exposure to crude oil. I have observed reversible water repellency in all three NW soils and two of the three CW soils. The only CW soil that did not display reversible water repellency is the one that may never have been exposed to crude oil contamination (i.e. BRU-CW soil). The ELL-PW soil tested also could not be made water-repellent by exposure to nonpolar solvent. The ELL-PW and BRU-CW soils likely contain only native soil organic matter, whereas the ELL-CW, DEV-CW and three NW soils contain petroleum residues in addition to native organic matter (Chapter 3).

The above considerations all support the hypothesis that petroleum residues or related partial degradation products are the principal source of water-repellent agents in the studied soils.

An important question raised by my observations is why substances that resist extraction with amphiphilic solvents do not impart water repellency to NW soils unless they are first exposed to nonpolar solvent. I discuss this question in terms of two competing hypotheses.

Solvent retention by soil vs. flexible interfacial conformation of water-repellent substances: two competing sets of hypotheses to explain reversible water repellency

There are only two plausible hypotheses for the removal of water repellency in NW soil and of solvent-inducible water repellency in amphiphilic solvent-extracted CW soil. The same two hypotheses apply as well to the generation of water repellency in nonextracted CW soil and to its partial restoration in amphiphilic solvent-extracted NW soil observed following exposure to nonpolar, non-H-bonding solvents. These are: (i) solvent retention by soil alters its wettability depending on the exposed functionality of sorbed solvent molecules, or (ii) partial solvation modifies the interfacial conformation of water-repellent substances, which in turn changes the affinity of soil for water. Chemical oxidation is not included here as an alternative hypothesis because it was deemed not a tenable hypothesis for all solvents tested (e.g. DCM and SDS). I found no evidence of a consistent mechanism by which air- or oven-drying alone could have eliminated soil water repellency following extraction in amphiphilic solvents.

Hudson *et al.* (1994) proposed that retention of nonpolar solvent molecules may explain why extraction with hexane increased the water repellency of wettable and nonwettable sandy soil samples taken from golf greens. My first alternative hypothesis basically proposes the same explanation. When considering this hypothesis to explain why exposure to DCM or CCH generates water repellency in nontreated CW soil and partially restores it in amphiphilic solvent-extracted NW soil, however, I find that I have more evidence against it than supporting it. This evidence can be summarised as follows: (i) in my work, exposure to nonpolar solvent restores or imparts water repellency to oil-contaminated CW and NW soil, but does not impart water repellency to pristine BRU-CW and ELL-PW soils or AW sand; (ii) nonpolar solvent molecules freshly sorbed by solid surfaces should readily volatilise during prolonged air- and oven-drying periods preceding the assessment of soil water repellency; and (iii) IPA and DCM solvent peaks were never detected in the gas chromatograms of solvent-extracted CW and NW soil samples that were subjected to thermal desorption-GC/EI/MS and -GC/CI/MS.

The observation that amphiphilic solvent-extracted ELL-CW and DEV-CW soils no longer acquire water repellency by exposure to nonpolar solvent is additional evidence against the hypothesis that retention of nonpolar solvent molecules by soil is sufficient in itself to generate measurable soil water repellency. The results of the six-step sequential extraction further help to discriminate between the two competing hypotheses. The solvent retention hypothesis is not consistent with the concurrent loss of soil water repellency and of solvent-extractable material that was observed during the six-step sequential extraction. This leaves changes in interfacial conformation of water-repellent substances as the only tenable hypothesis.

Proposed mechanism

Water-repellent substances may be present exclusively in hydrocarbon-contaminated soil (e.g. petroleum asphaltenes), or they may be unusually concentrated in such soils (e.g. long-chain alkanes of mixed petroleum, plant and microbial origin). I account for these observations in a re-formulated flexible conformation hypothesis that places greater focus on the proposed mechanism. This hypothesis states that nonpolar moieties of water-repellent substances exposed at the interface between solid and fluid phases in soil are structurally flexible and susceptible to solvent-induced conformational changes. It is their conformation and surface coverage density that determines how readily water spreads on soil surfaces.

Data presented show that strong H-bonding solvents typically reduced soil water repellency, whereas weaker or non-H-bonding solvents typically increased it. They also indicate that none of the solvents used for a single exhaustive extraction removed all water-repellent substances from NW soil. The mechanism I invoke to explain these observations is analogous to that which was proposed by Ma'Shum and Farmer (1985) and Ma'Shum *et al.* (1988). I hypothesise that removal of non-H-bonding solvents from soil favours extension at the interface between soil particle surfaces and interstitial pore fluids of the loose alkyl chains of nonextracted water-repellent substances. In contrast, removal of H-bonding organic solvent from soil should not favour their extension and should therefore leave more polar or ionic functional groups exposed at the solid-fluid interface. It follows that soils with a higher relative surface density of structurally flexible alkyl chains (e.g. oil-contaminated soils) should be more susceptible to solvent-induced soil water repellency than soils with a lower relative surface density of such moieties (e.g. pristine soils). Zisman (1964) demonstrated that the nature of surface-exposed chemical groups and their packing density is what determines wettability. The mechanism I propose is consistent with my experimental observations and with the findings of Zisman (1964).

Evidence in support of structural flexibility in complex organic macromolecules

My observation that exposure to various solvents can affect bulk soil physical properties, such as soil wettability, has had its parallel in the coal chemistry literature for at least a decade. A considerable amount of work has been done on the solvent swelling of coals, which has given rise to similar hypotheses of solvent-induced conformational flexibility in these macromolecular networks (Brenner 1984; Larsen and Mohammadi 1990; Glass and Stevenson 1996; Glass and Wenger 1998). The fewer reports on the solvent swelling behaviour of peats and soil organic matter have generally yielded similar support to the hypothesis of conformational flexibility (Chen and Schnitzer 1989; Lyon and Rhodes 1993; Lyon 1995). Many solvents with differing functionalities have some affinity for at least parts of "insoluble" organic macromolecules. These interactions can compete with intermolecular forces, such as H bonding forces, which are largely responsible for the structure of macromolecular networks, such as coal, peat and soil organic matter.

The coal chemistry literature contains reports that exposure to organic solvents can induce structural rearrangements in coal macromolecular networks, which are retained following solvent removal. Pyridine-extracted coals, for example, swell more and faster than "raw" or nonextracted coals upon exposure to pyridine or various non-H-bonding solvents (e.g. benzene, tetralin and toluene) (Larsen *et al.* 1985; Milligan *et al.* 1997). They also do not return to their original shape on removal of solvent and solvent-soluble components, but remain smaller when measured in the direction of the bedding plane and larger normal to it (Brenner 1984; Cody *et al.* 1988). The fact that pyridine-extracted coal swells more in pyridine than "raw" coal indicates that interactions occur between pyridine and pyridine-insoluble components of coal. It would appear that pyridine competes with intermolecular forces responsible for the structure of coal. Reports of solvent-induced swelling support the hypothesis that solvents can induce conformational changes in solvent-insoluble organic structures.

According to Larsen *et al.* (1985), swelling is not completely reversible in pyridine-extracted coal samples because not all "broken" coal-coal H bonds re-form on pyridine removal and because some solvent molecules become trapped in pores of the coal network during its collapse. Larsen and Mohammadi (1990) later suggested that removal of pyridine from swollen coals might be leaving parts of coal macromolecules free to rearrange and adopt a new lower-energy conformation. The flexible conformation hypothesis I propose is analogous to that invoked by Larsen and Mohammadi (1990). I propose that nonpolar moieties stretch in evaporating nonpolar, non-H-bonding solvent and coil in evaporating polar, H-bonding solvents in a free energy-minimising response to changing competing intermolecular forces.

CONCLUSION

I presented evidence that exposure to H-bonding, amphiphilic and non-H-bonding solvents eliminates and restores soil water repellency only in soils that were once exposed to oil contamination. From this, I infer that causative agents of soil water repellency occur at high surface density only in my soils that were previously contaminated by petroleum hydrocarbons.

The evidence presented, in combination with that published in the literature, leads me to conclude that the fractional coverage and conformation of surface-exposed alkyl chains determines the severity of measurable soil water repellency. On one hand, I demonstrated that the amphiphilic extractants SDS, IPA/NH_4OH, and IPA/CH_3COOH are equally effective at eliminating soil water repellency. On the other, I showed that exposure to the nonpolar, non-H-bonding solvents CCH, DCM, and $CHCl_3$ generates water repellency in wettable oil-contaminated (i.e. CW) soil, and partially restores it in amphiphilic solvent-extracted soil. From these observations, I propose that causative agents of soil water repellency are amphiphilic molecules that interact strongly with soil through their polar or ionic functional groups. Solvent-induced, reversible water repellency is a macroscale manifestation of solvent-induced changes in the conformation of their surface-exposed alkyl chains.

Table 4.1. Physicochemical properties of the three CW and NW soils (0-15 cm)

	ELL		BRU		DEV	
Property	CW[x]	NW[x]	CW	NW	CW	NW
Sand $(g\cdot kg^{-1})$	290	300	860	860	380	400
Silt $(g\cdot kg^{-1})$	350	370	20	20	320	350
Clay $(g\cdot kg^{-1})$	360	330	120	120	300	250
CEC (cmol $(+)\cdot kg^{-1}$)	42	34	3	3	43	28
Water at -33 kPa $(g\cdot kg^{-1})$	360	360	50	40	340	250
Total C $(g\cdot kg^{-1})$	61	68	2	5	39	41
Mineral N $(mg\cdot kg^{-1})$	101	83	5	12	9	119
pH (in 0.01 *M* $CaCl_2$, 2:1)	5.3	5.4	5.5	5.4	7.3	5.8
Residual oil $(g\cdot kg^{-1})$[z]	1.0	9.8	<0.1	2.3	1.5	6.5

[x] CW = control wettable; NW = nonwettable
[y] Adapted from Tables 2.2 and 2.3
[z] Adapted from Table 3.4

Table 4.2. Solvent classification scheme

Solvents	Polarity (ε_r)[z]	Amphiphilic character	H-bonding capacity
Water	75.2	No	Strong
0.05 *M* SDS[x]	75.2	Yes	Strong
0.5 *M* SDS	74.9	Yes	Strong
IPA/15.7 *M* NH_4OH	24.2	Yes	Strong
IPA/5.2 *M* CH_3COOH	23.2	Yes	Strong
Ethanol	16.5	Yes	Strong
*Iso*propanol	13.4	Yes	Strong
Dichloromethane	8.9	No	Weak
Chloroform	4.8	No	Weak
Cyclohexane	2.0	No	Weak

[z] Measured at 20 °C at the average frequency of 915 MHz. System set with the dielectric constant (relative permittivity) value of water as its upper limit.
[y] Adapted from Barton (1989)
[x] Sodium dodecyl sulphate

Table 4.3. Molarity of ethanol droplet (MED) index of soils after extraction with sodium dodecyl sulphate (SDS) and after SDS extraction followed by treatment in chloroform ($CHCl_3$). The $CHCl_3$ treatment entailed immersing soil in excess $CHCl_3$ and vortexing the slurry until complete $CHCl_3$ evaporation

Soil	Prior to SDS extraction	After SDS extraction		After SDS extraction and $CHCl_3$ treatment	
		0.05 *M*	0.5 *M*	0.05 *M*	0.5 *M*
Nontreated					
BRU-CW	0.0 ±0.0[z]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
BRU-NW	3.5 ±0.1	0.0 ±0.0	0.0 ±0.0	3.3 ±0.1	3.4 ±0.0
DEV-CW	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
DEV-NW	4.2 ±0.0	0.0 ±0.0	0.0 ±0.0	4.1 ±0.1	2.9 ±0.2
IPA/NH_4OH-extracted					
BRU-CW	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
BRU-NW	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	1.3 ±0.1	1.3 ±0.3
DEV-CW	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.1 ±0.1	0.0 ±0.0
DEV-NW	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.9 ±0.2	0.0 ±0.2
DCM-extracted					
BRU-CW	0.0 ±0.0[y]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
BRU-NW	3.3 ±0.1[y]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
DEV-CW	2.1 ±0.1[y]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
DEV-NW	3.6 ±0.1[y]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0

[z] Standard deviation

[y] Data from Table 3.3

Table 4.4. Molarity of ethanol droplet (MED) index of soils during two-step extraction with IPA/NH_4OH (1st) followed by DCM (2nd) and IPA/CH_3COOH (1st) followed by CCH (2nd)

		IPA/NH_4OH^z-DCM^y		IPA/CH_3COOH^x-CCH^w	
Soil	Before	After 1st	After 2nd	After 1st	After 2nd
ELL-CW	1.2 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
ELL-NW	3.9 ±0.1	0.1 ±0.2	1.5 ±0.6	0.0 ±0.0	0.7 ±0.3
BRU-CW	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
BRU-NW	3.5 ±0.1	0.0 ±0.0	2.5 ±0.4	0.0 ±0.0	2.2 ±0.3
DEV-CW	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
DEV-NW	4.2 ±0.0	0.0 ±0.0	0.7 ±0.1	0.3 ±0.3	0.7 ±0.4
ELL-PW	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0

[z] *Iso*propanol/15.7 *M* NH_4OH (7:3, v/v)
[y] Dichloromethane
[x] *Iso*propanol/5.2 *M* CH_3COOH (7:3, v/v)

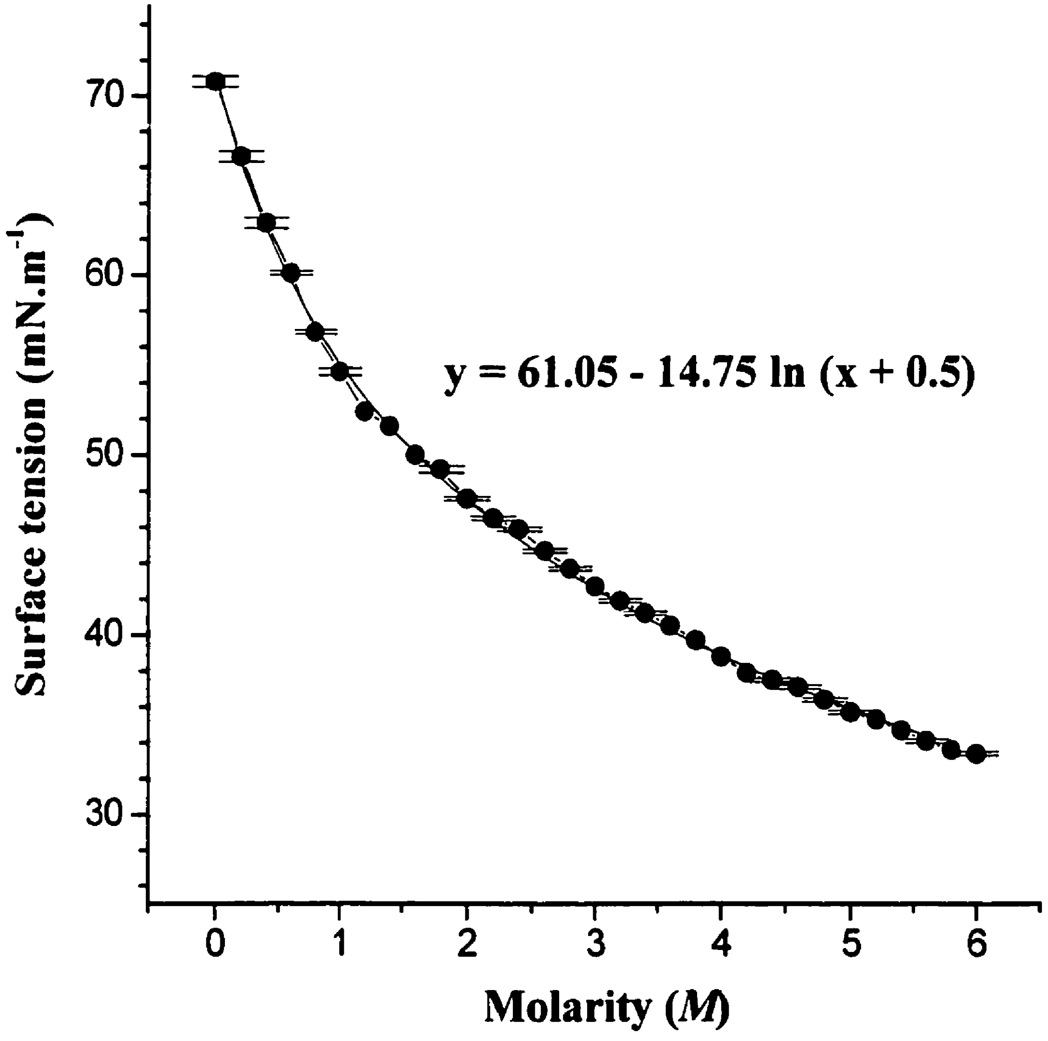

Figure 4.1. Surface tension versus molarity of aqueous ethanol solution. Error bars represent standard deviation of corrected surface tension measurements. x = molarity of ethanol solution (*M*) and y = corrected surface tension (mN·m^{-1}). The lowest molarity of ethanol solution (*M*) that is absorbed by soil within 10 s is the molarity of MED index of the soil.

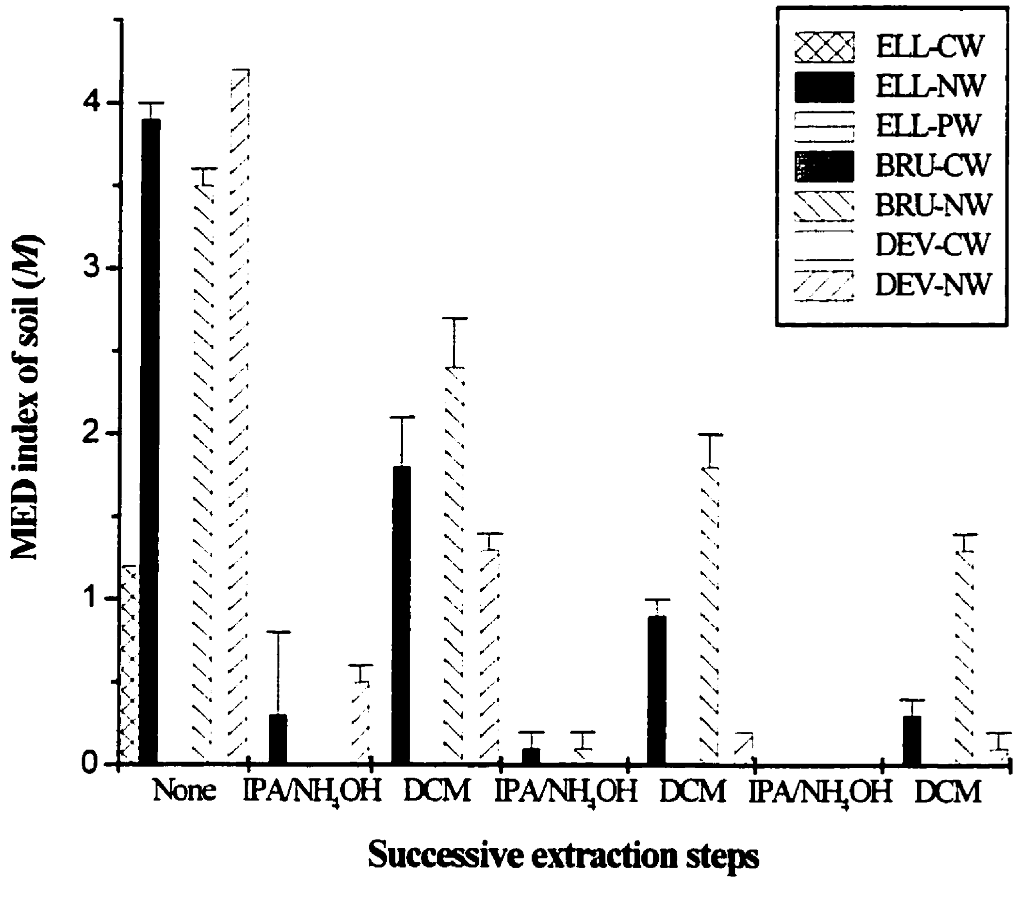

Figure 4.2. Changes in the MED index of soils during the six-step sequential extraction alternating between IPA/NH$_4$OH and DCM. "Missing" error bars are too small to be seen. The seven soils on the x axis follow from left to right the order depicted from top to bottom in the legend. None=before extraction.

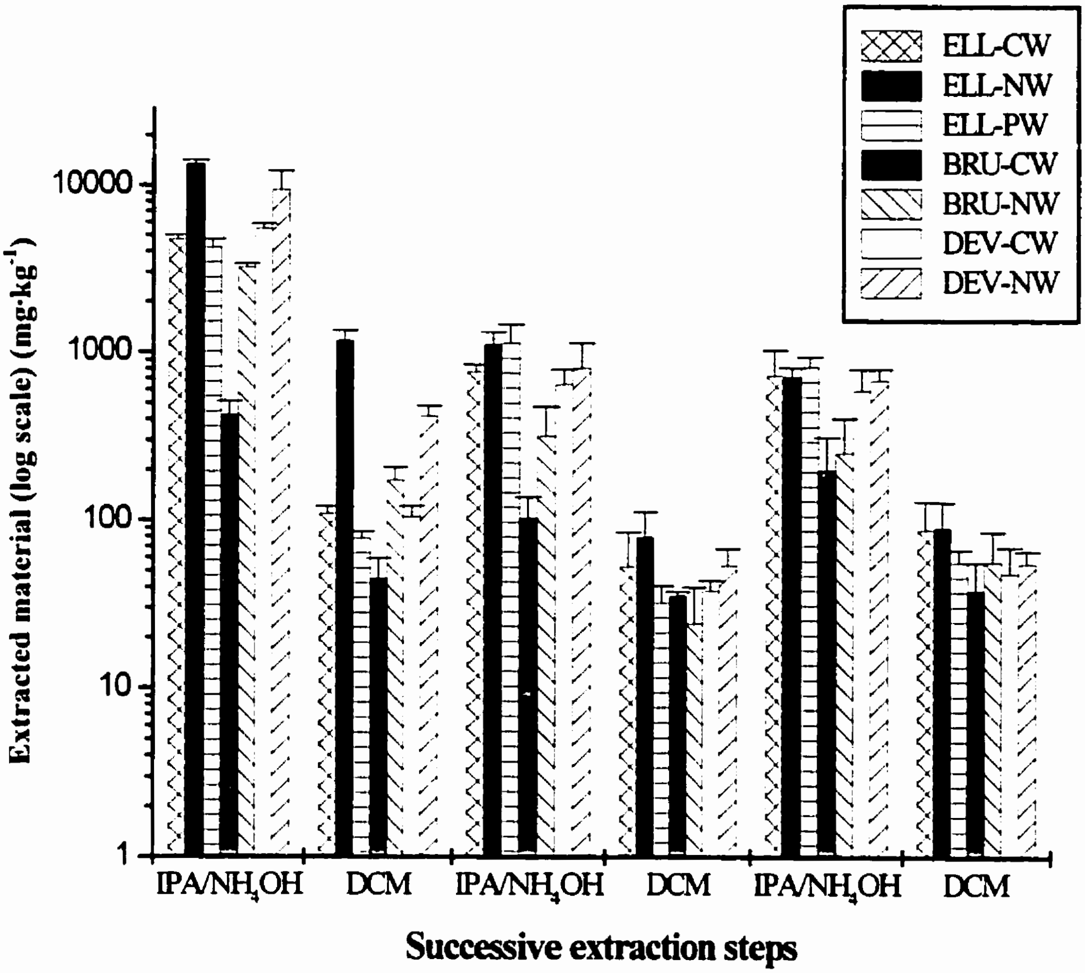

Figure 4.3. Mass of material extracted from soil during the six-step sequential extraction alternating between IPA/NH$_4$OH and DCM. The seven soils on the x axis follow from left to right the order depicted in the legend from top to bottom.

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CHAPTER 5

Processes leading to the development of soil water repellency following crude oil contamination[1]

INTRODUCTION

Soils that become severely water-repellent several years or decades following oil contamination have been described in previous chapters. Over 20 such soils (0.1 to > 2 ha) have been inventoried since 1990 in Alberta, Canada (G. Dinwoodie, Alberta Environmental Protection, pers. commun.). To my knowledge, reports on the development of soil water repellency following oil contamination have only come from Alberta. The phenomenon, however, is likely encountered in other parts of the world as well.

The principal objective of the work presented here was to test hypotheses regarding processes that may have led to the development of soil water repellency at old crude oil spill sites. These hypotheses were formulated on the basis of available circumstantial and experimental evidence suggesting that crude oil residues contribute to the development of soil water repellency (Chapter 3). I tested the alternative hypotheses that the development of soil water repellency following oil contamination is initiated by sorption of vapour- or liquid-phase petroleum residues onto soil particle surfaces. The vapour-phase sorption hypothesis states that volatile petroleum compounds entrapped in subsoil horizons migrated up the soil column and gradually accumulated on particle surfaces of upper soil horizons. This hypothesis was suggested by: (1) evidence that manifestation of soil water repellency typically succeeds oil contamination by several years or decades (Chapter 2), (2) detection of a strong petroleum odour in subsoil at water-repellent sites, and (3) anecdotal reports of gradually-expanding water-repellent areas, especially in cultivated fields. The liquid-state sorption hypothesis states that causative agents of soil water repellency sorbed to surface soil from the crude oil (liquid) phase during or soon following the contamination event, but, for some reason, delayed to impart water repellency to soil. This hypothesis was suggested by reports stating that: (1) soil water repellency resists nondestructive extraction procedures (Chapter 4), (2) crude oil did not penetrate below the layer of water-repellent soil at some spill sites (N. Sawatsky, Alberta Environmental Protection, pers. commun.), and (3) some of the least

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volatile constituents of crude oil impart water repellency to rock surfaces in petroleum reservoirs (Crocker and Marchin 1988; Powers and Tamblin 1995).

I proceeded to test the vapour-phase sorption hypothesis as follows. First, I characterised the distribution pattern of residual petroleum contamination in the soil profile underneath a patch of water-repellent soil ≈ 1500 m^2 in area. Then, I tested whether diffusion of vapour-phase petroleum compounds from oil-contaminated subsoil could impart water repellency to readily wettable pristine and oil-contaminated soils. I tested the liquid-phase sorption hypothesis as follows. I analysed water-repellent soils for the presence of crude oil constituents that would likely have sorbed to soil from the liquid phase during or soon following oil contamination. I assessed the role of petroporphyrins as causative agents of soil water repellency because these are suspected of causing water repellency in some petroleum reservoirs. The role of complex crude oil fatty acids was investigated because fatty acids can form water-insoluble soaps with multivalent soil cations (Elliott 1946) and impart water repellency to soil (Wander 1949).

The water-repellent character of the 20- to 50-yr old oil-contaminated soils under study is unusually resistant to physical, chemical and biological removal processes. This observation inspired me to test the hypothesis that causative agents of water repellency in these soils are associated with humin or soil minerals, rather than with humic or fulvic acids. I concluded the present work with an estimation of the potential role that water erosion in the lateral expansion of water-repellent soil patches at old crude oil spill sites. This was done by measuring the fractional mass of water-repellent soil that would be required to induce severe water repellency in adjacent soil. This work was suggested by anecdotal reports from landowners and environmental protection officers that patches of water-repellent soil at some old crude oil spill sites have been enlarging over the past several years.

MATERIALS AND METHODS

Study sites

The three sites that were selected for my studies are old crude oil spill sites located within a 100-km radius of the city of Edmonton, Alberta, Canada. The ELL site (53°25'N, 113°33'W) is a fallowed agricultural field that was contaminated by crude oil in 1973. The DEV site (53°20'N, 113°42'W) is a fallowed agricultural field that was contaminated in 1947. The BRU site (53°51'N, 112°58'W) is an industrial site that was contaminated in the mid-1970s. Soil from the ELL site consists of Malmo silty clay loam (Eluviated Black Chernozemic); from the BRU site of aeolian dune sand (Orthic Regosolic); and from the DEV site, of Ponoka loam (Eluviated Black Chernozemic). More detailed information about site characteristics can be found in Chapter 2.

The ELL, BRU and DEV sites each contains at least one patch of water-repellent soil 0.1 to several ha in area. Subsoil (≈20 to 100 cm depth, > 100 cm not checked) underneath water-repellent and adjacent wettable soil releases a distinct petroleum odour at the DEV site only.

Information about the volume and composition of crude oil that was spilled at the three study sites is not available. The only known common factor is that the product spilled was crude oil and not more refined petroleum products. Some of the oil pooling on the soil surface at the DEV site was burnt and some was pumped within the year following the spill (Kerr 1986). This was not sufficient, however, to prevent oil percolation deeper into the soil column. At the ELL site, the water-repellent soil was contaminated once with crude oil at the rate of 11% (w/w) and left untreated for the subsequent five years (Toogood 1977). During the following 15 years, it was tilled, fertilised and seeded. Management was interrupted after 15 years because water repellency had become apparent and original site productivity had not been restored (J. Thurston, University of Alberta, pers. commun.). At the Bruderheim (BRU) site, oil contamination may have occurred on several occasions. It is not known whether anything was done to accelerate soil remediation after the last known oil contamination event (D. Trenholm, Overall Reclamation Services Ltd., pers. commun.). Intrinsic or enhanced soil remediation failed to eliminate water repellency at the three study sites.

Soil sampling and sample preparation

Nonwettable and adjacent control wettable soil

Samples of control wettable (CW) and nonwettable (NW) soil (0-15 cm) from the three selected sites were collected and processed as described in Chapter 2. Readily wettable soil to be used as CW soil was sampled within a 25 m-perimeter outside the boundaries of the NW soil at each site. CW soil was taken as that which supported some plant growth and which, at field moisture content, absorbed water droplets placed on its surface in 10 s or less. DEV-CW soil was sampled from underneath a growing wheat crop, whereas ELL-CW and BRU-CW soils were sampled in areas that were only sparsely covered with weeds. Field-moist ELL-CW soil was readily wettable at the time of sampling, but slightly water-repellent following indoor air-drying. It was nevertheless kept as the ELL-CW soil. Slight water repellency in air-dried ELL-CW soil may have been acquired as a result of contamination by adjacent ELL-NW soil.

It is known that ELL-CW soil was contaminated with crude oil at the same time as was ELL-NW soil. In contrast, the dimension of the oil-contaminated area at the DEV and BRU sites is less precisely known. According to anecdotal reports, however, the sampled DEV-CW soil was also contaminated by crude oil in 1947, but the sampled BRU-CW soil is probably pristine. The contaminated area at the

BRU site seems to be confined to a relatively large, flat-bottomed depression in the landscape. BRU-NW soil was obtained from within the depression, whereas BRU-CW soil was obtained 25 m away from the edge of the depression.

Air-dried soil was sieved to pass a 1-mm sieve and thoroughly mixed to produce uniform composite samples of CW and NW soil for each site. These samples were stored in sealed glass jars in the dark at 4 °C prior to analysis (i.e. up to one year). Selected chemical and physical properties of the three NW and corresponding CW soils, as reported in Chapter 2, are listed in Table 5.1.

Pristine wettable soil used for comparison

Pristine wettable (PW) soil (Ap horizon) was obtained from agricultural fields that have not been exposed to crude oil contamination. The ELL-PW soil belongs to the same Malmo soil series as the ELL-CW and ELL-NW soils. The Therien soil (THE-PW) was obtained from LSD NW 14-61-9-W4 (54°17'N, 111°15'W) and Millet soil (MIL-PW) from LSD NE 9-47-25-W4 (53°03'N, 113°35'W). The THE-PW soil is classified as a Dark Grey Luvisol and the MIL-PW soil Black Chernozemic soil. Air-dried PW soil was sieved to pass a 1-mm sieve and stored at ≈21 °C before use (i.e. up to one year). Some chemical and physical properties of the PW soils used are reported in Table 5.1 (J.R. Robertson, University of Alberta, pers. commun.).

Assessment of soil water repellency

Soil water repellency was assessed using the Molarity of Ethanol Droplet (MED) test (King 1981). Soil was always air-dried to constant mass, oven-dried at 105 °C for 24 h, and then cooled to room temperature before MED assessment. Balls of soil that had cemented together following MED testing on air-dried soil were always removed before MED testing was performed on oven-dried soil. A total of 51 solution concentrations were prepared to include 0 and 6 *M* and all of the 0.2-*M* increments in between. Fresh aqueous ethanol solutions were prepared every three months and stored at 4 °C between periods of use. The solutions were always allowed to equilibrate overnight at ≈21 °C before use. The test was performed by placing droplets (2-3 mm diameter) of increasing ethanol solution concentration on the levelled soil surface. MED indices were recorded as the molarity of the droplets of lowest ethanol solution concentration to penetrate completely into soil within 10 s or less.

The surface tension of the 51 ethanol solution concentrations can be estimated using the following logarithmic function:

$$y = 61.05 - 14.75 \ln (x + 0.5) \qquad (1)$$

where x = molarity of ethanol solution *or* MED index in *M*, and y = surface tension in $mN \cdot m^{-1}$ (Fig. 4.1).

Processes leading to the development of soil water repellency

A. Sorption of petroleum compounds from the vapour phase

Residual oil in the profile underneath DEV-NW soil

A 54 m × 24 m area at the centre of a larger patch of water-repellent soil at the DEV site was selected for this work. The rectangular section was divided using a grid pattern that produced 27 cells 48 m^2 (6 m × 8 m) in area. Soil cores (3 cm wide × 100 cm deep) were taken at each grid line intersection, except those at the four corners of the 54 m × 24 m area. Sampling was performed using a hydraulic core sampler. Each 100-cm core was sliced while still inside the sampler. Soil from the following six depth sections was scooped into labelled moisture tin cans (9 cm wide × 4 cm high): 0-10, 20-30, 30-40, 50-60, 70-80, 90-100 cm. Lids were hermetically sealed onto the cans with 3M Tartan tape. The sealed cans were stored at 4 °C until further analysis (up to two years).

The total 216 (36 cores × 6 depths) soil samples were analysed for residual oil contamination and soil moisture content. Residual oil contamination was determined as the concentration of DCM-extractable organics remaining in the soil. Soil moisture content was determined gravimetrically by oven-drying field-moist (stored) soil at 105 °C for 24 h.

The concentration of DCM-extractable organics was determined on moist soil to minimise loss of volatile petroleum residues. The detailed procedure used was as follows: two subsamples of the same moist soil (≈25 g, oven-dried basis) were taken and weighed while still cold. One was immediately oven-dried to determine soil moisture content and the other prepared for determination of residual oil content. The moist subsample to be extracted was placed in a mortar and thoroughly mixed with an approximately equal volume of anhydrous $MgSO_4$. A stainless steel fork was used to break clumps and homogenise the mixture. The soil was placed in a cellulose thimble and Soxhlet-extracted for 24 h at the rate of 10 cycles h^{-1} using glass-distilled DCM. The DCM extracts were concentrated on a rotary evaporator, transferred into preweighed aluminum dishes, and allowed to dry to constant weight in a fume hood. The concentration of DCM-extractable organics was determined gravimetrically, as described in McGill and Rowell (1980). Only single determinations of DCM-extractable organics and moisture content were made.

Generation of water repellency by sorption of vapour-phase petroleum compounds

Petroleum-contaminated subsoil was used as the source of vapour-phase petroleum compounds in this study. The soil used was taken from the 0-90 cm depth section of the sampled 54 m × 24 m area of the DEV site. Concentrations of DCM-extractable organics in these subsoil samples ranged from 22 to 31 $g \cdot kg^{-1}$ (110 to 140 $g \cdot kg^{-1}$ water plus volatile organic compounds or VOCs).

Approximately 30 g (oven-dry basis) of field-moist contaminated subsoil was poured at the bottom of glass jars (≈90 mL). Twenty-gram samples (oven-dried basis) of air-dried readily wettable soil from pristine and oil-contaminated areas were then loosely wrapped into three-layered nylon bags and placed one per jar on top of the contaminated subsoil. The jars were sealed tightly and placed in dark storage at ≈21 °C for 60 d. The wettable soil treatment was triplicated, but the same source of contaminated subsoil was used for each triplicated wettable soil treatment. During the 60-d exposure period, the jars were gently shaken at 7-d intervals to improve gas diffusion.

I measured the water repellency of the bagged wettable soil after 30 and 60 d. Each jar was opened only long enough to remove the bag of wettable soil. The bag of wettable soil remained out of the jar only for as long as it took to untie the bag, take a ≈10-g subsample, tie the bag again and return it to the jar. Water repellency was assessed on the air-dried subsamples, and again after they were oven-dried (24 h, 105 °C). The DEV subsoil samples used as source of petroleum vapours in this experiment all had an MED index > 5 before and after the 60-d exposure period, as measured in the oven-dried state (data not shown).

B. Sorption of petroleum compounds from the liquid phase

Petroleum asphaltenes as causative agents

Petroleum asphaltenes are operationally defined as the *n*-alkane (C_5 to C_7)-insoluble fraction of crude oil mixtures. When crude oil is mixed with porous reservoir rock or soil, asphaltenes are defined as the fraction that is soluble in aromatic solvents, such as alkylbenzenes, tetralins or naphthalenes, but that precipitates in large excesses of low-boiling liquid *n*-alkane (C_5 to C_7) (40:1, *n*-alkane:extract, v/v) (Calemma *et al.* 1995; Yan *et al.* 1997).

Soil was Soxhlet-extracted for 72 h using toluene (6 $cycles \cdot h^{-1}$) to remove petroleum asphaltenes (Buckley and Liu 1998). The extracts were concentrated by rotary evaporation and filtered through a 0.22-µm cellulose acetate filter (AcetatePlus* Supported Cellulose Membrane, Micron Separations, Inc.) to remove as much fine clay particles as possible. The concentrated extracts were brought to 50-

mL volume using fresh toluene (HPLC grade). Ten-millilitre aliquots were air-dried 1 mL at a time into 1.5 mL polyethylene vials for use in instrumental neutron activation analysis (INAA). The other 40 mL was air-dried in preweighed aluminum dishes to determine the gravimetric content of toluene-extractable organics in soil. The extracted soil was allowed to air-dry before it was oven-dried and assessed for soil water repellency. All extractions and analyses were performed in triplicate.

I analysed for the presence of petroleum asphaltenes in soil by analysing for V of petroporphyrin origin in toluene extracts obtained from soil. INAA was performed by Dr. M.J.M. Duke at the SLOWPOKE nuclear reactor facility of The University of Alberta. The principle of the analysis is that elements (isotopes) irradiated with neutrons emit gamma-rays during their decay. These gamma rays can be radioassayed and the ratio of decay-corrected count rates used to determine the masses of the elements in the samples and standards (Helmke 1996).

Metallic salts of fatty acids as causative agents

Exhaustive Soxhlet extraction was used to extract metallic salts of fatty acids from soil. It was performed using HPLC-grade ethanol, which contained 95% (v/v) denatured ethanol 3A and 5% (v/v) IPA (Sigma-Aldrich). Soxhlet refluxing was set at the rate of 6 cycles·h^{-1} and maintained for 48 h. Approximately 25 g of soil (oven-dry basis) was extracted with 200 mL solvent.

Metal salts of fatty acids were also extracted using a mixture of a 1:1 (v/v) denatured ethanol and 0.1 *M* HCl in one instance, and 1:1 (v/v) denatured ethanol and 0.1 *M* NaOH under N_2 in the other. The composition of the denatured ethanol was 85:15 (v/v) ethanol:methanol. Approximately 20 g of oven-dried soil was suspended in 100-mL extraction mixture and shaken in a gyratory shaker at 280 rotations·min^{-1} for 24 h at ≈21 °C. The next day, the residue was separated by centrifugation and decantation. Centrifugation was performed at 8 800 × *g* for 20 min for every rinse. In the case of the ethanol:acid mixture, two extraction protocols were followed: (i) a one-time 24-h extraction with no rinse, and (ii) a one-time 24-h extraction with 75 × 50-mL rinses with fresh ethanol:acid mixture. In the case of the ethanol:alkali mixture, extraction was performed under N_2 to minimise risk of organic matter oxidation. A single extraction protocol was tested: a one-time 24-h extraction followed by three rinses with 0.01 *M* $CaCl_2$ and three rinses in deionised water. The rinses in 0.01 *M* $CaCl_2$ and water were necessary to re-aggregate the soil and prevent the precipitation of water-soluble sodium salts on the surface of the drying soil.

All Soxhlet extracts and supernatant solutions were discarded without analysis. The extracted soil samples were allowed to air-dry to constant weight at ≈21 °C. A ceramic mortar and pestle was used to break crusts that had formed during drying and homogenise the soil before MED assessment. Water repellency was assessed on both air-dried and oven-dried (105 °C, 24 h) extracted soil samples. Water repellency was again assessed after soil had been saturated with chloroform ($CHCl_3$), stirred to dryness, and gently homogenised again using a mortar and pestle. Treatment with $CHCl_3$ was applied because earlier work indicated that it can restore water repellency in extracted soil (Chapter 4). Restoration of water repellency by treatment with $CHCl_3$ indicates that potential to display water repellency has been conserved by the soil. All extractions and MED assessments were performed in triplicate.

C. Stabilisation of causative agents by association with the humin or mineral soil fractions

Humic and fulvic acids were extracted from soil as follows: ≈20 g soil (oven-dry basis) was weighed into a 200-mL propylene flask and 100 mL of 0.1 *M* NaOH was added to it. Air was displaced by N_2 before the flasks were stoppered. The soil-NaOH suspensions were shaken at ≈21 °C for 24 h on a gyratory shaker at 280 rotations·min^{-1}. The next day, the insoluble (mineral+humin) residue was separated by centrifugation at 13 800 × *g* for 30 min and subjected to either of the following rinsing protocols: (i) three 100-mL rinses with fresh 0.01 *M* $CaCl_2$ followed by three rinses with fresh deionised water, and (ii) 40 × 100-mL rinses with fresh 0.1 *M* NaOH under N_2 followed by three 100-mL rinses with fresh 0.01 *M* $CaCl_2$ and three rinses with fresh deionised water. Centrifugation speed had to be increased from 13 800 to 23 000 × *g* toward the end of the 40 rinses protocol because soil was becoming increasingly dispersed. Supernatant solutions were all decanted and discarded without analysis.

The extracted soil samples were allowed to air-dry to constant weight at ≈21 °C. Crusts that had formed during drying were gently broken using a mortar and pestle before MED testing. Soil water repellency was assessed both after air-drying and after oven-drying at 105 °C for 24 h. It was again assessed after soil had been saturated with $CHCl_3$, stirred to dryness, and gently homogenised using a mortar and pestle. All extractions and MED assessments were performed in triplicate.

D. Lateral spreading by mechanical dispersal of water-repellent soil

Fixed mass fractions of air-dried nonwettable and adjacent wettable soil from the three study sites were mixed together to simulate the outcome of mechanical soil dispersal. A total of 11 mass fractions of nonwettable soil were tested: 0, 0.1, 0.2, ..., 1.0. The soil mixtures were prepared in triplicate, oven-dried at 105 °C for 24 h, and assessed for soil water repellency using the MED test.

Potential water erosion rates at the three study sites were estimated using a modified Universal Soil Loss Equation. The purpose of the exercise was to estimate the rate at which spreading of severe water repellency may occur in all directions at each site due to water erosion alone. Values for the different factors were estimated following the guidelines provided in Tajek *et al.* (1985).

RESULTS

Processes leading to the development of soil water repellency

A. Sorption of petroleum compounds from the vapour phase

Residual oil in the profile underneath DEV-NW soil

I found DCM-extractable organics in concentrations ranging from <1 to 60 g·kg^{-1} throughout the sampled 54 m × 24 m × 1 m section of DEV site. The average DCM-extractable and soil moisture content for each depth section are presented in Fig. 5.1. Depth sections obtained below 30 cm released a strong petroleum odour and presented characteristic symptoms of low redox conditions; i.e. greyish blue colour. Soil from the 20-30 cm depth section sometimes had a hard consistence and needed to be broken down into smaller pieces with a hammer before it could be ground using a mortar and pestle.

The average concentration of DCM-extractables did not vary much with depth. The average concentration of water and VOCs, however, was significantly less in the 0-10 cm depth section than in other depth sections (Fig. 5.1). These values were obtained by averaging measured concentrations at each of the 36 sampling points. The error bars represent the standard error of those means.

Generation of water repellency by sorption of vapour-phase petroleum compounds

MED indices measured on air-dried soil had a high variance (large standard error of the mean) (Fig. 5.2a). Only the two soils that were previously exposed to oil contamination (DEV-CW and ELL-CW) acquired significant water repellency after 30 and 60 d of exposure to contaminated subsoil. The pristine (PW) soils, including BRU-CW, displayed more severe water repellency after 60 d than after 30 d of exposure, but variability was also greater after 60 d. Oven-drying reduced both the variability and the severity of induced water repellency symptoms in soil (Fig. 5.2b). Again, only the two soils that were previously exposed to oil contamination (DEV-CW and ELL-CW) acquired significant water repellency after 30 and 60 d of exposure to contaminated subsoil. BRU-CW soil was made readily wettable by oven-drying, and ELL-PW and MIL-PW soil nearly so. Water repellency was less after 60 than after 30 d in the case of the ELL-CW soil.

B. Sorption of petroleum compounds from the liquid phase

Petroleum asphaltenes as causative agents

Extraction with toluene did not eliminate water repellency in the three NW soils or in the ELL-CW soil, and it generated water repellency in DEV-CW soil (Table 5.2). Concentrations of V were higher in the toluene extracts obtained from the NW soils. This suggests that toluene extraction removed more petroleum asphaltenes from these soils than it did from the oil-contaminated CW soils. The toluene-soluble V found in ELL-PW soil may be clay-associated V that passed through the 0.22-µm filter. This V concentration may be taken as an estimate of the maximum mineral-associated V contamination that is to be expected in any of the analysed soil extracts. This is because the ELL-PW soil was never exposed to crude oil contamination and because soil from the ELL site contains a larger clay-size particle fraction than soil from the other two sites.

Metallic salts of organic acids as causative agents

Based on the results of MED measurements made on oven-dried soil, extraction with ethanol, ethanol:0.1 *M* HCl (1:1, v/v) or ethanol: 0.1 *M* NaOH (1:1, v/v) did not completely eliminate water repellency in ELL-NW and DEV-NW soils (Table 5.3). Based on the results of MED measurements made on $CHCl_3$-treated soil, extraction with ethanol, ethanol:0.1 *M* HCl (1:1, v/v) or ethanol: 0.1 *M* NaOH (1:1, v/v) did not remove the potential to display water repellency in any of the oil-contaminated soils; that is, the ELL-CW, ELL-NW, BRU-NW, DEV-CW and DEV-NW soils (Table 5.3).

C. Stabilisation by association with humin and mineral soil fractions

On the basis of the results of MED measurements made on oven-dried soil, removal from soil of humic and fulvic acids with 0.1 *M* NaOH did not completely eliminate water repellency in any of the NW soils (Table 5.4). However, it reduced soil water repellency considerably in ELL-NW, BRU-NW and DEV-NW soil and completely eliminated it in ELL-CW soil. On the basis of the results of MED measurements made on $CHCl_3$-treated soil, removal from soil of humic and fulvic acids with 0.1 *M* NaOH also did not completely eliminate the potential to display water repellency in any of the NW soils (Table 5.4). Only the more exhaustive NaOH extraction completely eliminated the potential to display water repellency in the oil-contaminated ELL-CW and DEV-CW soils. A single NaOH extraction partially reduced actual (i.e. oven-dried) and potential (i.e. $CHCl_3$-treated) water repellency in ELL-NW, BRU-NW and DEV-NW soils to a similar extent as did the more exhaustive NaOH extraction.

D. Lateral expansion due to mechanical dispersal

A 0.1 mass fraction of nonwettable soil in adjacent soil was sufficient to cause a sharp increase in water repellency in the DEV-CW and ELL-CW soils, but not in the BRU-CW soil (Fig. 5.3). It took as little as a 0.2 mass fraction of nonwettable soil to spread severe water repellency, defined by King (1981) as MED > 2.2, in adjacent soil at the relatively fine-textured ELL and DEV sites. In the coarser-textured soil of the BRU site, water repellency increased more gradually with increasing mass fraction of nonwettable soil. At this site, severe water repellency was not displayed until a 0.5 mass fraction of BRU-NW soil was surpassed.

According to my estimates of water erosion potential, severe soil water repellency may spread laterally at the rate of 0.0078 $m^2 \cdot yr^{-1}$ for each m^2 of original water-repellent area present at the ELL site (15 cm deep), 0.0014 $m^2 \cdot yr^{-1}$ at the BRU site, and 0.024 $m^2 \cdot yr^{-1}$ at the DEV site (Table 5.5). Using these estimates, I calculated the number of years it would take for circular 1, 0.5 and 0.1 ha patches of water-repellent soil (15 cm deep) to spread severe water repellency to a 3-m wide strip (15 cm deep) of adjacent soil at the ELL, BRU and DEV sites. For a circular 0.5 ha original water-repellent area, the calculation gave ≈17 yr at the ELL site, ≈81 yr at the BRU site and ≈6 yr at the DEV site (Table 5.6).

DISCUSSION

Processes leading to the development of soil water repellency

A. Sorption of petroleum compounds from the vapour phase

I hypothesised that subsoil-entrapped volatile petroleum compounds migrate upward over time and sorb onto the drier, organic matter-coated surfaces of upper soil horizons. Sorption imparts water repellency to surface soil and leads to lateral expansion of patches of water-repellent soil. Three conditions are needed for this mechanism to contribute to soil water repellency. First, there must exist a source of petroleum hydrocarbons below the surface. Second, the source must contain volatile hydrocarbons that can migrate to the surface. Third, volatile hydrocarbon compounds must sorb to surface soil and render it water-repellent. I tested these conditions using contaminated subsoil from the DEV site and wettable surface soil from five sites. I did not, however, measure the diffusivity of volatile compounds in the soil profile, as would have been necessary to determine the rate at which upward diffusion occurs. My results confirm the presence of residual oil in the top 1-m profile of DEV-NW soil patches. Concentrations of volatile petroleum compounds were not recorded separately, but concentrations of DCM-extractable organics presented in Fig. 5.1 were obtained so as to account for as much semivolatile petroleum compounds as possible.

The results presented in Fig. 5.2a and 5.2b indicate that soil water repellency can be generated by sorption of vapour-phase petroleum compounds emanating from subsoil. All three conditions stated above appear to have been met. Prior exposure to oil contamination seems to have predisposed ELL-CW and DEV-CW soils to acquire more severe water repellency from exposure to vapour-phase petroleum compounds. The four pristine soils acquired only slight water repellency in comparison. It is possible that petroleum residues remaining on the surface of wettable oil-contaminated soil increased the sorption capacity of these soils for volatile petroleum hydrocarbons. This seems a likely explanation considering that the ELL-PW and ELL-CW soils should not vary substantially in native physicochemical properties (Table 5.1). Concomitant diffusion of water vapour from the petroleum-contaminated subsoil during the 60-d exposure period must have reduced the sorption capacity of both contaminated and PW soils for vapour-phase petroleum compounds (Chiou and Shoup 1985). This could not be avoided as removal of moisture from contaminated subsoil samples would have resulted in substantial undesirable loss of volatile petroleum compounds.

Soil water repellency generated during the 60-d exposure to petroleum-contaminated subsoil was not as resistant to thermal extraction as is naturally-occurring soil water repellency (Chapter 2). This discrepancy, however, does not constitute sufficient evidence to refute the hypothesis that soil water repellency can be generated by sorption of vapour-phase petroleum compounds. Sorbate-soil contact times of 60 d *versus* decades may not be comparable because sorbate resistance to thermal desorption typically increases with increasing contact time. In addition, sorption of water vapour molecules by soil may have temporarily prevented the formation of stronger intermolecular associations between vapour-phase petroleum compounds and soil mineral surfaces (Ong and Lion 1991; Pennell *et al.* 1992).

B. Sorption of petroleum compounds from the liquid phase

The causative agents of soil water repellency may be compounds that sorbed to soil from the liquid crude oil phase during or soon following the time of oil contamination. These compounds would have to have resisted natural biotic and abiotic weathering processes for several years or decades following oil contamination, as well as gained increased resistance to removal by nondestructive extraction processes. This is needed to explain why exhaustive extraction of NW soil with solvents used to dissolve crude oil does not eliminate soil water repellency (Chapter 3). Mechanisms to explain the delayed appearance of water repellency that is initiated by sorption of liquid-phase petroleum compounds are discussed in a later section.

Causative agents of water repellency that may have sorbed to soil from the liquid crude oil phase include interfacially-active compounds of the asphaltene and resin fractions and high-molecular-weight nonpolar compounds of the saturate and aromatic fractions. I chose to investigate only the role of petroleum asphaltene constituents because petroleum asphaltenes are operationally defined as a solubility class. This functional definition is of analytical benefit because it allows statements to be made about the complete *removal* of petroleum asphaltenes from soil and the impact this has on soil water repellency. In Chapter 3, I demonstrated that solvents typically used to extract saturate and aromatic hydrocarbons from soil fail to eliminate soil water repellency completely and irreversibly.

Petroleum asphaltenes commonly occur in crude oils, oil shales, and bituminous sands, but are usually absent in light refined petroleum products, such as gasoline, kerosene and diesel fuel (Xu *et al.* 1994). Petroporphyrins are constituents of crude oil asphaltene fractions that can be used as markers because they are uniquely enriched in V (Filby 1994; Xu *et al.* 1994). Constituents of crude oil asphaltene fractions are suspected of causing water-wettability problems in petroleum reservoir rocks (Crocker and Marchin 1988; Hasiba and Jessen 1968). In soils, they are known to resist microbial degradation and sometimes persist long after the disappearance of other crude oil constituents (Song *et al.* 1990; Atlas 1981; McGill *et al.* 1981). According to Pollard *et al.* (1992), crude oil asphaltene fractions typically include extended polyaromatics, naphthenic acids, sulphides, polyhydric phenols, fatty acids and petroporphyrins.

I hypothesised that interfacially-active crude oil constituents can impart water repellency to soil by one of two mechanisms. One is by sorbing strongly to soil through their polar or ionic functional group and in turn leaving their nonpolar parts exposed at the solid-fluid interface. The other is by forming water-insoluble metallic soaps that precipitate on soil surfaces. Metallic soaps are formed when the acid H or its equivalent in a complex organic acid is replaced by a metal cation (Elliott 1946). Carboxyl groups are found in constituents of asphaltene crude oil fractions and polyvalent metal cations, such as Ca, Mg, Fe, and Al abound in most soils.

Extraction of petroleum asphaltenes

I used the presence of V of petroleum origin in toluene extracts obtained from NW and adjacent CW and PW soils to obtain confirmation that toluene extraction removes petroleum asphaltenes from oil-contaminated soils. The results of INAA indicate that toluene-soluble petroleum asphaltenes are absent from ELL-PW soil and that more are removed from oil-contaminated NW soils than from oil-contaminated CW soils. The MED results indicate that removal of petroleum asphaltenes from soil does not eliminate soil water repellency. This suggests that petroleum asphaltenes, operationally defined as toluene-soluble material, does not alone cause water repellency in the studied soils. The possibility remains that compounds causing soil water repellency are petroleum asphaltenes that have become irreversibly sorbed to soil due to polycondensation reactions or multiplication of noncovalent bonds with the soil. Such compounds would no longer be expected to dissolve or suspend readily in solvent. They would also lose their identity as petroleum asphaltenes.

Extraction of metallic soaps

I chose to extract metallic soaps from soil using ethanol and ethanol mixtures of dilute acid or base based on theoretical considerations. The H^+ or Na^+ ions might disrupt soap-soil cation bridges and release salts in solution. The H^+ ions of the acid mixture might cause hydrolysis of some of the salts and liberate protonated fatty acids. The Na^+ ions of the alkaline mixture might improve dispersion of soap molecules in solution, and its OH ions, scavenge metal cations to liberate ionised fatty acids in solution. Ethanol was mixed with the alkali and acidic extractants to provide a better phase than water for the dissolution or suspension of liberated metallic soaps, protonated fatty acids and deprotonated fatty acids. This alcohol was chosen because previous work indicated that extraction with strong H-bonding solvents (e.g. methanol, *n*-propanol and IPA) reduces soil water repellency to a greater extent than extraction with nonpolar, non-H-bonding solvents (e.g. DCM and CCH) (Chapter 3). Jacobson and Holmes (1916) also presented evidence that some metallic soaps are slightly more soluble in ethanol and methanol than they are in weaker H-bonding solvents (e.g. ether).

If as predicted metal salts of fatty acids were removed by any of the solvents tested, then metal salts of fatty acids are not the sole causative agents of soil water repellency in the studied soils. Water repellency was neither completely nor irreversibly eliminated following extraction with these solvents. The ethanol:0.1 *M* NaOH extraction was performed with one rinse only because the earlier ethanol:0.1 *M* HCl results indicated that multiplying the number of rinses does not cause substantial further decreases in soil water repellency. Wander (1949) successfully eliminated soil water repellency by extracting soil with ether followed by methanol. This author attributed removal of soil water repellency to removal of metallic soaps based on two observations: release of fat globules on acidification and heating of air-dried methanol extract, and strong calcium and magnesium tests of the water-soluble heat-oxidised residue of methanol extract. In this study, I did not attempt to confirm removal from soil of metallic cations, metallic soaps, protonated or deprotonated fatty acids. This is because metallic cations and fatty acids not associated with the formation of hydrophobic soaps would likely have also been extracted by ethanol:0.1 *M* NaOH solutions, ethanol:0.1 *M* HCl and ethanol alone (Hudson *et al.* 1994).

C. Stabilisation by association with the humin or mineral soil fractions

The causative agents of soil water repellency may have originally sorbed to soil from the vapour or liquid phase. Both mechanisms can impart water repellency to soil or soil minerals. This was shown with vapours in the present report and with nonvolatile crude oil constituents in reports by Crocker and

Marchin (1988), Powers *et al.* (1996) and Yan *et al.* (1997). I have observed, however, that freshly sorbed vapour-phase petroleum compounds impart water repellency to soil that is not as resistant to thermal extraction, at least in the short term, as is naturally-occurring soil water repellency. It is likely that freshly sorbed liquid-phase petroleum residues also impart water repellency to soil that is less resistant than is naturally-occurring soil water repellency. This is because organic compounds typically become increasingly recalcitrant the longer they reside in soil (Alexander 1995). Resistance to desorption is thought to build over time through free radical-initiated polycondensation reactions and multiplication of noncovalent intermolecular associations (e.g. H bonds, dipole interactions, cation bridges, ligand exchange, and protonation) in the organic phase and between the organic phase and mineral soil surfaces (Sposito 1984; Paul and Clark 1989; Larsen and Mohammadi 1990).

In this part of the study, I tested the hypothesis that water-repellent substances are bound to the humin or mineral soil fractions. This hypothesis was suggested by evidence that water repellency seems to be associated predominantly with the fraction of organic soil constituents that is not extractable in aqueous and organic solvents (Chapter 4). Because removal of fulvic and humic acids did not completely and irreversibly eliminate soil water repellency, I conclude that water-repellent substances are associated with humin or with soil minerals in the studied soils. Water-repellent substances may not require strong association with the soil to *impart* water repellency to soil. Strong association with humin or with soil minerals probably occurs naturally over time and imparts recalcitrance to induced water repellency symptoms.

D. Lateral expansion of water-repellent soil

Anecdotal reports from landowners and environmental protection officers indicate the lateral expansion of water-repellent areas. There is no experimental evidence to support or refute these claims because soil water repellency at old crude oil spill sites was little studied before the past few years. I nevertheless investigated potential mechanisms of lateral expansion of water-repellent soil based on data obtained at the three study sites. I postulated that lateral expansion of water-repellent soil occurs through mechanical dispersal of existing water-repellent soil or through creation of more water-repellent soil over time. I tested the mechanical dispersal hypothesis by measuring what mass fraction of water-repellent soil is required to spread severe water repellency to adjacent wettable soil. Severe water repellency was defined as a MED test result of ≥ 2.2 (King 1981). For the finer-textured ELL-CW and DEV-CW soils, a fractional mass of water-repellent soil of 0.2 was sufficient to impart severe water repellency to adjacent soil. Water repellency in these soils increased most steeply in the 0 to 0.2 fractional mass range. Water repellency increased in a less steep and more linear fashion with increasing mass fraction of nonwettable soil in the coarser-textured BRU-CW soil. In this soil, a 0.6 mass fraction of nonwettable soil was required to generate severe water repellency in adjacent soil. The estimates of water erosion potential at the three study sites suggest that it is quite possible that natural erosion processes cause measurable lateral expansion of water-repellent areas over time. I calculated that a circular 1 ha area of water-repellent soil (15 cm deep) may increase its radius by 3 m within 5 yr at the DEV site and 12 yr at the ELL site (Table 5.6).

Water-repellent soils containing reserves of petroleum compounds at shallow depth in their profile may also be at risk of expanding laterally due to creation of more water-repellent soil over time. I have shown that sorption of vapour-phase petroleum compounds can impart water repellency to soil within 60 d. The degree of induced water repellency was more severe in surface soil known to contain residues from oil contamination. The severity and persistence of vapour-induced water repellency would likely increase with increasing exposure time (e.g. decades). Creation of new water-repellent soil over time is not likely to be occurring through sorption of liquid-phase petroleum residues. This is because a high-rising water table would be required to transport residual oil remaining in subsoil to coat of the pore walls of the 0-15 cm top layer. Water table rises near the surface, however, would be expected to promote upward diffusion of subsoil-entrapped vapour-phase petroleum residues.

E. Manifestation of soil water repellency

The reason I propose for why several years or decades must pass before manifestation of soil water repellency differs for the two alternative hypotheses. If soil water repellency is generated by sorption of vapour-phase petroleum compounds, time is required for the manifestation of water repellency because enough volatile petroleum compounds must migrate through soil, sorb, and increase their fractional coverage on particle surfaces of upper soil horizons. According to this hypothesis, the development of soil water repellency requires that an indeterminate, but presumably large, amount of liquid-phase petroleum compounds have accumulated in shallow subsoil horizons. On the other hand, if sorption of petroleum compounds from the liquid phase is what initiates the development of soil water repellency, time may be required because the outer layer of sorbed petroleum compounds must undergo chemical or physical transformation over time (i.e. partial oxidation or dehydration accompanied by re-orientation). There is evidence that removal of water and VOCs over time can induce conformational changes in the outer layer of organic material that is left behind (Ma'Shum and Farmer 1985). Removal of water and VOCs is thought to promote the formation of stronger association of sorbed petroleum compounds with one another and with native organic and mineral soil constituents.

SUMMARY OF KEY OBSERVATIONS

1. PW and CW soils acquired slight water repellency following a 60-d exposure at ≈21 °C to vapour-phase petroleum compounds. More severe water repellency was generated in CW soils that were previously exposed to oil contamination.

2. Petroleum asphaltenes are present in oil-contaminated CW and NW soils, but their removal from soil by toluene extraction does not eliminate soil water repellency.

3. Removal of metallic soaps by extraction with ethanol, ethanol:0.1 *M* NaOH or ethanol:0.1 *M* HCl and removal of humic and fulvic acids by extraction in 0.1 *M* NaOH under N_2 do not completely and irreversibly eliminate soil water repellency.

4. Relatively little mixing is required to impart severe water repellency to adjacent soil at sites where the soil is fine-textured. Lateral expansion of patches of water-repellent soil may be caused by mechanical dispersal of existing water-repellent soil or by generation of new VOC-coated water-repellent soil.

CONCLUSION

Two alternative, but not mutually exclusive, scenarios are proposed to explain the development, spreading and persistence of soil water repellency at old crude oil spill sites:

1. Soil water repellency is generated by VOC sorption over many years. Appearance of soil water repellency is controlled by the degree of fractional coverage achieved by VOCs on the surface of particles of upper soil horizons. Lateral expansion occurs over time due to erosion and, possibly also, to generation of new VOC-coated water-repellent soil. Expansion caused by generation of new water-repellent soil stops when reserves of volatile petroleum compounds in subsoil horizons have been depleted. Sorbed petroleum vapours become increasingly resistant to biological, physical and chemical removal processes by becoming more strongly associated with humin or with soil minerals over time.

2. Soil water repellency is generated by sorption of nonvolatile petroleum compounds during or soon following the time of oil contamination. The condition is not manifested for another several years or decades because extensive evaporation of water and VOCs is required to induce the re-organisation of less volatile, sorbed petroleum compounds. Lateral expansion may occur through mechanical dispersal of existing water-repellent soil, or to generation of new VOC-coated water-repellent soil where sufficient liquid crude oil has persisted have persisted in shallow subsoil horizons. The recalcitrance of

water-repellent character is attributed to ageing; that is, to an increase in the number and strength of bonds formed between sorbed petroleum compounds, humin and mineral soil surfaces.

Soils that do not develop water repellency following oil contamination may have contained enough water at the time of contamination to prevent crude oil penetration into soil or strong association of petroleum compounds with the soil. Alternatively, they may have received only a low concentration of causative agents because only a small volume of oil was spilled or because the oil that was spilled contained only a small concentration of causative agents of soil water repellency. Bioremediation of causative agents may have been more effective where small volumes of oil were spilled and moisture, nutrients and oxygen did not become deficient soon following oil contamination. Soils that are left untreated following crude oil contamination seem to be at greater risk of developing water repellency over time (Chapter 2).

Table 5.1. Physicochemical characteristics of the studied soils (0-15 cm)

Soil	Sand ($g \cdot kg^{-1}$)	Clay ($g \cdot kg^{-1}$)	Texture[z]	pH	Org. C[y] ($g \cdot kg^{-1}$)	Min. N[x] ($mg \cdot kg^{-1}$)
ELL-CW[w]	290	360	CL	5.3	54.5	100.7
ELL-NW[w]	300	330	CL	5.4	63.2	82.6
BRU-CW[w]	860	120	LS	5.5	1.6	4.9
BRU-NW[w]	860	120	LS	5.4	4.8	12.3
DEV-CW[w]	380	300	L	7.3	37.4	8.6
DEV-NW[w]	400	250	L	5.8	37.9	118.8
ELL-PW	260	310	CL	5.1	63.5[v]	5700[u]
THE-PW	410	160	L	6.0	33.4[v]	3000[u]
MIL-PW	500	200	L-SCL	5.8	44.0[v]	3800[u]

[z] CL = clay loam, LS= loamy sand, L = loam, L-SCL =loam-silty clay loam
[y] Organic C
[x] Mineral N
[w] Adapted from Tables 2.1, 2.2 and 2.3
[v] Calculated from organic matter content assuming 50 g C per 100 g organic matter
[u] Total N values available only

Table 5.2. Extraction of petroleum asphaltenes

Soil	Toluene-extractables ($g \cdot kg^{-1}$ soil)	MED after extraction (*M*)	Vanadium[z] ($\mu g \cdot kg^{-1}$ soil)
ELL-CW	1.2 ± 0.1[y]	0.9 ± 0.3	6.4 ± 0.4
ELL-NW	11.3 ± 1.6	3.2 ± 0.2	136.0 ± 2.0
BRU-CW	0.0 ± 0.0	0.0 ± 0.0	0.7 ± 0.3
BRU-NW	2.5 ± 0.6	3.2 ± 0.2	38.2 ± 1.0
DEV-CW	1.2 ± 0.1	1.2 ± 0.0	2.0 ± 0.7
DEV-NW	6.9 ± 0.7	3.8 ± 0.0	11.7 ± 1.1
ELL-PW	0.4 ± 0.0	0.0 ± 0.0	1.1 ± 0.2

[z] Toluene-extractable V in soil
[y] Standard deviation

Table 5.3. Soil water repellency after extraction to remove metallic salts of fatty acids listed in order of decreasing extractant effectiveness

	ELL			BRU		DEV	
Extractant	CW	NW	PW	CW	NW	CW	NW
None	1.2 ±0.0[a]	3.9 ±0.1	0.0 ±0.0	0.0 ±0.0	3.5 ±0.1	0.0 ±0.0	4.2 ±0.0
Ethanol (95%)							
Air-dried	0.0 ±0.0	0.4 ±0.2	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.8 ±0.0
Oven-dried	0.0 ±0.0	0.5 ±0.2	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.8 ±0.3
CHCl$_3$-treated	0.0 ±0.0	2.9 ±0.2	0.0 ±0.0	0.0 ±0.0	3.4 ±0.3	0.0 ±0.0	1.8 ±0.3
Ethanol:0.1 *M* NaOH (1:1, v/v) (1×)							
Air-dried	0.0 ±0.0	1.2 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	2.7 ±0.1
Oven-dried	0.8 ±0.0	3.5 ±0.1	0.0 ±0.0	0.0 ±0.0	0.8 ±0.0	0.0 ±0.0	3.1 ±0.1
CHCl$_3$-treated	3.2 ±0.2	5.5 ±0.1	0.1 ±0.1	0.0 ±0.0	2.9 ±0.0	1.2 ±0.5	4.3 ±0.1
Ethanol: 0.1 *M* HCl (1:1, v/v) (75×)							
Air-dried	0.0 ±0.0	1.2 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	1.3 ±0.1
Oven-dried	0.2 ±0.0	4.0 ±0.0	0.0 ±0.0	0.0 ±0.0	1.9 ±0.3	0.0 ±0.0	3.5 ±0.1
CHCl$_3$-treated	1.0 ±0.0	4.9 ±0.1	0.0 ±0.0	0.0 ±0.0	3.1 ±0.1	0.7 ±0.1	4.7 ±0.3
Ethanol: 0.1 *M* HCl (1:1, v/v) (1×)							
Air-dried	0.0 ±0.0	1.5 ±0.1	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	2.3 ±0.2
Oven-dried	1.8 ±0.0	4.1 ±0.1	0.0 ±0.0	0.0 ±0.0	2.8 ±0.0	1.0 ±0.0	4.3 ±0.1
CHCl$_3$-treated	4.8 ±0.0	4.7 ±0.1	0.0 ±0.0	0.0 ±0.0	3.2 ±0.0	2.2 ±0.0	4.8 ±0.0

[a] Standard deviation

Table 5.4. Soil water repellency after extraction of humic and fulvic acids

	ELL			BRU		DEV	
Extractant	CW	NW	PW	CW	NW	CW	NW
None	1.2 ±0.0[z]	3.9 ±0.1	0.0 ±0.0	0.0 ±0.0	3.5 ±0.1	0.0 ±0.0	4.2 ±0.0
0.1 *M* NaOH (1×)							
Air-dried	0.0 ±0.0	1.1 ±0.1	0.0 ±0.0	0.0 ±0.0	0.3 ±0.1	0.0 ±0.0	1.9 ±0.2
Oven-dried	0.0 ±0.0	2.4 ±0.1	0.0 ±0.0	0.0 ±0.0	1.5 ±0.2	0.0 ±0.0	2.2 ±0.2
$CHCl_3$-treated	0.5 ±0.4	3.6 ±0.0	0.0 ±0.0	0.0 ±0.0	3.6 ±0.0	0.4 ±0.2	3.6 ±0.0
0.1 *M* NaOH (40×)							
Air-dried	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.6 ±0.2
Oven-dried	0.0 ±0.0	2.0 ±0.7	0.0 ±0.0	0.0 ±0.0	1.2 ±0.0	0.0 ±0.0	1.6 ±0.2
$CHCl_3$-treated	0.0 ±0.0	4.3 ±0.6	0.0 ±0.0	0.0 ±0.0	3.6 ±0.0	0.0 ±0.0	3.4 ±0.3

[z] Standard deviation

Table 5.5. Calculation of water erosion potential using a modified Universal Soil-Loss Equation

Soil	R[z]	K[z]	LS[z]	C[z]	Water erosion $(Mg \cdot ha^{-1}) \cdot yr^{-1}$	Spreading rate[y] $(m^2 \cdot yr^{-1}) \cdot m^{-2}$
ELL	600	0.013	0.4	1.0	3.1	0.0078
BRU	600	0.007	0.4	1.0	1.7	0.0014
DEV	600	0.026	0.6	1.0	9.4	0.024

[z] From Tajek *et al.* (1985)

[y] The denominator (in m^2) refers to the fixed value of the original area of water-repellent soil (15 cm deep). Calculated using a soil bulk density of 1.33, a soil volume per hectare of 1500 m^3, and a required mass fraction of 0.2 at the DEV and ELL sites and of 0.6 at the BRU site.

Table 5.6. Estimation of time required for erosion to spread severe water repellency to 3 m-wide strip of surrounding soil from circular areas of water-repellent soil at the three study sites

Site	Radius before (m)	Radius after (m)	Mass of invaded area[z] (Mg)	Mass of NW soil needed[y] (Mg)	Erosion rate ($Mg \cdot yr^{-1}$)	Time needed (yr)
ELL	56.42 (1 ha)	59.42 (1.11 ha)	217.80	43.56	3.10	14
	39.89 (0.5 ha)	42.89 (0.58 ha)	155.66	31.13	1.55	20
	17.84 (0.10 ha)	20.84 (0.14 ha)	72.73	14.55	0.31	47
BRU	56.42 (1 ha)	59.42 (1.11 ha)	217.80	130.68	1.70	77
	39.89 (0.5 ha)	42.89 (0.58 ha)	155.66	93.40	0.85	110
	17.84 (0.10 ha)	20.84 (0.14 ha)	72.73	43.64	0.17	260
DEV	56.42 (1 ha)	59.42 (1.11 ha)	217.80	43.56	9.40	5
	39.89 (0.5 ha)	42.89 (0.58 ha)	155.66	31.13	4.70	7
	17.84 (0.10 ha)	20.84 (0.14 ha)	72.73	14.55	0.94	16

[z] Calculated using a bulk density of 1.33 and a volume per hectare of 1500 m^3

[y] Calculated using a mass fraction of 0.2 at DEV and ELL and 0.6 at BRU

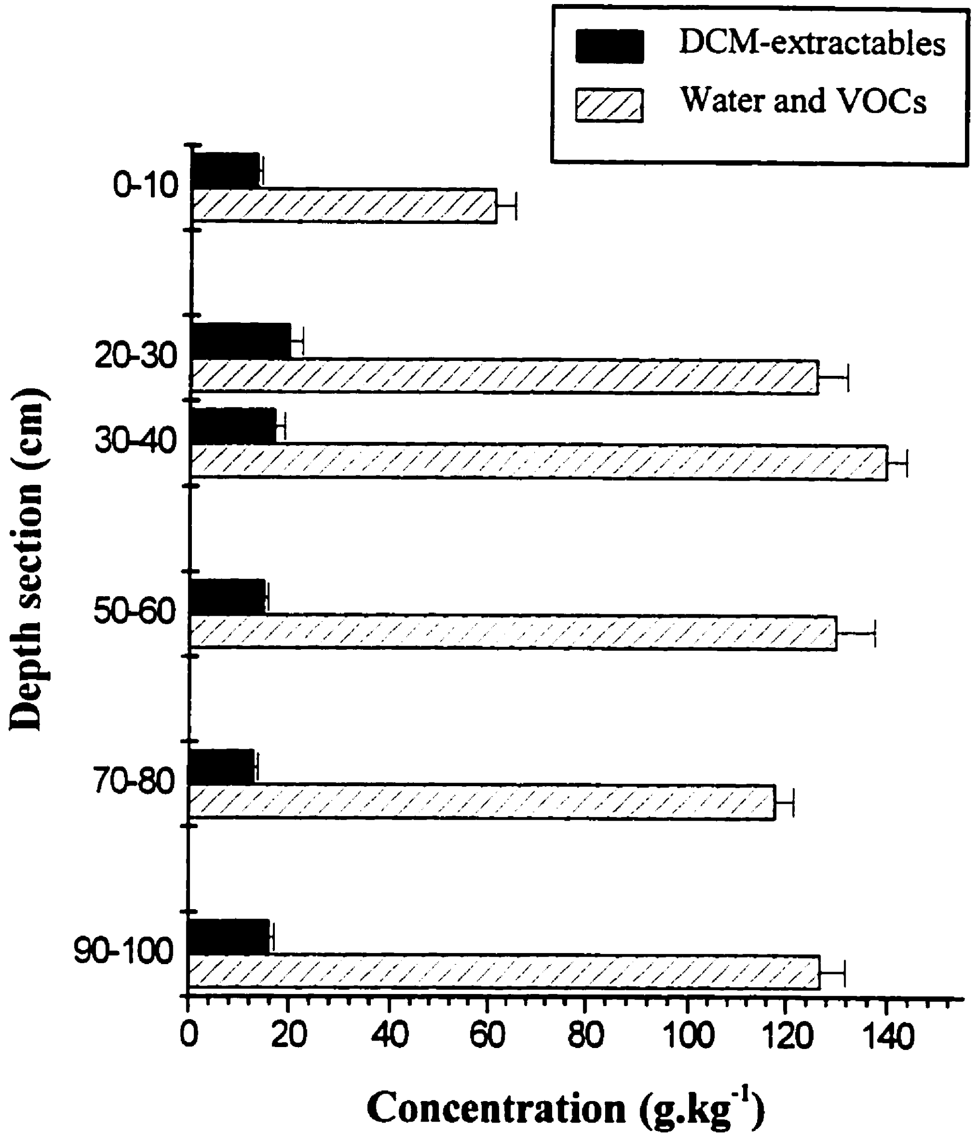

Figure 5.1. DCM-extractable and water and VOCs in Devon soil profile (0-100 cm). Values represent depth section averages for 36 sampling points located within a 54 m × 24 m area. The error bars represent the standard error of the mean.

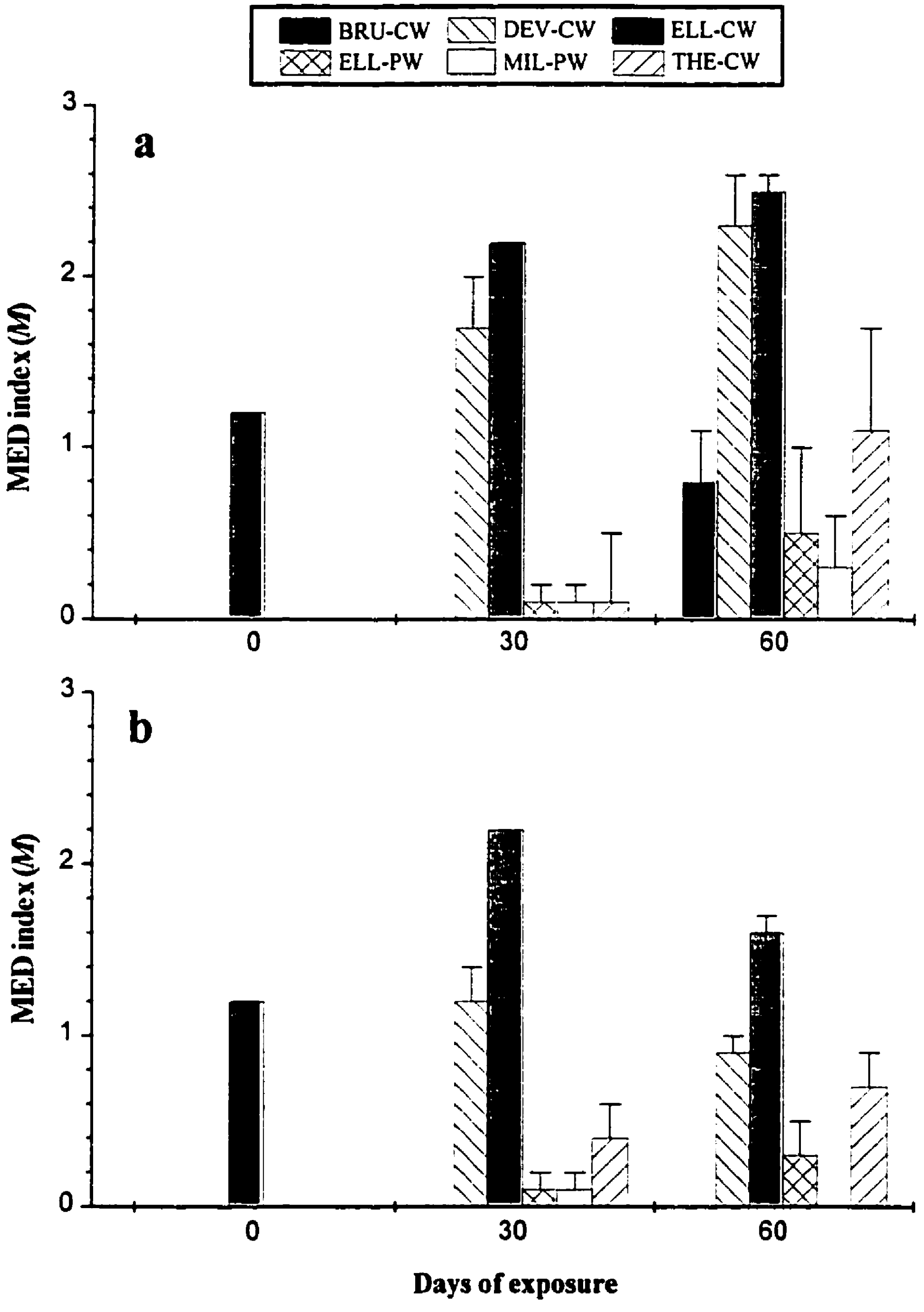

Figure 5.2. Soil water repellency generated in wettable pristine and oil-contaminated soil during exposure to petroleum-contaminated subsoil for 60 d. Contaminated subsoil is from the 90-100 cm depth section of the sampled 54 m × 24 m water-repellent area of the DEV site. The error bars represent the standard error of the mean. a = air-dried, b = oven-dried.

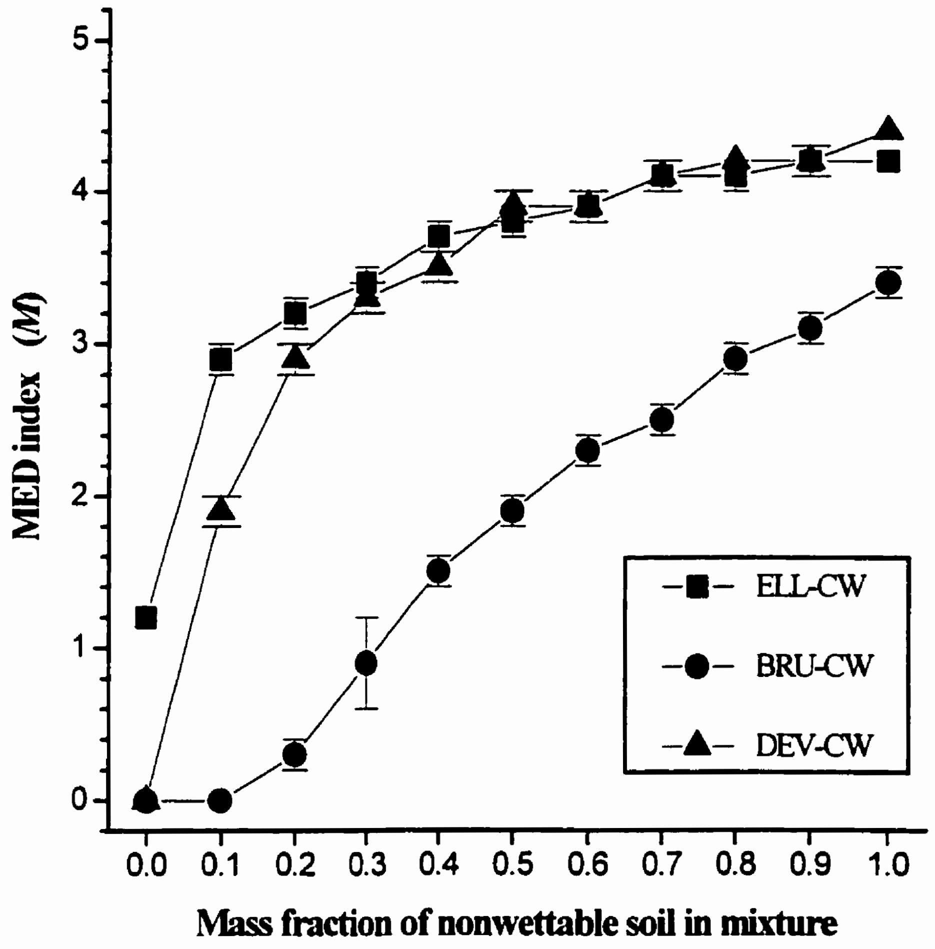

Figure 5.3. Soil water repellency resulting from increasing the mass fraction of ELL-NW, BRU-NW and DEV-NW soil in ELL-CW, BRU-CW and DEV-CW soil from 0 to 1. The error bars represent the standard error of the mean.

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CHAPTER 6

Synthesis

INTRODUCTION

Water-repellent soils have been encountered in diverse environments in many parts of the world. They include soils that display water repellency symptoms ranging from complete resistance to wetting to slightly reduced infiltration rates compared to readily wettable soils. My doctoral research focussed on soils that become severely water-repellent several years or decades following contamination by crude oil. These soils no longer look, feel or smell like they contain any oil, but they remain dry even under heavy rainfalls. The overall objective of my doctoral research was to identify the causative agents and the mechanism by which these agents impart water repellency to soil. To my knowledge, this was the first study focussing on the occurrence and cause of soil water repellency at old crude oil spill sites.

Three NW soils (0-15 cm that were contaminated by crude oil between 1947 and 1980 were selected for this research. Readily wettable soil surrounding NW soil patches was also sampled at the three sites to be used as corresponding CW soil. The research was divided into four phases: (1) characterisation of three NW and corresponding CW soils (Chapter 2), (2) isolation and characterisation of causative agents of soil water repellency (Chapter 3), (3) investigation into the cause of reversible soil water repellency (Chapter 4), (4) identification of processes leading to the development of soil water repellency at old crude oil spill sites (Chapter 5). The results of this work are summarised below.

SUMMARY

Chapter 2: Characterisation of water-repellent soil

Characterisation of three NW and corresponding CW soils was accomplished using routine soil characterisation procedures. The objective of this phase was to obtain background information about these poorly known soils. This information would assist in the development of testable hypotheses concerning the development and persistence of soil water repellency. Some striking differences were found between the NW and adjacent CW soils examined. A smaller dry aggregated MWD and a higher total C and mineral N content, in particular, characterised the NW soils. CEC, pH, and water-holding capacity were comparable in NW and corresponding CW soils. No evidence of high exchangeable Na^+ or high SAR was found in any of the NW and CW soils studied. Counts of viable and culturable CFU were lower in ELL-NW soil, but of the same order of magnitude as that found in ELL-CW soil. These results suggested that inability of native soil microorganisms to remediate water-repellent soil is not due to their absence in soil, but to impeded metabolism because of limited water availability. Complete elimination of soil water repellency was achieved by heating soil in a fan oven at 200 °C for 16-18 h. Prolonged heating for 14 d at 105 or 150 °C in the same fan oven failed to eliminate soil water repellency. The reported characterisation work indicated that the main difference between NW and adjacent CW soil lies in the quality and quantity of organic material they contain, and not in the properties of their inorganic constituents.

Chapter 3: Characterisation of causative agents of soil water repellency

Isolation of causative agents of soil water repellency was attempted using SFE and Soxhlet extraction with various polar, nonpolar and amphiphilic solvents. Solvents were selected to include ones that are commonly used to remove petroleum hydrocarbons and other lipidic material from soil. The four SFE protocols tested failed to eliminate soil water repellency. Soxhlet extraction with nonpolar, non-H bonding solvent was as ineffective as SFE at reducing soil water repellency. Elimination of soil water repellency was achieved by Soxhlet extraction with the amphiphilic solvent mixture IPA/NH_4OH. Ma'Shum et al. (1988) were the first to report that this mixture completely eliminates water repellency in water-repellent sands. Compounds extracted from DEV-NW soil using IPA/NH_4OH were applied to AW sand and characterised using thermal desorption-GC/MS in electron impact and positive chemical ionisation modes. They were identified as consisting mostly of homologous series of long-chain and polycyclic aliphatic organic compounds (C_{24} to C_{32}); namely, *n*-fatty acids, *n*-alkanes, and cycloalkanes, with no phenolic or polycyclic aromatic compounds and scarcely any polar compounds detected. Three- to 5-ring cycloalkanes (e.g. terpanes and steranes) predominated, followed by 1- to 2-ring cycloalkanes and long-chain *n*-alkanes. These findings led me to conclude that compounds removed from DEV-NW soil by IPA/NH_4OH are predominantly compounds of petroleum origin rather than of plant or microbial origin. On the condition that elimination of soil water repellency occurs through removal of causative agents, I concluded that causative agents of soil water repellency at old crude oil spill sites are compounds of petroleum origin.

Chapter 4: Reversibility of water-repellent character and its cause

In Chapter 4, I report on the reversibility of water repellency in three old petroleum-contaminated soils. This study was suggested by results from work presented in Chapter 3. The intriguing observation was that Soxhlet extraction with nonpolar, non-H-bonding solvent leaves oil-contaminated CW soil slightly water-repellent. Inspiration for this study also came from reports by McGhie and Posner (1980) and Ma'Shum and Farmer (1985) indicating that soil water repellency can be eliminated and in turn restored without addition of organic compounds to soil.

I reported in Chapter 3 that soil water repellency is eliminated by extraction with amphiphilic solvents and barely reduced by extraction with nonpolar solvents. In Chapter 4, I observed reversible soil water repellency following extraction with amphiphilic and nonpolar solvents used alone and in sequence. My results indicated that: (i) water repellency is completely eliminated following extraction with amphiphilic solvent, but partially restored following subsequent exposure to nonpolar, non-H-bonding solvent; (ii) extraction with nonpolar, non-H-bonding solvent generates water repellency in readily wettable CW soil, but does not in PW soil, and (iii) repeated sequential extractions alternating between amphiphilic and nonpolar, non-H-bonding solvent increase extractable material and reduce the magnitude of reversible soil water repellency with time.

I attribute reversible soil water repellency to solvent-induced changes in the conformation of causative agents of soil water repellency. Recent literature reports on the structural flexibility of "insoluble" organic macromolecules are discussed for supporting evidence. I propose that exposure to nonpolar, non-H-bonding solvents induces stretching of nonpolar moieties (i.e. alkyl chains), whereas exposure to polar, H-bonding solvents induces their coiling. These solvent-induced conformational changes are retained upon solvent removal. My results indicate that the wettability of oil-contaminated soils depends on both the interfacial conformation and the fractional coverage of their surface-exposed nonpolar moieties.

Chapter 5: Processes leading to the development of soil water repellency

In Chapter 5, I investigated mechanisms to explain how soil water repellency develops, spreads and persists at old crude oil spill sites. My results indicate that soil water repellency can be generated by soil sorption of vapour-phase petroleum compounds. Literature reports are cited that support the hypothesis that sorption of liquid-phase petroleum compounds can also impart water repellency to soil. The hypotheses that soil water repellency is solely caused by sorption of petroleum asphaltenes or formation of metal salts of fatty acids, however, are rejected on the basis that their removal from soil does not eliminate soil water repellency completely and irreversibly.

I estimated the potential role of water erosion as a mechanism of lateral expansion of water-repellent areas. My results indicate that expansion of water-repellent areas likely occurs predominantly through mechanical dispersal (i.e. erosion and cultivation). However, where sufficient reserves of petroleum compounds remain at shallow subsoil depths, the possibility remains that it also occurs through generation of new water-repellent soil over time.

Resistance of soil water repellency to exhaustive extraction with 0.1 *M* NaOH indicates that at least some causative agents are irreversibly bound to humin or to mineral surfaces. I infer from these data that permanent remediation of soil water repellency at old crude oil spill sites may require destruction of its causative agents. On the positive side, however, these data also suggest that prompt intervention to reduce the concentration and residence time of petroleum residues in soil should prevent the development or reduce the spread of soil water repellency.

ADVANCE IN KNOWLEDGE

Soil water repellency is not solely a function of the presence of causative agents in soil

The processes by which soil water repellency develops in some areas and not in others are largely unknown. This is because the fundamental cause of soil water repellency has not been clearly established. I mentioned in Chapter 1 that there are at least five technical or logical difficulties impeding efforts to identify the causative agents of soil water repellency. Not least of them is the fact that there are no decisive means of obtaining confirmation that causative agents of soil water repellency have been removed from soil. My research further confirmed that this investigative approach is inadequate because it assumes that the sole cause of soil water repellency is the *presence* of water-repellent substances in soil. Horne and McIntosh (1998) recently showed that compounds extracted from readily wettable and nonwettable soil using IPA/NH_4OH are equally effective at imparting water repellency to soil. I obtained similar results by applying ≈800 $mg \cdot kg^{-1}$ of IPA/NH_4OH extract obtained from CW and NW soils to AW sand (Appendix B). Such results demonstrate that some readily wettable soils contain sufficient water-repellent substances to display water repellency under certain conditions. They also indicate that ability to impart soil water repellency under controlled experimental conditions is not the same as ability to impart soil water repellency under natural field conditions. Finally, they confirm that presence of water-repellent substances in soil is a necessary, but not sufficient condition, to give rise to soil water repellency.

Soil water repellency is a function of both the packing density and chain conformation of amphiphilic organic molecules in the outermost layer of soil organic matter coatings

My research supports the following postulate: amphiphilic organic molecules interact with soil mostly through their polar or ionic functional groups. This leaves alkyl chain substituents dangling at the solid/fluid interface. The polar or ionic group interactions anchoring the amphiphilic molecules to soil are not readily disrupted by change in fluid composition (i.e. they resist complete solvation). Different fluids can still, however, partially solvate these molecules and affect the conformation of their weakly interacting, alkyl chain substituents. Chain conformation varies from coiled (to minimise exposed surface area) to stretched (to maximise exposed surface area) depending on fluid properties. The alkyl chains stretch in weakly hydrophilic fluid (e.g. nonpolar, non-H-bonding solvent or air) and coil in strongly hydrophilic fluid (e.g. water or polar organic, H-bonding solvent) (Fig. 6.1). Soil water repellency is a function of the conformation and number of chains that are exposed at the solid/fluid interface in soil. The stretched chain conformation at high packing density generates the most severe water repellency symptoms (Table 6.1).

Table 6.1. Variables controlling the severity of soil water repellency

	Packing density of amphiphilic molecules	
Chain conformation	High	Low
Coiled	moderately water-repellent	not water-repellent
Stretched	severely water-repellent	slightly water-repellent

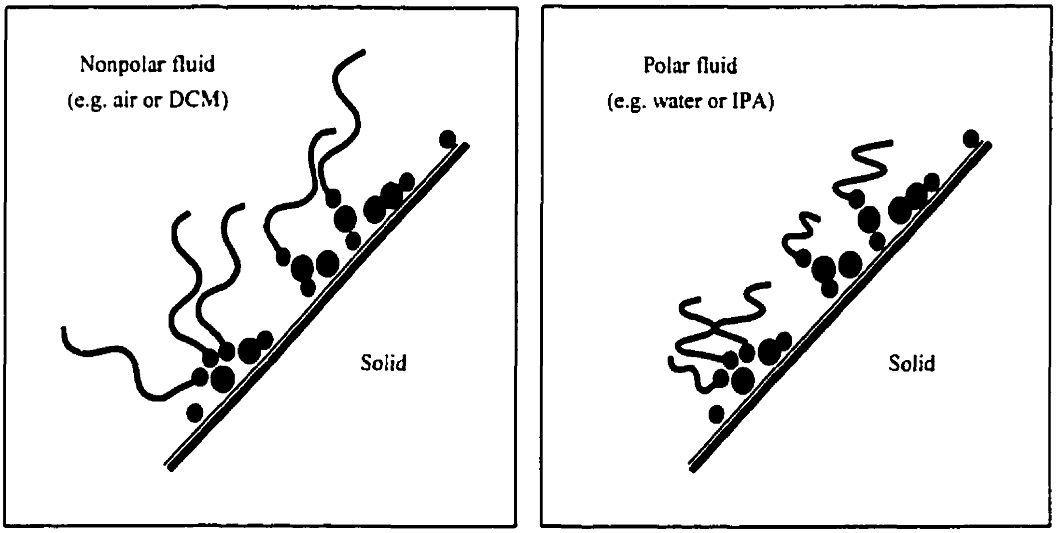

Figure 6.1. Solvent-induced conformational flexibility in surface-exposed alkyl chains. Depending on fluid properties, surface-exposed alkyl chains stretch or coil to minimise free energy.

Elimination of soil water repellency must not be taken as evidence that causative agents of soil water repellency have been removed from soil

My work indicates that complete elimination of soil water repellency cannot be taken as confirmation of removal of causative agents from soil. This is because elimination of soil water repellency that is achieved by solvent extraction can usually be reversed without addition of organic compounds to soil. Reversible soil water repellency has been repeatedly observed in this research (Chapter 4). Knowledge that soil water repellency is reversible under controlled laboratory conditions comes heavy with practical implications for those concerned with achieving its permanent remediation under field conditions. What can be rapidly simulated under controlled laboratory conditions may naturally occur at a slower rate under natural field conditions.

Causative agents should be suspected of remaining in soil when elimination of soil water repellency can be reversed without addition of organic compounds to soil. In Chapter 4, I presented evidence indicating that soil water repellency can be restored by exposing soil to solvents for which polar or ionic functional groups have little affinity. I proposed a mechanism to explain how soil water repellency can be generated and in turn eliminated without removal or addition of organic compounds from and to soil. The latter states that surface-exposed alkyl chain substituents in oil-contaminated soils can stretch and coil, and thereby modify their fractional coverage, in response to change in fluid composition.

The causative agents of soil water repellency in the studied soils are compounds of petroleum origin

In Chapter 3, I described how IPA/NH_4OH extraction eliminates water repellency in oil-contaminated soils. I also described the identity of compounds removed from DEV-NW soil using IPA/NH_4OH. These consisted predominantly of long-chain and polycyclic aliphatic hydrocarbons typical of weathering crude oil mixtures. In Chapter 4, I observed that extraction with IPA/NH_4OH eliminates the potential for solvent-induced water repellency in oil-contaminated CW soils (Chapter 4). This was inferred to indicate that petroleum residues extracted from oil-contaminated soils using IPA/NH_4OH include some causative agents of soil water repellency.

In Chapter 4, I observed that some causative agents also remain in NW soil following extraction with IPA/NH_4OH. This was inferred from the observation that water repellency can be restored in IPA/NH_4OH-extracted NW soils by exposure to nonpolar, non-H-bonding solvent. This observation indicated that compounds resisting extraction in IPA/NH_4OH also contribute to the expression of soil water repellency. I was unable to isolate, characterise or confirm the petroleum or natural origin of IPA/NH_4OH-insoluble causative agents of soil water repellency. However, two pieces of evidence suggest that the latter are probably of petroleum origin. First, there is the observation that, among the soils studied, only petroleum-contaminated ones displayed solvent-induced reversible water repellency. Second, there is the circumstantial evidence implicating petroleum residues rather than natural organic compounds as causative agents of soil water repellency. Since the early 1980s in Alberta, water-repellent soil patches (0.1 to >10 ha) have been discovered at over 20 old crude oil spill sites.

Additional items of new knowledge

- Water-repellent soils are disaggregated and enriched in organic C compared to adjacent normal soil (Chapter 2)
- Water-repellent soils do not present a salt toxicity or N deficiency problem (Chapter 2)
- Water-repellent soils contain a substantial community of viable, although apparently dormant, microorganisms (Chapter 2)
- Soil water repellency is completely and irreversibly eliminated by heating soil in a fan oven at 200 °C for 16-18 h. Exposure soil to 150 °C for 14 d does not eliminate soil water repellency (Chapter 2)
- Extraction of water-repellent soil using IPA/NH_4OH removes mostly long-chain and polycyclic aliphatic hydrocarbons of petroleum origin (Chapter 3)
- Repeated sequential extraction with alternate amphiphilic and nonpolar, non-H-bonding solvent gradually eliminates soil water repellency completely and irreversibly (Chapter 4)
- Soil water repellency is completely and irreversibly eliminated by Soxhlet extraction with DCM followed by room-temperature extraction in 0.05 *M* SDS (Chapter 4)
- The mathematical relationship between surface tension and molarity of ethanol in aqueous solution obeys the following logarithmic function: $y = 61.05 - 14.75 \ln (x + 0.5)$, where y is the surface tension of the liquid in $mN \cdot m^{-1}$ and x is the molarity of the aqueous ethanol solution in $moles \cdot L^{-1}$ (Chapter 4)
- Exhaustive extraction of soil with 0.1 *M* NaOH under N_2 or with the amphiphilic solvents IPA/NH_4OH, IPA/CH_3COOH, IPA/H_2O, and 0.5 *M* SDS reduces soil water repellency considerably, but not irreversibly (Chapters 4 and 5)
- Exposure to nonpolar, non-H-bonding solvent favours expression of water repellency in crude oil-contaminated soils (Chapters 3, 4, and 5)
- IPA/NH_4OH extracts obtained from CW and NW soils are equally effective at imparting water repellency to AW sand (Appendix B)
- Causative agents in 20- to 50-yr-old water-repellent soils are associated with humin or soil minerals, and not with humic or fulvic acids (Chapter 5)
- Petroleum asphaltenes, as defined operationally on the basis of solubility in toluene, are not the sole causative agents of soil water repellency (Chapter 5)
- Metallic salts of fatty acids, unless they are not removed from soil by ethanol, ethanol:acid, ethanol:alkali or alkali alone, are not the sole causative agents of soil water repellency (Chapter 5)

- Sorption of vapour-phase petroleum compounds can induce water repellency in PW and CW soils (Chapter 5)
- Some water-repellent sites contain residual volatile petroleum compounds at shallow subsoil depths (Chapter 5 and Appendix D)
- Water-repellent soil is prone to dispersal by mechanical cultivation and wind and water erosion (Chapter 5)

FUTURE RESEARCH

Most researchers agree that soil water repellency is caused by the presence of a coating of hydrophobic organic substances on soil particle surfaces (Wallis and Horne 1992). Efforts to identify these substances, however, have not yet yielded the expected definite answers. It does not help that most attempts to identify causative agents of soil water repellency have been made without concern for the mechanism by which causative agents impart water repellency to soil. This has resulted in a variety of proposed causative agents that induce water repellency when added to soil, but that also occur naturally in readily wettable soils.

Identification of the causative agents of soil water repellency may not be as crucial as identification of the mechanism by which hydrophobic organic substances impart water repellency to soil. It may even be a futile enterprise unless the goal is identification of a common chemical structure rather than common source for these substances in soil. For example, it would be of little practical or theoretical value to know that humic substances or petroleum compounds are the causative agents of soil water repellency. This is because such compounds also occur in soils that do not display water repellency. The fundamental question that should be addressed is not what compounds cause soil water repellency, but rather why water repellency is only displayed by certain soils. There is enough evidence to suggest that organic compounds having the potential to impart at least transient water repellency to soil occur naturally in readily wettable soils. My research indicates that the explanation for the peculiar character of water-repellent soil lies in the composition and conformational flexibility of the outermost layer of organic material coating soil particle surfaces. Exciting new knowledge may be derived from the characterisation of the three-dimensional organisation and dynamic behaviour of this outer organic layer. Future research may, for instance, reveal that permanent remediation of soil water repellency does not require removal of causative agents from soil.

My research suggests that the fractional coverage of alkyl chains on soil particle surfaces determines the degree of water repellency that is displayed by soil. This fractional coverage is determined by both the chain conformation and packing density of organic molecules possessing such chains. Direct physical evidence is needed to test the validity of model predictions, such as that the stretched chain conformation at high packing density should produce the most severe soil water repellency symptoms. In addition, research is needed to identify the scale at which the ratio of hydrophobic:hydrophilic surface area in soil most closely correlates with macroscale soil water repellency symptoms (Fig. 6.2).

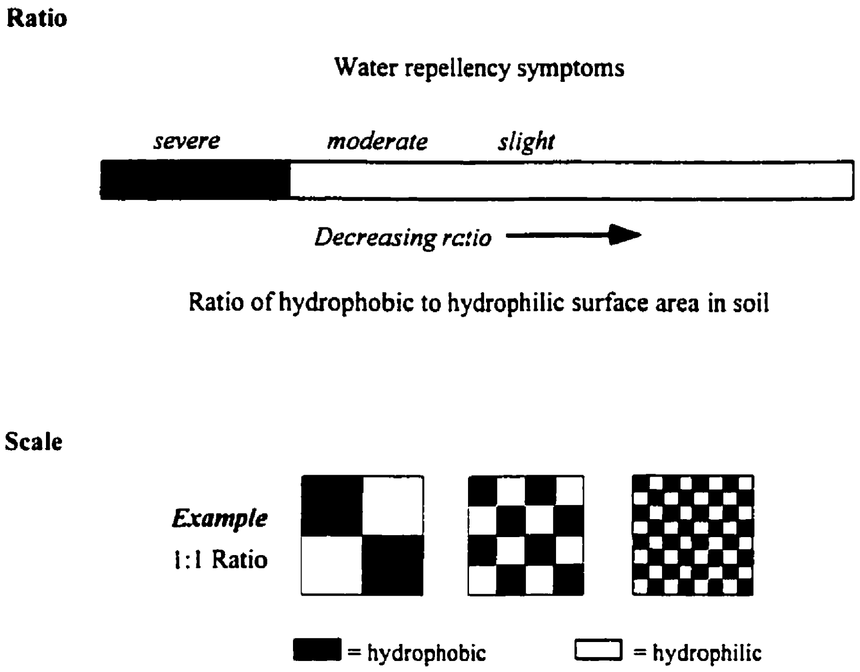

Figure 6.2. Illustration of the need to know the ratio of hydrophobic to hydrophilic surface area in soil and the scale of magnitude at which measurement of this ratio best correlates with macroscale soil water repellency symptoms. Both the fraction and the distribution of hydrophobic surface area in soil are likely to be controlling variables of soil wetting behaviour.

Measurement of the average ratio of hydrophobic:hydrophilic surface area in soil could replace average solid surface tension as an indicator of soil affinity for water. To be useful, however, this new measurement should also take into account spatial heterogeneity at the molecular scale. This is because knowledge that 1 cm^3 of soil has an average hydrophobic:hydrophilic surface area ratio of 0.10 may not be informative if all it takes to inhibit wetting is contiguity of 1/20 of this hydrophobic surface area ahead of the wetting front. Ideally, surface area ratios in soil should be determined at a scale that permits quantification of hydrophobic surface area at the scale of the cross-sectional area of a water molecule (i.e. nm^2). Because it would be impractical to perform this measurement on every unit of surface area in a soil, a simpler and still useful alternative may be to determine the scale at which measured hydrophobic:hydrophilic surface area ratios correlate best with macroscale soil water repellency symptoms.

In the introduction chapter of this thesis, I discussed the fact that the development of soil water repellency seems to necessitate a sequence of two and sometimes three processes. At old crude oil spill sites, accumulation, re-distribution or re-organisation, and stabilisation of hydrophobic organic substances seem all to be required for the development of soil water repellency. Accumulation is apparently of crude oil constituents in the vapour or liquid phase. Re-distribution and re-organisation is to increase the surface coverage of hydrophobic moieties at the fluid/solid interface. Stabilisation is for the soil-sorbed portion of vapour- or liquid-phase petroleum compounds to multiply noncovalent bonds with humin or soil minerals and become increasingly resistant to extraction over time. All three processes are poorly documented in the soil water repellency and other pertinent literature. Further studies into the mechanisms and forces driving organic molecule re-organisation and stabilisation at the solid/fluid interface in soil would fill prominent gaps in our understanding of organic contaminant interactions with soil. My work with water-repellent soils, for example, suggests that stabilisation of organic contaminants can occur at the solid/air interface in soil and does not require diffusion of organic contaminants into inaccessible nanopores (Scow 1993; Pignatello and Xing 1995).

PRACTICAL IMPLICATIONS

My research indicates that causative agents of water repellency in the studied soils are relatively resistant to nondestructive extraction procedures. For example, exhaustive extraction with 0.1 *M* NaOH under N_2 and Soxhlet extraction with DCM, toluene, CCH, methanol, ethanol, IPA and a variety of amphiphilic solvent mixtures failed to remove soil water repellency completely and irreversibly. Two nondestructive extraction protocols were nevertheless identified that removed soil water repellency completely and irreversibly. These were extraction with DCM followed by SDS, and repeated sequential extraction of water-repellent soil using IPA/NH_4OH followed by DCM. Such results indicate that permanent remediation of soil water repellency does not necessitate use of destructive oxidative techniques, such as heating soil in a fan oven at 200 °C for 16-18 h or treating soil with hydrogen peroxide. Destruction of causative agents of soil water repellency by chemical or thermal oxidation is not usually considered an appealing remediation option because it also destroys soil.

The recalcitrance of causative agents of soil water repellency is probably largely an acquired property. In Chapter 2, I discussed how prompt remediation of some oil-contaminated plots at the Ellerslie site effectively prevented the development of soil water repellency. This suggests that stimulation of bioremediation of oil contaminants soon following spillage may be the most effective means of preventing the development of soil water repellency at crude oil spill sites.

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APPENDIX A

Gravimetric determination of solvent-extractable material

Concentration ($mg{\cdot}kg^{-1}$) = mass of a.d. extract (mg)/(mass of o.d. soil extracted - mass of a.d. extract) (kg)

where a.d.= air-dried under ambient conditions and o.d.= oven-dried at 105 °C for 24 h.

Example Two air-dried soil samples are taken out of storage. Sample 1 is weighed, placed in a cellulose thimble and Soxhlet extracted for 24 h. Sample 2 is weighed in a preweighed aluminium dish and placed in an oven at 105 °C for 24 h. The oven-dried mass of Sample 2 is recorded. The oven-dried mass of sample 1 is calculated from knowledge of the moisture content of air-dried Sample 2 soil. Following Soxhlet extraction, the extract obtained from Sample 1 is concentrated by roto-evaporation and transferred into a preweighed aluminium drying dish. The extract is air-dried in a fume hood until its mass has become constant. The air-dried extract mass is recorded.

APPENDIX B

Generation of soil water repellency by addition of IPA/NH_4OH-extractable material obtained from readily wettable and water-repellent oil-contaminated soils

Table B.1. MED index of initially wettable solids treated with ≈800 mg·kg^{-1} of material extracted from CW and NW soils using IPA/NH_4OH

	MED (*M*) of recipient of extract	
Source of extract	AW sand[z]	ELL-PW soil
ELL-CW	2.7 ±0.1	0.0 ±0.0
DEV-CW	3.6 ±0.0	0.0 ±0.0
ELL-NW	3.6 ±0.0	0.0 ±0.0
DEV-NW	3.5 ±0.1	0.0 ±0.0

[z] Acid-washed sand

APPENDIX C

Field layout of Devon site

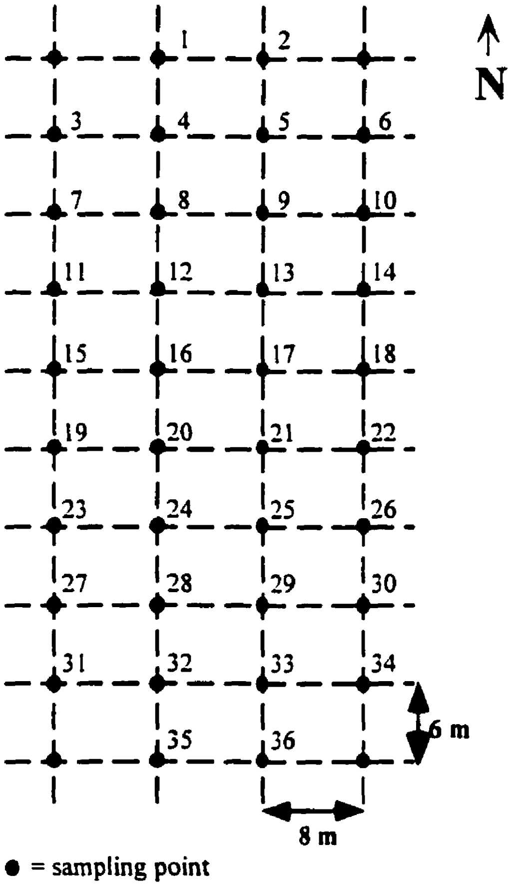

Figure C.1. Field layout of the patch of water-repellent soil (54 m × 24 m) that was sampled for residual DCM-extractable organics at the Devon site.

APPENDIX D

Data obtained from characterisation of moisture and residual oil content in Devon soil profile

Table D.1. Data used to calculate the concentration of DCM-extractable organics in DEV soil

Spot[a]	Depth (cm)	Rep 1 (mg·kg^{-1})	Rep 2 (mg·kg^{-1})	Rep 3 (mg·kg^{-1})	Average (mg·kg^{-1})	Std Dev (mg·kg^{-1})
1	0-10	12991.53	-	-	12991.53	-
	20-30	14899.03	-	-	14899.03	-
	30-40	25635.53	-	-	25635.53	-
	50-60	19854.14	-	-	19854.14	-
	70-80	13822.31	12508.37	12424.05	12918.24	784.08
	90-100	15385.78	12874.04	-	14129.91	1776.07
2	0-10	16592.30	-	-	16592.30	-
	20-30	29587.39	-	-	29587.39	-
	30-40	21073.65	-	-	21073.65	-
	50-60	15960.66	-	-	15960.66	-
	70-80	11078.11	-	-	11078.11	-
	90-100	15339.35	-	-	15339.35	-
3	0-10	13352.99	-	-	13352.99	-
	20-30	16175.01	20808.41	-	18491.71	3276.31
	30-40	34888.07	-	-	34888.07	-
	50-60	25898.54	-	-	25898.54	-
	70-80	12334.36	-	-	12334.36	-
	90-100	16173.49	15697.83	18832.44	16901.25	1689.28
4	0-10	19618.39	-	-	19618.39	-
	20-30	15220.57	-	-	15220.57	-
	30-40	25767.75	25634.59	-	25701.17	94.16
	50-60	21719.59	25626.63	-	23673.11	2762.69
	70-80	17255.66	17665.48	-	17460.57	289.79
	90-100	12612.46	-	-	12612.46	-
5	0-10	10033.93	-	-	10033.93	-
	20-30	57084.66	59775.97	-	58430.32	1903.04
	30-40	17644.52	-	-	17644.52	-
	50-60	16415.04	-	-	16415.04	-
	70-80	13460.82	-	-	13460.82	-
	90-100	8819.76	-	-	8819.76	-
6	0-10	14983.29	-	-	14983.29	-
	20-30	15922.90	-	-	15922.90	-
	30-40	1402.02	-	-	1402.02	-
	50-60	20518.78	-	-	20518.78	-
	70-80	19052.51	-	-	19052.51	-
	90-100	11550.14	-	-	11550.14	-
7	0-10	16311.80	-	-	16311.80	-
	20-30	23083.30	-	-	23083.30	-
	30-40	25788.30	-	-	25788.30	-
	50-60	20497.72	-	-	20497.72	-
	70-80	14539.58	13050.41	-	13795.00	1053.00
	90-100	15610.46	14561.02	-	15085.74	742.07
8	0-10	21927.26	-	-	21927.26	-
	20-30	13481.34	-	-	13481.34	-
	30-40	46436.88	41120.16	-	43778.52	3759.49
	50-60	17849.58	-	-	17849.58	-
	70-80	10160.00	-	-	10160.00	-
	90-100	16216.06	-	-	16216.06	-
9	0-10	10668.91	-	-	10668.91	-
	20-30	26216.50	-	-	26216.50	-

	30-40	19398.25	-	-	19398.25	-
	50-60	18045.24	-	-	18045.24	-
	70-80	8149.23	-	-	8149.23	-
	90-100	12103.18	-	-	12103.18	-
10	0-10	8993.10	-	-	8993.10	-
	20-30	26294.67	27233.82	-	26764.25	664.08
	30-40	35431.17	36915.78	-	36173.48	1049.78
	50-60	21309.53	-	-	21309.53	-
	70-80	18609.75	-	-	18609.75	-
	90-100	14146.67	-	-	14146.67	-
11	0-10	14200.28	12561.88	-	13381.08	1158.52
	20-30	20711.55	21534.47	-	21123.01	581.89
	30-40	33504.38	-	-	33504.38	-
	50-60	13044.64	-	-	13044.64	-
	70-80	11956.05	13214.45	-	12585.25	889.82
	90-100	-	-	-	-	-
12	0-10	12659.58	-	-	12659.58	-
	20-30	28708.41	30190.28	-	29449.35	1047.84
	30-40	24754.77	-	-	24754.77	-
	50-60	15106.87	-	-	15106.87	-
	70-80	12906.13	-	-	12906.13	-
	90-100	12716.55	-	-	12716.55	-
13	0-10	14783.81	-	-	14783.81	-
	20-30	13824.81	-	-	13824.81	-
	30-40	21887.31	-	-	21887.31	-
	50-60	12208.55	-	-	12208.55	-
	70-80	11242.09	-	-	11242.09	-
	90-100	12074.17	-	-	12074.17	-
14	0-10	9940.35	-	-	9940.35	-
	20-30	7239.91	-	-	7239.91	-
	30-40	151.33	-	-	151.33	-
	50-60	18915.53	-	-	18915.53	-
	70-80	14222.36	-	-	14222.36	-
	90-100	15989.44	-	-	15989.44	-
15	0-10	14552.60	11087.24	-	12819.92	2450.38
	20-30	18566.13	-	-	18566.13	-
	30-40	13511.99	13334.28	14453.04	13766.44	601.22
	50-60	14920.43	-	-	14920.43	-
	70-80	12587.75	-	-	12587.75	-
	90-100	14761.92	-	-	14761.92	-
16	0-10	12098.15	-	-	12098.15	-
	20-30	19570.82	-	-	19570.82	-
	30-40	14601.32	-	-	14601.32	-
	50-60	11308.07	-	-	11308.07	-
	70-80	9107.19	-	-	9107.19	-
	90-100	14588.19	-	-	14588.19	-
17	0-10	12594.64	-	-	12594.64	-
	20-30	6552.98	-	-	6552.98	-
	30-40	115.05	127.40	-	121.23	8.73
	50-60	12091.88	-	-	12091.88	-
	70-80	8359.26	-	-	8359.26	-
	90-100	8200.42	-	-	8200.42	-
18	0-10	15518.54	-	-	15518.54	-
	20-30	14824.47	15817.02	-	15320.75	701.84
	30-40	1269.14	-	-	1269.14	-
	50-60	13940.14	-	-	13940.14	-
	70-80	9297.61	-	-	9297.61	-
	90-100	11117.82	-	-	11117.82	-
19	0-10	11814.59	-	-	11814.59	-
	20-30	19593.18	19422.48	-	19507.83	120.70
	30-40	21627.29	-	-	21627.29	-
	50-60	12687.48	-	-	12687.48	-
	70-80	7812.57	8308.01	-	8060.29	350.33
	90-100	10748.65	11284.07	10958.54	10997.09	269.78
20	0-10	10973.70	-	-	10973.70	-
	20-30	16539.50	-	-	16539.50	-

	30-40	13107.88	-	-	13107.88	-
	50-60	7927.53	-	-	7927.53	-
	70-80	8904.85	-	-	8904.85	-
	90-100	9943.31	-	-	9943.31	-
21	0-10	16115.49	-	-	16115.49	-
	20-30	18119.35	-	-	18119.35	-
	30-40	14149.74	-	-	14149.74	-
	50-60	9148.03	-	-	9148.03	-
	70-80	6248.82	-	-	6248.82	-
	90-100	7821.24	-	-	7821.24	-
22	0-10	13933.70	-	-	13933.70	-
	20-30	2732.75	-	-	2732.75	-
	30-40	114.32	-	-	114.32	-
	50-60	10789.47	-	-	10789.47	-
	70-80	8702.52	-	-	8702.52	-
	90-100	7783.24	-	-	7783.24	-
23	0-10	14467.42	12831.17	-	13649.30	1157.00
	20-30	23867.00	25346.97	-	24606.99	1046.50
	30-40	11289.86	19420.62	-	15355.24	5749.32
	50-60	15147.76	14800.05	14304.41	14750.74	423.83
	70-80	12970.36	-	-	12970.36	-
	90-100	18402.90	18960.94	-	18681.92	394.59
24	0-10	11881.41	-	-	11881.41	-
	20-30	35135.89	29605.70	-	32370.80	3910.43
	30-40	18145.58	-	-	18145.58	-
	50-60	9780.78	-	-	9780.78	-
	70-80	11831.43	-	-	11831.43	-
	90-100	16647.89	-	-	16647.89	-
25	0-10	18160.97	-	-	18160.97	-
	20-30	12170.56	-	-	12170.56	-
	30-40	11293.41	-	-	11293.41	-
	50-60	8880.82	-	-	8880.82	-
	70-80	11058.01	-	-	11058.01	-
	90-100	14442.05	-	-	14442.05	-
26	0-10	9900.22	-	-	9900.22	-
	20-30	146.50	-	-	146.50	-
	30-40	189.31	-	-	189.31	-
	50-60	11336.46	-	-	11336.46	-
	70-80	7133.84	-	-	7133.84	-
	90-100	15880.84	-	-	15880.84	-
27	0-10	16535.70	-	-	16535.70	-
	20-30	38922.52	-	-	38922.52	-
	30-40	20173.17	-	-	20173.17	-
	50-60	17216.42	16301.49	-	16758.96	646.95
	70-80	10226.38	-	-	10226.38	-
	90-100	27706.20	30236.63	-	28971.42	1789.28
28	0-10	36523.16	36051.60	-	36287.38	333.44
	20-30	10713.26	-	-	10713.26	-
	30-40	9470.70	-	-	9470.70	-
	50-60	12047.48	-	-	12047.48	-
	70-80	20090.06	-	-	20090.06	-
	90-100	25408.69	-	-	25408.69	-
29	0-10	7920.32	-	-	7920.32	-
	20-30	14947.85	-	-	14947.85	-
	30-40	9037.84	-	-	9037.84	-
	50-60	7376.96	-	-	7376.96	-
	70-80	14031.47	-	-	14031.47	-
	90-100	26579.37	25932.22	-	26255.80	457.60
30	0-10	7689.06	-	-	7689.06	-
	20-30	89.51	-	-	89.51	-
	30-40	33007.69	39311.91	-	36159.80	4457.76
	50-60	13938.26	-	-	13938.26	-
	70-80	16580.48	-	-	16580.48	-
	90-100	11707.08	-	-	11707.08	-
31	0-10	14471.37	14867.20	-	14669.29	279.89
	20-30	77778.83	77449.59	-	77614.21	232.81

	30-40	27323.23	26448.57	-	26885.90	618.48
	50-60	21250.11	-	-	21250.11	-
	70-80	16392.95	-	-	16392.95	-
	90-100	-	-	-	-	-
32	0-10	5495.63	-	-	5495.63	-
	20-30	12008.60	-	-	12008.60	-
	30-40	9637.65	-	-	9637.65	-
	50-60	10097.66	-	-	10097.66	-
	70-80	24393.88	-	-	24393.88	-
	90-100	35162.19	30699.93	-	32931.06	3155.29
33	0-10	5344.64	-	-	5344.64	-
	20-30	7977.50	-	-	7977.50	-
	30-40	9636.73	-	-	9636.73	-
	50-60	12460.22	-	-	12460.22	-
	70-80	10818.18	-	-	10818.18	-
	90-100	19795.46	-	-	19795.46	-
34	0-10	7742.34	-	-	7742.34	-
	20-30	5518.50	-	-	5518.50	-
	30-40	3616.62	-	-	3616.62	-
	50-60	8050.13	-	-	8050.13	-
	70-80	15396.93	15581.46	-	15489.20	130.48
	90-100	23190.54	-	-	23190.54	-
35	0-10	8526.73	10366.54	-	9446.64	1300.94
	20-30	29794.97	34144.78	-	31969.88	3075.78
	30-40	15745.58	-	-	15745.58	-
	50-60	15739.35	-	-	15739.35	-
	70-80	22181.26	-	-	22181.26	-
	90-100	28546.73	-	-	28546.73	-
36	0-10	6032.83	-	-	6032.83	-
	20-30	12672.82	-	-	12672.82	-
	30-40	11819.67	-	-	11819.67	-
	50-60	13969.92	-	-	13969.92	-
	70-80	10220.02	-	-	10220.02	-
	90-100	15193.13	-	-	15193.13	-

[z] Refers to sampling point number in Figure C.1.

Table D.2. Calculation of mean DCM-extractable concentration per depth section

Depth (cm)	Sum ($mg \cdot kg^{-1}$)	Mean	$SumY_i^2$	$(Sum\ Y_i)^2/n$	n-1	Std Dev	SEM
0-10	472 863	13 135	7 281 642 344	6 211 088 737	35	5 530.57	921.76
20-30	712 374	19 788	22 108 759 087	14 096 574 056	35	15 130.09	2521.68
30-40	607 706	16 881	14 905 048 919	10 258 511 002	35	11 522.08	1920.35
50-60	528 549	14 682	8 521 029 220	7 760 106 646	35	4 662.69	777.11
70-80	462 660	12 852	6 586 007 246	5 945 957 840	35	4 276.34	712.72
90-100	540 551	15 898	9 912 492 822	8 593 966 290	33	6 321.02	1084.05

Table D.3. Data used to calculate H_2O and VOCs content in DEV soil

Spot[z]	Depth (cm)	Rep 1 (g·kg^{-1})	Rep 2 (g·kg^{-1})	Rep 3 (g·kg^{-1})	Average (g·kg^{-1})	Std Dev (g·kg^{-1})
1	0-10	110.00	-	-	110.0	-
	20-30	183.1	-	-	183.1	-
	30-40	169.5	-	-	169.5	-
	50-60	137.2	-	-	137.2	-
	70-80	105.6	109.4	118.4	111.1	6.6
	90-100	115.7	111.2	-	113.4	3.2
2	0-10	67.0	-	-	67.0	-
	20-30	193.0	-	-	193.0	-
	30-40	141.6	-	-	141.6	-
	50-60	111.1	-	-	111.1	-
	70-80	102.5	-	-	102.5	-
	90-100	117.2	-	-	117.2	-
3	0-10	43.5	-	-	43.5	-
	20-30	86.8	87.7	-	87.2	0.6
	30-40	180.5	-	-	180.5	-
	50-60	190.3	-	-	190.3	-
	70-80	158.9	-	-	158.9	-
	90-100	147.2	213.1	160.6	173.6	34.8
4	0-10	116.1	-	-	116.1	-
	20-30	96.5	-	-	96.5	-
	30-40	135.5	125.1	-	130.3	7.4
	50-60	126.4	73.8	-	100.1	37.2
	70-80	133.9	175.8	-	154.8	29.6
	90-100	113.8	-	-	113.8	-
5	0-10	59.2	-	-	59.2	-
	20-30	138.1	135.7	-	136.9	1.7
	30-40	148.7	-	-	148.7	-
	50-60	121.9	-	-	121.9	-
	70-80	115.0	-	-	115.0	-
	90-100	101.2	-	-	101.2	-
6	0-10	76.1	-	-	76.1	-
	20-30	208.9	-	-	208.9	-
	30-40	186.8	-	-	186.8	-
	50-60	159.4	-	-	159.4	-
	70-80	126.4	-	-	126.4	-
	90-100	113.0	-	-	113.0	-
7	0-10	47.3	-	-	47.3	-
	20-30	102.0	-	-	102.0	-
	30-40	190.1	-	-	190.1	-
	50-60	138.6	-	-	138.6	-
	70-80	152.6	158.1	-	155.4	3.9
	90-100	125.6	122.4	-	124.0	2.3
8	0-10	42.7	-	-	42.7	-
	20-30	75.0	-	-	75.0	-
	30-40	127.9	127.4	-	127.6	0.4
	50-60	107.4	-	-	107.4	-
	70-80	108.3	-	-	108.3	-
	90-100	113.3	-	-	113.3	-
9	0-10	92.9	-	-	92.9	-
	20-30	168.6	-	-	168.6	-
	30-40	161.5	-	-	161.5	-
	50-60	145.6	-	-	145.6	-
	70-80	30.4	-	-	30.4	-
	90-100	138.5	-	-	138.5	-
10	0-10	67.9	-	-	67.9	-
	20-30	168.9	166.9	-	167.9	1.4
	30-40	169.4	175.9	-	172.6	4.6
	50-60	149.9	-	-	149.9	-
	70-80	142.1	-	-	142.1	-
	90-100	113.5	-	-	113.5	-

11	0-10	56.3	57.4	-	56.8	0.8
	20-30	123.7	121.7	-	122.70	1.4
	30-40	172.1	-	-	172.1	-
	50-60	133.4	-	-	133.4	-
	70-80	112.7	115.8	-	114.2	2.2
	90-100	-	-	-	-	-
12	0-10	48.8	-	-	48.8	-
	20-30	118.5	120.7	-	119.6	1.6
	30-40	138.9	-	-	138.9	-
	50-60	109.3	-	-	109.3	-
	70-80	114.4	-	-	114.4	-
	90-100	113.2	-	-	113.2	-
13	0-10	59.4	-	-	59.4	-
	20-30	173.7	-	-	173.7	-
	30-40	144.2	-	-	144.2	-
	50-60	133.1	-	-	133.1	-
	70-80	130.3	-	-	130.3	-
	90-100	122.0	-	-	122.0	-
14	0-10	100.1	-	-	100.1	-
	20-30	166.1	-	-	166.1	-
	30-40	143.3	-	-	143.3	-
	50-60	138.9	-	-	138.9	-
	70-80	121.5	-	-	121.5	-
	90-100	124.5	-	-	124.5	-
15	0-10	76.2	76.3	-	76.2	0.1
	20-30	175.6	-	-	175.6	-
	30-40	172.0	171.6	165.7	169.8	3.5
	50-60	116.0	-	-	116.0	-
	70-80	105.4	-	-	105.4	-
	90-100	187.9	-	-	187.9	-
16	0-10	56.7	-	-	56.7	-
	20-30	143.5	-	-	143.5	-
	30-40	115.1	-	-	115.1	-
	50-60	111.7	-	-	111.7	-
	70-80	107.3	-	-	107.3	-
	90-100	104.3	-	-	104.3	-
17	0-10	56.7	-	-	56.7	-
	20-30	109.9	-	-	109.9	-
	30-40	126.8	125.4	-	126.1	1.0
	50-60	101.6	-	-	101.6	-
	70-80	99.7	-	-	99.7	-
	90-100	90.8	-	-	90.8	-
18	0-10	49.6	-	-	49.6	-
	20-30	101.0	97.5	-	99.2	2.5
	30-40	119.4	-	-	119.4	-
	50-60	368.2	-	-	368.2	-
	70-80	101.1	-	-	101.1	-
	90-100	108.0	-	-	108.0	-
19	0-10	38.7	-	-	38.7	-
	20-30	57.7	57.6	-	57.6	0.1
	30-40	121.8	-	-	121.8	-
	50-60	113.0	-	-	113.0	-
	70-80	111.0	105.6	-	108.3	3.8
	90-100	113.6	102.8	112.4	109.6	5.9
20	0-10	42.1	-	-	42.1	-
	20-30	93.3	-	-	93.3	-
	30-40	135.8	-	-	135.8	-
	50-60	109.5	-	-	109.5	-
	70-80	105.2	-	-	105.2	-
	90-100	103.0	-	-	103.0	-
21	0-10	53.7	-	-	53.7	-
	20-30	107.2	-	-	107.2	-
	30-40	104.4	-	-	104.4	-
	50-60	118.8	-	-	118.8	-
	70-80	108.6	-	-	108.6	-
	90-100	97.7	-	-	97.7	-

22	0-10	42.6	-	-	42.6	-
	20-30	99.8	-	-	99.8	-
	30-40	129.2	-	-	129.2	-
	50-60	106.9	-	-	106.9	-
	70-80	109.0	-	-	109.0	-
	90-100	108.3	-	-	108.3	-
23	0-10	46.6	47.5	-	47.0	0.6
	20-30	110.4	94.8	93.2	99.5	9.5
	30-40	132.8	131.6	-	132.2	0.8
	50-60	125.5	129.3	125.3	126.7	2.2
	70-80	119.4	-	-	119.4	-
	90-100	118.2	116.5	-	117.4	1.2
24	0-10	40.9	-	-	40.9	-
	20-30	113.2	113.1	-	113.2	0.1
	30-40	147.5	-	-	147.5	-
	50-60	103.9	-	-	103.9	-
	70-80	103.0	-	-	103.0	-
	90-100	128.5	-	-	128.5	-
25	0-10	47.3	-	-	47.3	-
	20-30	111.8	-	-	111.8	-
	30-40	131.1	-	-	131.1	-
	50-60	104.0	-	-	104.0	-
	70-80	141.4	-	-	141.4	-
	90-100	131.5	-	-	131.5	-
26	0-10	79.8	-	-	79.8	-
	20-30	95.2	-	-	95.2	-
	30-40	111.2	-	-	111.2	-
	50-60	109.3	-	-	109.3	-
	70-80	108.5	-	-	108.5	-
	90-100	122.1	-	-	122.1	-
27	0-10	147.5	-	-	147.5	-
	20-30	121.8	-	-	121.8	-
	30-40	159.7	-	-	159.7	-
	50-60	127.6	124.6	-	126.1	2.1
	70-80	105.7	-	-	105.7	-
	90-100	186.5	-	-	186.5	-
28	0-10	70.2	69.5	-	69.8	0.5
	20-30	141.4	-	-	141.4	-
	30-40	122.0	-	-	122.0	-
	50-60	117.2	-	-	117.2	-
	70-80	127.5	-	-	127.5	-
	90-100	139.9	-	-	139.9	-
29	0-10	40.0	-	-	40.0	-
	20-30	129.2	-	-	129.2	-
	30-40	131.7	-	-	131.7	-
	50-60	134.5	-	-	134.5	-
	70-80	135.2	-	-	135.2	-
	90-100	111.9	108.9	-	110.4	2.1
30	0-10	47.0	-	-	47.0	-
	20-30	101.6	-	-	101.6	-
	30-40	116.9	117.6	-	117.2	0.5
	50-60	99.8	-	-	99.8	-
	70-80	124.6	-	-	124.6	-
	90-100	114.5	-	-	114.5	-
31	0-10	64.7	65.2	-	65.0	0.4
	20-30	129.0	-	-	129.0	-
	30-40	116.7	-	-	116.7	-
	50-60	122.7	-	-	122.7	-
	70-80	113.9	-	-	113.9	-
	90-100	-	-	-	-	-
32	0-10	41.1	-	-	41.1	-
	20-30	118.3	-	-	118.3	-
	30-40	133.1	-	-	133.1	-
	50-60	111.3	-	-	111.3	-
	70-80	129.4	-	-	129.4	-
	90-100	139.4	137.3	-	138.4	1.5

33	0-10	41.0	-	-	41.0	-
	20-30	106.3	-	-	106.3	-
	30-40	119.4	-	-	119.4	-
	50-60	119.4	-	-	119.4	-
	70-80	120.1	-	-	120.1	-
	90-100	134.9	-	-	134.9	-
34	0-10	40.4	-	-	40.4	-
	20-30	155.7	-	-	155.7	-
	30-40	133.3	-	-	133.3	-
	50-60	137.4	-	-	137.4	-
	70-80	129.4	132.3	-	130.8	2.0
	90-100	135.1	-	-	135.1	-
35	0-10	50.4	45.9	-	48.2	3.2
	20-30	120.7	121.2	-	121.0	0.4
	30-40	108.1	-	-	108.1	-
	50-60	116.2	-	-	116.2	-
	70-80	133.6	-	-	133.6	-
	90-100	134.4	-	-	134.4	-
36	0-10	43.8	-	-	43.8	-
	20-30	100.7	-	-	100.7	-
	30-40	133.1	-	-	133.1	-
	50-60	120.3	-	-	120.3	-
	70-80	116.3	-	-	116.3	-
	90-100	228.3	-	-	228.3	-

[z] Refers to sampling point number in Figure C.1.

Table D.4. Calculation of mean H_20 and VOCs concentration per depth section

Depth (cm)	Sum ($g \cdot kg^{-1}$)	Mean ($g \cdot kg^{-1}$)	$SumY_i^2$ ($(g \cdot kg^{-1})^2$)	$(Sum\ Y_i)^2/n$ ($(g \cdot kg^{-1})^2$)	n-1	Std Dev ($g \cdot kg^{-1}$)	SEM ($g \cdot kg^{-1}$)
0-10	2203.00	61.19	156785.85	134811.36	35	25.06	4.18
20-30	4532.02	125.89	613733.12	570532.64	35	35.13	5.86
30-40	5025.72	139.60	720030.47	701606.33	35	22.94	3.82
50-60	4670.70	129.74	676811.63	605984.40	35	44.98	7.50
70-80	4239.43	117.76	515903.51	499244.31	35	21.82	3.64
90-100	4312.68	126.84	574092.51	547036.40	33	28.63	4.91

APPENDIX E

Measurement of the surface tension of ethanol solutions

Surface tension measurements were obtained using a Fisher surface Tensiomat Model 21, Catalog No. 14-814 (Fisher Scientific). This model utilises principles of operation originally devised by Dr. Pierre Lecomte du Nouy. Essentially a torsion-type balance, it is the kind of instrument currently specified by the American Society for Testing Materials in Methods D-971 (interfacial tension of oil against water) and D-1331 (surface and interfacial tension of detergents (Fisher Scientific 1996). The Surface Tensiomat shows "apparent" surface tension on a calibrated dial. The dial readings can be converted to "absolute" values (S) by multiplying the "apparent" value (P) by a correction factor (F).

$$S = P \times F$$

The formula to calculate the correction factor (F) is:

$$F= 0.7250 + \mathrm{SQRT}\{[(0.01452)(P)/C^2(D-d)] + 0.04534 - [(1.679)(r/R)]\}$$

where:

F= correction factor
R= radius of the ring (cm)
r= radius of the wire of the ring (cm)
P= apparent value or dial reading (dynes·cm^{-1})
D= density of lower phase (air) (g·mL^{-1})
d= density of upper phase (test liquid) (g·mL^{-1})
C= circumference of the ring (cm)

Values for the circumference and R/r ratio of the ring were provided by the manufacturer (C= 5.920 cm, R/r= 53.0322424). I used a density of air of 0.0001 g·mL^{-1}. The units of S were converted from dynes·cm^{-1} to mN·m^{-1} (1 dynes·cm^{-1} = 1 mN·m^{-1}). I used denatured ethanol 95% (v/v) from Sigma-Aldrich (Cat. No. 27,074-1). This ethanol contains 95 parts denatured ethanol and 5 parts *iso*propyl alcohol (mol. wt. = 46.07 g·mole^{-1}, density= 0.785 g·mL^{-1}). Molarity of ethanol solution was not corrected for presence of denaturing agent.

Reference: Fisher Scientific. 1996. Instructions Manual, Fisher Surface Tensiomat Model 21.

Table E.1. Data used to calculate the corrected surface tension of ethanol solutions

Molarity (M)	Flask (g)	Flask+sol (g)	Density ($g \cdot mL^{-1}$)	Rep 1 ($dynes \cdot cm^{-1}$)	Rep 2 ($dynes \cdot cm^{-1}$)	Rep 3 ($dynes \cdot cm^{-1}$)	P ($dynes \cdot cm^{-1}$)	Std Dev ($dynes \cdot cm^{-1}$)	F	S ($dynes \cdot cm^{-1}$)	Std Dev ($dynes \cdot cm^{-1}$)
0.0	29.5893	79.3204	0.9946	75.7	75.1	75.7	75.5	0.3	0.9	70.8	0.3
0.2	29.5893	79.2244	0.9927	71.2	71.0	71.7	71.3	0.4	0.9	66.6	0.3
0.4	29.5893	79.1516	0.9912	67.6	68.0	67.3	67.6	0.4	0.9	62.9	0.3
0.6	29.5893	79.0639	0.9895	65.0	64.8	64.6	64.8	0.1	0.9	60.1	0.1
0.8	29.5893	78.9660	0.9875	61.6	61.5	61.4	61.5	0.1	0.9	56.8	0.1
1.0	29.5893	78.8826	0.9859	59.2	59.5	59.1	59.3	0.2	0.9	54.6	0.2
1.2	29.5893	78.7756	0.9837	57.0	57.0	57.1	57.0	0.1	0.9	52.4	0.0
1.4	29.5893	78.7085	0.9824	56.2	56.2	56.2	56.2	0.0	0.9	51.6	0.0
1.6	29.5893	78.6404	0.9810	54.4	54.6	54.6	54.5	0.0	0.9	50.0	0.0
1.8	29.5893	78.5600	0.9794	53.4	54.2	53.7	53.8	0.3	0.9	49.2	0.2
2.0	29.5893	78.4887	0.9780	51.9	52.0	52.3	52.1	0.2	0.9	47.6	0.1
2.2	29.5893	78.3952	0.9761	50.8	50.9	51.2	51.0	0.2	0.9	46.5	0.1
2.4	29.5893	78.3172	0.9746	50.4	50.2	50.3	50.3	0.1	0.9	45.9	0.1
2.6	29.5893	78.2544	0.9733	49.3	49.0	49.0	49.1	0.1	0.9	44.7	0.1
2.8	29.5893	78.1993	0.9722	48.0	48.2	48.0	48.1	0.1	0.9	43.7	0.1
3.0	29.5893	78.1153	0.9705	47.0	47.0	47.1	47.0	0.1	0.9	42.7	0.0
3.2	11.1314	58.8324	0.9540	46.1	46.2	46.0	46.1	0.1	0.9	41.9	0.1
3.4	11.1816	59.1954	0.9603	45.2	45.3	45.6	45.4	0.2	0.9	41.2	0.1
3.6	11.2236	59.2364	0.9603	44.7	44.7	44.7	44.7	0.0	0.9	40.5	0.0
3.8	11.2476	59.1846	0.9587	43.8	43.8	43.8	43.8	0.0	0.9	39.7	0.0
4.0	11.2314	59.0485	0.9563	42.9	43.0	42.9	42.9	0.1	0.9	38.8	0.0
4.2	10.3702	58.2386	0.9574	42.0	42.0	42.0	42.0	0.0	0.9	37.9	0.0
4.4	11.2523	58.9090	0.9531	41.4	41.7	41.4	41.5	0.2	0.9	37.5	0.1
4.6	11.2446	58.9710	0.9545	41.2	41.0	41.2	41.1	0.1	0.9	37.1	0.1
4.8	11.2031	58.6405	0.9487	40.2	40.5	40.3	40.3	0.1	0.9	36.4	0.1
5.0	11.1785	58.6636	0.9497	39.7	39.6	39.5	39.6	0.1	0.9	35.7	0.1
5.2	14.2010	61.7756	0.9515	39.2	39.2	39.1	39.2	0.1	0.9	35.3	0.0
5.4	13.7180	61.1307	0.9483	38.7	38.5	38.5	38.6	0.0	0.9	34.7	0.0
5.6	14.6680	61.8727	0.9441	37.8	37.8	38.1	37.9	0.2	0.9	34.1	0.1
5.8	13.2128	60.3129	0.9420	37.3	37.4	37.4	37.4	0.0	0.9	33.6	0.0
6.0	14.1049	61.2883	0.9437	37.3	37.2	37.1	37.2	0.1	0.9	33.4	0.1
17.0	-	-	0.7850	25.8	25.7	25.7	25.7	0.0	0.9	22.9	0.0