Studies of the molecular basis of soil water repellency.

Llewellyn, Christopher Thomas

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Studies of the molecular basis of soil water repellency

by

Christopher Thomas Llewellyn

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Abstract

To identify the causes of water repellency in soils, a range of water repellent soils and wettable control soils, sampled from five countries (Australia, Greece, Portugal, The Netherlands, U.K.), were studied. Water repellency was assessed using the water drop penetration time (WDPT) test whilst total organic carbon (TOC) analysis and diffuse reflectance infrared spectroscopy (DRIFT) were used to measure the TOC and aliphatic content respectively in the soils. Water repellency correlated slightly better with aliphatic content than TOC content, although neither correlated well with water repellency.

The efficiency of Soxhlet extractions with isopropanol: aqueous ammonia (7:3, v:v) in extracting compounds associated with water repellency was examined. Extraction efficiency was examined by determining: extract mass; severity of water repellency post-extraction; amounts of organic carbon and aliphatic C-H removed; and by assessing the ability of extracts to cause repellency in acid washed sand. Extraction removed repellency completely from 12 of 14 repellent samples and extracts from all soils (including the wettable control samples) were capable of inducing repellency. Samples were rendered wettable regardless of the mass extracted or the quantity of organic carbon removed, suggesting that provided there is some aliphatic material present, the amount is less important than its constitution and/or molecular arrangement. Low polarity solvents caused sample repellency to increase despite the removal of non-polar hydrocarbons, suggesting that compounds such as alkanes are not, in themselves, the main cause of repellency.

Kinetics and selectivity of the extraction procedure (using isopropanol: aqueous ammonia) was also examined. Increasing extraction time caused an increase in extract mass and a decrease in soil water repellency. The same compound types were detected by GC-MS in all extracts, but their proportions varied with extraction time. In particular, the removal of alkanes from the soil sample was less rapid than that of more polar compounds.

Abbreviations

Aq. NH_3	Aqueous ammonia
AU	Australian soil sample
AWS	Acid washed sand
$CHCl_3$	Chloroform
DRIFT	Diffuse reflectance infrared Fourier transform spectroscopy
DSC	Differential scanning calorimetry
FID	Flame ionisation detection
FTIR	Fourier transform infrared
GC	Gas chromatography
GC-FID	Gas chromatography – flame ionisation detection
GC-MS	Gas chromatography – mass spectrometry
GK	Greek soil sample
HPLC	High performance liquid chromatography
IPA	Isopropanol
IPA/NH_3	Isopropanol: aqueous ammonia (7:3, v:v) solvent mixture
LC	Liquid chromatography
LDS	Localised dry spot
M	Mol dm^{-3}
MED	Molarity of an ethanol droplet test
NL	Dutch soil sample
PT	Portuguese soil sample
RI	Repellency index
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TC	Total carbon
TOC	Total organic carbon
SG	Specific gravity
UK	British soil sample
WDPT	Water drop penetration time test

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Chapter 3: Characterization of water repellent soils and assessment of extraction procedures

Chapter 4: DRIFT and TOC analysis of water repellent and wettable soils

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Chapter 6: Conclusions and implications

Chapter 1

Introduction

1.1 Introduction to water repellency in soils

Soils are generally considered to wet readily under rainfall or irrigation; water enters the soil matrix under the influence of gravity and capillary action (Doerr 1997). However, some soils exhibit a reduced affinity for water sometimes to the extent that the soil matrix is not wettable at all, *i.e.* water repellency (or hydrophobicity) (Fig 1.1a). Water repellency in soils generally occurs at low to moderate moisture contents (Doerr *et al.* 2000a) and has been reported for soils under a range of vegetation types from many regions worldwide. This phenomenon can have serious environmental implications including reduced infiltration capacity leading to poor seed germination and plant growth, accelerated surface run-off, soil erosion by wind and water and enhanced leaching of nutrients and agrochemicals through preferential flow (De Bano 2000a, Doerr *et al.* 2000a).

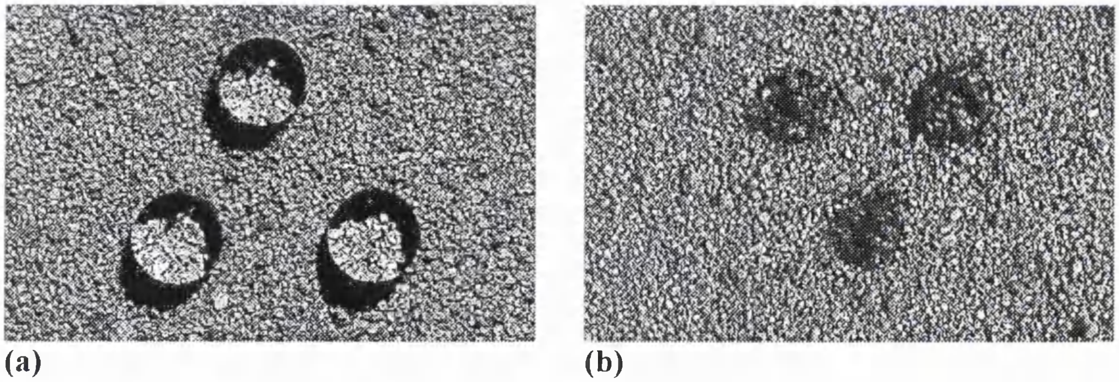

Figure 1.1: Water drops on (a) a water repellent soil and (b) a wettable soil.

It has been proposed that water repellency is caused by the accumulation of hydrophobic organic compounds originating from organic matter released as root exudates (Dekker and Ritsema 1996, Doerr *et al.* 1998), as fungal or microbial by-products (Savage *et al.* 1969, Jex *et al.* 1985), or directly from decomposing organic matter (McGhie and Posner 1981). The compounds responsible are generally thought to be present as a coating on the soil mineral or aggregate surfaces (Bisdom *et al.*

1993, Doerr *et al.* 2000a), although additional material may also be present as interstitial matter (Franco *et al.* 2000a). Achieving a fundamental understanding of the (bio)chemical causes of water repellency is critical not only in the amelioration of repellency by, for example, developing more effective and environmentally friendly wetting agents. It is also important in allowing mankind to balance the detrimental effects of repellency with its beneficial effects such as the enhanced stability of soil organic carbon (Piccolo *et al.* 1999), reduced evaporative losses or increased aggregate stability (DeBano 2000a, Doerr *et al.* 2000a).

This study is an investigation of water repellent soils from a wide range of locations (Australia, Greece, The Netherlands, Portugal, U.K.) in order to gain a better understanding of soil water repellency at a molecular level. Characterization is achieved by various methods but primarily by assessing water repellency levels, measuring organic matter content and isolation of compounds associated with soil water repellency by Soxhlet extraction. Some of the results have formed the basis of publications, Doerr *et al.* (in press) and Llewellyn *et al.* (2004) and have also contributed to related publications Morley *et al.* (in press) and Mainwaring *et al.* (2004). A full list of publications and conference contributions is given in Appendix A.

In the following sections of this chapter, previous work relevant to the characterisation and the origin of water repellency in soils is reviewed. Firstly, the principles of water repellency are discussed followed by a review of the most common techniques used to measure and classify water repellency in soils. A background to soil water repellency is presented discussing its causes, factors affecting its severity and consequences. The chemical principles underlying the water repellent effect are then summarised in terms of the types of compounds responsible and mechanisms associated with soil water repellency. Research gaps are then identified and aims formulated. Finally, an outline of the thesis is presented.

1.2 Principles of water repellency

Repellency of a liquid by a solid material is a function of the free energy of the solid/gas interface (Roy and McGill 2002), and the surface tension of the solid. Solids that resist wetting are said to have low energy surfaces (or low surface tensions). These solids do not actually exert a repelling force on a liquid; there is always a degree of attraction between a liquid and a solid with which it is in contact; it can be said they attract too weakly rather than repel. Thus, an entirely hydrophobic surface does not exist (Tschapek 1984).

Young (1805) was the first to relate the contact angle to the free energies of the three interfaces meeting at the solid/liquid/gas contact line with the balance of a drop of water on a solid surface being defined by the equation:

$$\cos\theta = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \qquad \textbf{(1)}$$

where γ_{sg} , γ_{sl} and γ_{lg} are the surface tensions (J m^{-2} or N m^{-1}) in the solid/gas, solid/liquid and liquid/gas interfaces respectively and θ is the contact angle. Fig. 1.2 shows the difference between a high and a low contact angle.

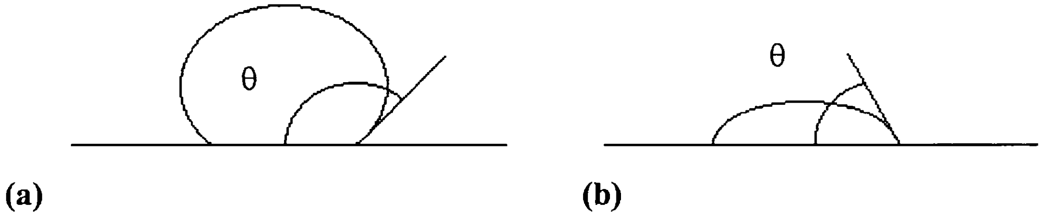

Figure 1.2: (a) High contact angle and (b) low contact angle.

In the case of uneven surfaces, such as a soil's, Young's equation is corrected (Wenzel 1936):

$$K\ (\gamma_{sg} - \gamma_{sl}) = \gamma_{lg} \cos\theta \qquad \textbf{(2)}$$

where K is the correction coefficient.

The following inequalities are present under (i) wetting conditions and (ii) non-wetting conditions:

$$\text{(i)} \quad \gamma_{sg} < \gamma_{sl} + \gamma_{lg} \qquad \text{(ii)} \quad \gamma_{sg} > \gamma_{sl} + \gamma_{lg} \qquad \textbf{(3)}$$

At room temperature (25 °C) most liquids have a surface tension of 20 – 40 mN m^{-1}. Water has an exceptionally high value of 72.75 mN m^{-1}, although the surface tension of soil water is always below this value indicating the presence of surface active substances in the soil water (Falasca and Tschapek 1992). The intermolecular forces in water are due to dispersion and polar forces (Fowkes 1964), as shown in equation 4:

$$\gamma_{\text{total}} = \gamma_{\text{dispersion}} + \gamma_{\text{polar}} \qquad \textbf{(4)}$$

where: $\gamma_{\text{total}} = 72$ mN m^{-1}, $\gamma_{\text{dispersion}} = 22$ mN m^{-1}, $\gamma_{\text{polar}} = 50$ mN m^{-1}

When interaction between water and a hydrophobic surface occurs it takes place predominantly through dispersion forces. A drop of water on a hydrophobic surface will form a sphere, minimising its area of contact with the surface (Adam 1963), as a result of its high surface tension. However, hydrocarbons will spread easily as their surface tension is considerably lower and similar to $\gamma_{\text{dispersion}}$ (22 mN m^{-1}).

A simplified way of characterizing the wetting process by assessing these forces is to consider them as forces of adhesion and cohesion, where adhesion is thought of as the attraction between the solid surface and water, and cohesion the attraction between individual water molecules.

1.3 Measurement and classification of soil water repellency

Measurement techniques that assess water repellency are extremely important for research and the communication of research findings. Repellency measurement techniques have long been established in the petroleum and textile engineering industries with American, British and German standards being established for some of them (Norris 1963, Anderson 1986). Although few of the methods used in these industries are employed by soil scientists, during the last century a variety of techniques have been developed to detect and quantify soil water repellency. The following sections outline those most commonly employed.

1.3.1 Contact angle method

When a liquid drop is placed on the surface of a solid, the shape of the drop is determined by the equilibrium between the three forces of the solid, liquid and gas. The tangent drawn at the curve of the drop to the point it intersects the solid surface forms the contact angle. A liquid drop with high surface tension resting on a low energy solid forms a spherical shape or high contact angle (Fig. 1.2 a) Conversely, when the solid surface energy exceeds the liquid surface tension, the drop forms a flatter, lower profile shape or low contact angle (Fig 1.2 b).

Measuring the contact angle, θ, of water drops on a soil's surface, provides a quantitative method of measuring soil water repellency and is a useful indicator of the free energy of the solid/gas interface. The general perception is that when $\theta < 90°$, water displaces air and wets the soil spontaneously, but when $\theta > 90°$, an external force is required to force the displacement of air to allow wetting of the soil by the water (Watson and Letey 1970, Roy and McGill 2002). Several workers have challenged this general perception. For example, Dyrness (1976) classified soils with $\theta = 70\text{-}80°$ as moderately repellent and those with $\theta > 80°$ as extremely repellent. Nakaya (1982) argued that any soil with $\theta > 0°$ was repellent to some degree whilst Wallis *et al.* (1991) believed that soils with $\theta < 90°$ could also exhibit hydrophobic properties of hydrological significance.

Measuring contact angles on smooth solid surfaces is relatively easy as the plane of the solid/liquid interface is easily recognizable. As soils are not planar surfaces the angle of the solid/liquid plane is more difficult to determine due to the surface roughness and therefore it is difficult to carry out a direct geometric measurement (Bachmann *et al.* 2000). A modification of the contact angle method was investigated by Bachmann *et al.* (2000) in order to overcome the problem created by surface roughness. Contact angle measurements were made on a thin layer of soil particles adhered to an adhesive tape in an attempt to create a more closely packed surface. It was found to be a simple and reproducible method for determining contact angles of sandy soils. Another variation of the contact angle method was used by Bond (1969) in which contact angles were measured from photographs of water drops on soils.

There are other limitations when considering the contact angle method. It is not only initially difficult to determine the solid/liquid plane on soil surfaces; other behavioural observations (such as water drops having many different stable contact angles (Anderson 1986)) have caused difficulties in the interpretation and comparison of contact angles between samples.

1.3.2 Capillary rise method

An indirect way of measuring the apparent contact angle, the capillary rise method, was developed by Letey *et al.* (1962, 2000). It was assumed that the hydrological characteristics of soil pores were comparable to those of a bundle of capillary tubes. Although an oversimplification, valuable insight was possible by assuming this capillary tube model. The rise of water into a soil column is therefore related to the capillary radius and the contact angle by the equation:

$$h = 2\gamma_l \cos \frac{\theta}{r\rho g} \tag{5}$$

where h is the height of liquid rise in the capillary of radius r, γ_l the liquid-air surface tension, θ the liquid-solid contact angle, ρ the liquid density and g the acceleration due to gravity. Both h and r are unknown. Letey *et al.* (1962) worked on the assumption that ethanol wets all soil with a contact angle of 0° (due to its low surface tension). According to equation (5) and using the subscript e to represent ethanol:

$$r = \frac{2\gamma_e}{h_e \rho_e g} \qquad \textbf{(6)}$$

The value of r obtained from equation (6) can be substituted into equation (5) when the height of rise is measured with water in the same soil. The contact angle for water, θ_w, can therefore be calculated using equation (7) where the subscript w represents water:

$$\cos\theta_w = \frac{h_w \gamma_e \rho_w}{\gamma_w h_e \rho_e} \qquad \textbf{(7)}$$

Letey *et al.* (1962) found this method gave reasonable and consistent measurements of θ, although the measured height reflects the sorptivity of the bulk soil as well as the repellency of the surface.

1.3.3 Repellency index (RI)

A similar technique to the capillary rise method is the repellency index technique. This gives an index of repellency (RI) through the measurement of a soil's intrinsic sorptivity. The rate of water infiltration is measured using an infiltrometer. In addition to this, the 'potential' rate of infiltration (as if the soil was wettable) can be determined by the same procedure using ethanol. After 5 minutes infiltration is stopped and the repellency index calculated by the equation:

$$RI = 1.95 \frac{S_e}{S_w} \qquad \textbf{(8)}$$

where 1.95 is an experimentally determined constant (which accounts for differences in the surface tension and viscosity between ethanol and water), S_e the potential sorptivity measured with ethanol and S_w the actual sorptivity with water. RI is a measure of the repellency of the soil surface combined with the sorptivity of the bulk soil and values range from 0 (wettable) to 100 (severely water repellent). Wallis *et al.* (1991) suggest that the index of repellency (RI) has a number of advantages over other tests; it is a physically significant parameter which can be used to calculate actual and 'potential' short-time water infiltration allowing comparison with rainfall and irrigation intensities. Limitations of this method are that it is not well suited to the rapid assessment of a large number of samples and it provides no information on the persistence or rate of decay of water repellency beyond 5 minutes.

1.3.4 Molarity of an Ethanol Droplet (MED) test

The MED test or % ethanol test measures the 'critical surface tension' of the substrate. It uses the known surface tensions of standardized solutions of ethanol in water (Doerr 1998). A classification system is used, whereby droplets of increasing surface tensions (decreasing ethanol concentrations) are applied to a soil until infiltration is resisted. The degree of repellency, or MED index, of a soil is expressed as the lowest concentration (mol dm^{-3}) or highest surface tension (mN m^{-1}) ethanol solution that infiltrates the soil within an arbitrary but fixed time. The time allowed for the droplet to infiltrate varies between studies; King (1981) used 5 s, Crockford *et al.* (1991) 3 s, whilst Harper and Gilkes (1994) used 10 s. The relationship between solution surface tension and molarity is given in the following equation (Roy and McGill 2000a):

$$y = 61.05 - 14.75 \ln (x + 0.5) \qquad \textbf{(9)}$$

where x is the molarity of ethanol solution (mol dm^{-3}) and y is the corrected liquid surface tension (mN m^{-1}). King (1981) proposed a classification where soils with a MED index ≤ 1.0 mol dm^{-3} (or ≥ 55 mN m^{-1}) are not significantly water repellent and soils with MED index ≥ 2.2 mol dm^{-3} (or ≤ 46 mN m^{-1}) are severely water repellent. Roy and McGill (2000a) suggested that the most useful range of MED test solution concentrations tends to be 0–6 mol dm^{-3}, corresponding to a surface tension range of *ca.* 72-33 mN m^{-1} at 21 °C. The relationship between surface tension and concentration of ethanol solution is shown in Fig. 1.3.

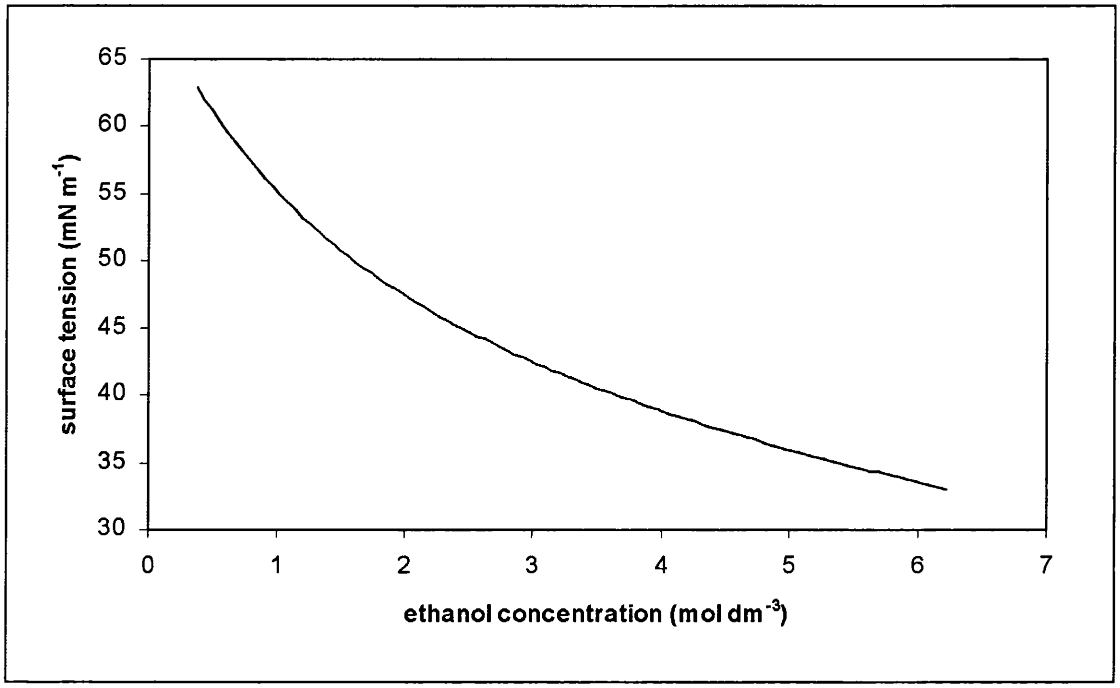

Figure 1.3: Relationship between surface tension and concentration of ethanol solutions (after Roy and McGill 2000a).

The main advantages of this test are its simplicity and speed of measurement. The water repellency of a large number of samples can be assessed in a short time and the test is suitable for both laboratory and field use. The MED test has therefore been used widely. However, this test is a measurement of the surface tension of a soil surface at the time of contact with a droplet of ethanol solution and is therefore a direct measure of the initial thermodynamic situation. It will not account for any change in water repellency which occurs with time as a consequence of the proximity of the water drop to the soil surface. It does not determine the time it takes for water to infiltrate (a kinetic measurement) but it might be expected that there is some relationship between these two properties.

1.3.5 Water Drop Penetration Time (WDPT) test

The WDPT test involves placing drops of water onto a soil surface and recording the time taken for complete infiltration (Letey 1969). The delay in droplet infiltration reflects the time the surface tension of the soil remains higher than that of the water drop (Doerr 1998). It is therefore a measure of the persistence time or stability (Letey *et al.* 2000) of the repellency and thus relates directly to the hydrological implications of soil water repellency, *e.g.* the generation of surface runoff is in principle dependent on the time required for rain drop to infiltrate (Wessel 1988).

WDPT can vary from instant infiltration to many hours and various researchers have used different classifications relating WDPT class to severity or persistence of water repellency. Roberts and Carbon (1971) and Ma'shum and Farmer (1985) used a threshold time of 1 s to distinguish between wettable and water repellent soils, whilst McGhie and Posner (1980) used a threshold time of 1 minute. In recent years the classification system most commonly used by researchers is that developed by Bisdom *et al.* (1993). In this system the threshold time to distinguish between wettable and water repellent conditions is 5 s. Other classes are: 5-60 s (slightly repellent); 60-600 s (strongly repellent); 600-3600 s (severely repellent); > 3600 s (extremely repellent).

Like the MED test, the WDPT test is also suitable for use in the laboratory or in the field and is probably the simplest and one of the most widely used methods for assessing soil water repellency. However, unlike the MED test, the WDPT test is not a direct measure of the initial degree of water repellency or the surface tension of a soil sample. It is a measure of the persistence of water repellency which may be of higher hydrological significance than the initial degree of water repellency, as it may be related to the rate of change in repellency as a consequence of rainfall (Doerr 1997). The WDPT test provides a measure of repellency but not a physical measure of water transport.

1.4 Background to water repellency in soils

1.4.1 Distribution of soil water repellency

Water repellent soils have been identified in a wide range of locations of varying climate. Most cases were initially reported from areas of semi-arid or Mediterranean climate such as South and Western Australia (Bond 1969, Roberts and Carbon 1971, Ma'shum *et al.* 1988), parts of the U.S.A. (Krammes and Osborn 1969, DeBano *et al.* 1970, Scholl 1971), New Zealand (Wallis *et al.* 1990a,b), South Africa (Scott 1992), Egypt (Bishay and Bakhati 1976), Italy (Giovannini *et al.* 1983) and Spain (Imeson *et al.* 1992).

However, more recently, many cases have been reported from areas with a wetter climate such as the U.K. (Mallik and Rahmann 1985, Doerr *et al.* 2000b), the Netherlands (Jungerius and de Jong 1989, Hendrickx *et al.* 1993, Dekker and Ritsema 1994a), north-central Portugal (Shakesby *et al.* 1993, Doerr *et al.* 1996), Columbia (Jaramillo *et al.* 2000), Sweden (Berglund and Persson 1996)) and British Columbia (Barrett and Slaymaker 1989). This suggests that water repellency is not confined to relatively dry climates (Doerr *et al.* 2000a).

De Bano (1981) concluded that water repellent soils are not isolated curiosities since they have been found in forests, grasslands, agricultural lands and on golf greens.

They are found worldwide on both uncultivated, as well as in intensively cultivated areas of land. Wallis *et al.* (1991) have even suggested that “water repellency is the norm rather than the exception, with the degree of repellency variable”.

Some detailed surveys have shown that soil water repellency affects large areas in some countries. According to Blackwell (2000) the three most westerly states of southern Australia have probably the largest areas of water repellent soils (with consequent limitation to agricultural animal and grain production) of any country in the world, amounting to *ca.* 5 million ha., equivalent to an area larger than the Netherlands. In the Netherlands itself 75% of the cropland and grassland topsoils exhibit water repellency (Dekker and Ritsema 1994a).

1.4.2 Consequences of soil water repellency

The main hydrological impacts of soil water repellency reported in the literature are summarised in this section.

1.4.2.1 Infiltration capacity and wetting patterns

The major effect of soil water repellency is a reduction in infiltration capacity. In wettable soils, infiltration rate decreases during water penetration, leading to Hortonian (infiltration-excess) overland flow if the infiltration capacity is exceeded (Doerr 1997). In water repellent soils, the infiltration rate is minimal during the initial phases of rainfall but often increases with time (DeBano 1981, Imeson *et al.* 1992) (Fig. 1.4). According to DeBano (1981), increased infiltration with time occurs because the substances responsible for water repellency are slightly water soluble and slowly dissolve, thereby increasing wettability.

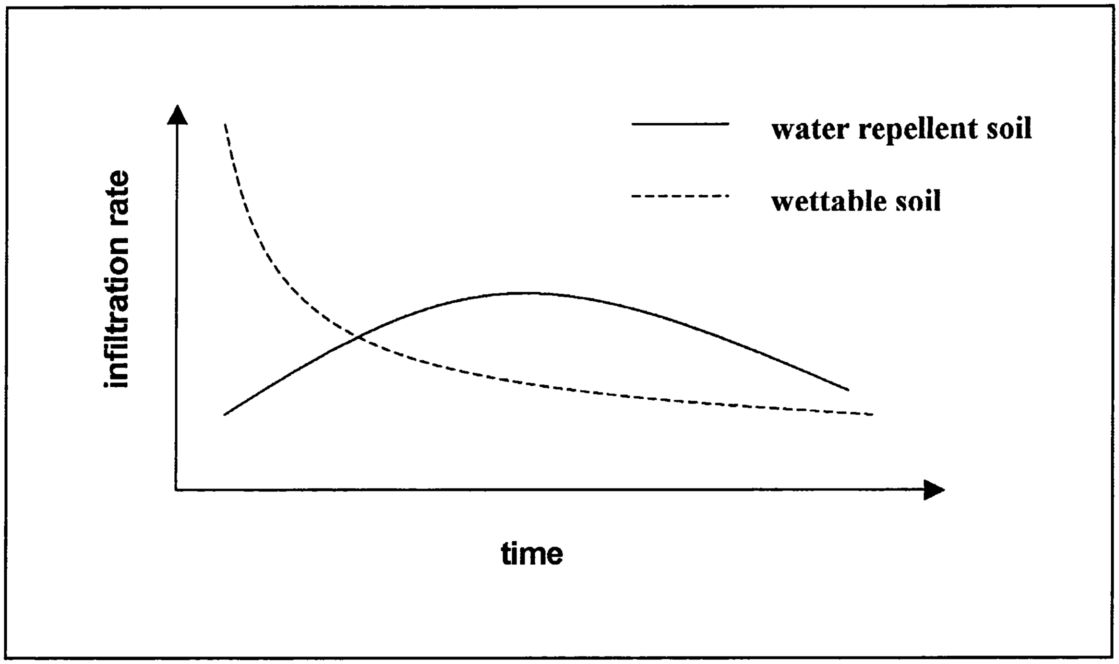

Figure 1.4: Infiltration curves for water repellent and wettable soils (after Imeson *et al.* 1992).

Meeuwig (1971) reported a reduced infiltration capacity in water repellent pine soils in California. Infiltration capacity has been found to increase six-fold from a water repellent dry soil (*ca.* 37 mm h^{-1}) to adjacent moist and less repellent soils (*ca.* 204 mm h^{-1}) by Wallis *et al.* (1990a). In addition to this, Wallis *et al.* (1991) have also shown, using the repellency index (RI) (or intrinsic sorptivity method), that within 5 minutes of measurement a water repellent soil had only 1% of its 'potential' infiltration rate when wettable.

Irregular or 'patchy' wetting patterns are often observed in areas of water repellent soils. DeBano (1981) attributed this to the fact that the water repellent layer covering the soil particles is not usually continuous. Water repellent soils in south and western

Australia studied by Bond and Harris (1964), had a grass covering. The pastures were patchy and well-grassed areas alternated with bare areas over small distances. On closer inspection it was found that water was only able to infiltrate the grassed areas of soil whilst the intervening areas remained dry even after heavy rain as the soil was extremely repellent. Repellency patchiness has even been observed at mm-scale in a Scottish grassland soil by Hallett *et al.* (2004).

Water repellency also leads to preferential flow pathways in the soil (Dekker and Ritsema 1995, 1996) as a result of unstable wetting fronts (Hendrickx *et al.* 1988). Preferential flow is the concentrated vertical movement of water *via* preferred pathways or channels through the soil matrix (Doerr *et al.* 2000a). This phenomenon is not restricted to water repellent soils (Ritsema and Dekker 1994a), however, water repellency can be particularly effective at preventing downward movement of water, directing it into structural or textural preferential flow paths or creating an unstable irregular wetting front (Doerr *et al.* 2000a). This can lead to accelerated transport (or leaching) of water and solutes such as nutrients and/or agrochemicals to the ground water and surface water (Hendrickx *et al.* 1993, Ritsema and Dekker 1994b). In the case of toxic substances this increases the risk of groundwater contamination (Dekker and Ritsema 1995). The mechanism by which preferential flow arises is by the movement of water through columns or 'fingers' of less repellent soil (preferential flow path). This has been termed 'fingered flow' (Dekker and Ritsema 1994b, Ritsema and Dekker 1994b).

1.4.2.2 Effects on plant growth

Reduced water infiltration due to repellency may affect the available soil water for seed germination and plant growth (Doerr *et al.* 2000a). The irregular or 'patchy' wetting patterns (discussed previously) can also cause poor germination and low crop yields, and the accelerated leaching of nutrients into groundwater reduces the amount of available nutrients required for plant growth.

Jamison (1942) observed a relationship between the decline of citrus trees in central Florida and soil water repellency whilst the growth of grass on localized dry spots found on golf greens was reported to have ceased entirely (Karnok *et al.* 1993). In some parts of Australia soil water repellency has been reported to impede agricultural production (McGhie and Posner 1981). According to Blackwell (2000), soil water repellency in Australia affects agricultural production on at least 5 million ha. of land.

1.4.2.3 Soil erosion

A result of the factors discussed previously (*i.e.* the reduction in infiltration capacity and increased overland flow during rainfall as well as poor plant growth) is enhanced soil erosion attributed to water repellency. Harper and Gilkes (1994) considered soil water repellency to be one of the main factors causing land degradation as enhanced overland flow is often linked to soil erosion as well as increased runoff (Burch *et al.* 1989). Osborn *et al.* (1964) monitored soil losses on plots of water repellent soil, some of which had been treated with wetting agent (and were therefore of low repellency) prior to rainfall. The amount of sediment removed from the untreated plots was more than thirteen times as much as that removed from the treated plots. Soil erosion caused by water repellency has also been reported by Krammes and

Osborn (1969) in southern California, Shakesby *et al.* (1996) in Portugal, Jungerius and ten Harkel (1994) in the Netherlands and Blackwell (2000) in Australia.

Runoff and erosion caused by soil water repellency probably contain large quantities of important plant nutrients which contributes to reducing vegetative cover and thus increased risk of further erosion. Nutrient losses are greatest in coarse textured soils which have a low exchange capacity because clay and organic matter are lacking (DeBano 1981). Increased erosion can also occur after wildfire (the effects of fire are discussed in section 1.5.1). Prosser and Williams (1998) stated that increased runoff alone can result in greater erosion following a fire although it is enhanced by the reduced vegetation and litter cover. However, Pradas *et al.* (1994) found that as soon as vegetation recovers and a litter cover develops, infiltration rates increase and potential erosion problems disappear.

In addition to water erosion, wind erosion can also be influenced by soil water repellency, although the erodibility by wind may not differ much between wettable and repellent soils when dry (Doerr *et al.* 2000a). However, the periods when soils are bare and dry (*i.e.* most susceptible to wind erosion) are likely to be longer and/or more frequent for water repellent soils.

1.4.3 Causes of soil water repellency

It is commonly accepted that soil water repellency is caused by organic compounds derived from living or decomposing plants or microorganisms (Doerr *et al.* 2000a). Roberts and Carbon (1972) stated that water repellent soils identified in Florida and California, New Zealand and South and Western Australia were found to occur only in the presence of organic matter. The identification of compounds causing water repellency has been the focus of much research in the last decade (Ma'shum *et al.* 1988, Franco *et al.* 1994, Hudson *et al.* 1994, McIntosh and Horne 1994, Spadek *et al.* 1994, Horne and McIntosh 2000). However, complete identification of specific compounds responsible and/or the mechanism by which water repellency is exhibited has yet to be achieved. A complicating factor in such studies is the natural abundance of various potentially responsible compounds in soils (Doerr *et al.* 2000a).

1.4.3.1 Origin of compounds associated with soil water repellency

As water repellency is caused by organic compounds, research has attempted to establish relationships between soil organic matter/organic carbon content and the degree of repellency. However, results have been inconsistent. Some studies have found positive correlation between the variables (Wallis *et al.* 1990a, Berglund *et al.* 1996, McKissock *et al.* 2003) whilst others have found no correlation (Jungerius and de Jong 1989, De Bano 1991). Wallis and Horne (1992) speculated that the inconsistency may be that the small amount of water repellent compounds necessary to cause water repellency may not be proportional to the actual amount of organic matter present in soil. Chen and Schnitzer (1978) and Wallis and Horne (1992) speculated that soil water repellency seems to be more closely related to the *type*, or fraction of the organic matter, rather than the *total amount* of organic matter or carbon. Only some organic matter will be hydrophobic, *e.g.* compounds consisting of long aliphatic chains with no polar groups (such as alkanes) would exhibit the most severe hydrophobicity. Previous research into the chemical characterisation of compounds associated with soil water repellency is discussed in more detail in Section 1.6.

(a) Vegetation

In many studies the occurrence of water repellency has been associated with particular vegetation types. One of the first studies into the effect of vegetation type on water repellency was by Jamison (1942) who found that soils under citrus groves in Florida were water repellent. Bond (1969) found differences in the wettability of soils beneath different plant cover. Since this initial interest, several studies have investigated the application of plant material or plant extracts to induce water repellency in previously wettable soils (Roberts and Carbon 1972, Reeder and Jurgensen 1979, McGhie and Posner 1980, 1981). However, conclusions drawn from these studies are somewhat limited by the fact the plant material had not undergone natural decomposition and incorporation into the soil, and the contribution of plant roots to soil organic matter was neglected.

It is thought that the important sources of organic material able to cause water repellency are by-products of living plants such as surface waxes (McIntosh and Horne 1994) and root exudates (Dekker and Ritsema 1996, Doerr *et al.* 1998), as well as decaying plant matter (McGhie and Posner 1981). Plants commonly associated with water repellency are trees such as the *Pinus* and *Eucalyptus* species, which have a considerable amount of resins, waxes or aromatic oils (Doerr *et al.* 2000a). Scott (1991) found that soils beneath eucalypts were much more repellent than those under pines. Water repellency under shrubs has also been reported (Mallik and Rahman 1985, DeBano 1991) as well as under grassland such as pasture, dune grass and turf (Barrett and Slaymaker 1989, Crockford *et al.* 1991, Karnok *et al.* 1993, Dekker and Ritsema 1994b, McIntosh and Horne 1994). As reported by Karnok *et al.* (1993), this is of considerable concern on areas of high economic value such as golf greens where localized dry spots (LDS) were found to persist after prolonged irrigation. Water repellency in soils has also been associated with certain crops such as barley and clover (McGhie and Posner 1981), and lucerne (Bond 1969, Roberts and Carbon 1972). It should be noted that some plant species induce water repellency only under exceptional conditions. In some studies, fire (see also section 1.5.1) has been necessary for certain types of vegetation to cause water repellency (*e.g.* Reeder and Jurgensen (1979), Mallik and Rahman 1985).

Scott (1992) suggested that the release of hydrophobic substances to the soil by plants, in the same way as allelopathy, is used to suppress the germination of competing vegetation nearby and to conserve water by channelling water deep into the soil profile whilst reducing surface evaporation. It was proposed that this may be the ecological "purpose" of water repellency in soils.

(b) Fungal and microbial action

Fungal and microbial species have also been associated with soil water repellency (Jex *et al.* 1985, Savage *et al.* 1969, 1972, Hallett *et al.* 2001). Compared with the input of organic material from higher plants, the input of biomass from fungi and organisms within the soil can also be considerable (Doerr 1997, Doerr *et al.* 2000a).

In south eastern Australia, Bond (1960) found that a sandy soil resisted wetting in areas where there were large volumes of fungal mycelia. Mycelia of some fungi are hydrophobic and observations suggest that substances produced by the mycelia become dispersed in the soil imparting a water repellent surface to the soil. Bond and Harris (1964) suggested that water repellency in sandy soils was associated with the growth of microorganisms, particularly basidiomycete fungi. It has been suggested that mycelia stimulate turf growth for a short time, exhausting the soil of moisture, but once soil is rendered dry fungal growth prevents rewetting (DeBano 1981). The soil cannot retain or absorb water and this kills the grass by the same processes as a drought, leaving the area bare (causing localized dry spots (LDS)).

1.5 Other factors affecting water repellency

It is commonly accepted that soil water repellency is caused by organic matter as discussed in section 1.4.3.1. However the severity of water repellency in soils is dependent on several factors, which are discussed here.

1.5.1 Fire and soil temperature

The most common way a soil may be exposed to heating in the field is by fire, either by burning of vegetation as part of land management practices or by ‘wildfire’. Fire can vaporise and alter organic matter. DeBano (2000b) summarised that after fire, water repellency is typically found as a discrete layer of variable thickness and spatial continuity. Fire-induced water repellency first became of research interest in the 1960s and 1970s in the U.S.A. The findings of DeBano and others are discussed here.

DeBano *et al.* (1970) studied the translocation of hydrophobic substances during the burning of organic litter and water repellent soils. Burning was found to increase water repellency in most of the soils tested. Hydrophobic substances in surface layers of litter and soil were found to vaporize by heat treatment. Some will be lost into the atmosphere whilst others will migrate downwards, condensing in cooler soil layers and creating a water repellent layer (DeBano and Krammes 1966). Savage *et al.* (1972) also observed extreme water repellency in burned soils. They suggested that products from heating surface soil litter were responsible for causing the repellency with aliphatic hydrocarbons being the most effective substances. In addition to this it was proposed that the condensation of volatile material on the sub-surface layers alone would not be sufficient to induce repellency, but rather the altering of the structures of these substances would be required for extreme water repellency to occur. The thickness of the resulting water repellent layer appears to be related to both the type of material burned on the surface and the specific surface area of the underlying soil (DeBano *et al.* 1970) as well as the intensity of the heat moving down the soil profile (Savage 1974).

DeBano and Krammes (1966) found that soil water repellency could be either intensified or destroyed by the temperatures existing during a wildfire. Fire temperatures would probably be high enough to destroy water repellency in the surface few cm of soil and the depth to which this occurs would be dependent on the intensity and duration of the fire. During wildfires, temperatures can be expected to reach 700-800 °C (DeBano 2000b). At around 5 cm below the soil surface, the temperature would be such that the repellency is not destroyed but intensified. DeBano *et al.* (1976) also examined the transfer of heat and hydrophobic substances during burning. Large temperature gradients developed in the upper part of the soils soon after the litter layer began burning with the upper 2.5 cm of the soils averaging *ca.* 270 °C cm^{-1} after 5 minutes of burning. However, in the 2.5-5.0 cm layer the temperature gradients did not exceed *ca.* 145 °C cm^{-1}. It was found that soil water also affected the translocation of organic substances by altering temperature gradients in sandy soils during a fire. Temperatures at the surface and in underlying layers were found to be much lower in wet samples than in dry samples. For example, maximum surface temperature in the dry soil was 350 °C but 285 °C in the initially wet soil. Temperature gradients also developed faster in the dry soils. As a result, burning wet soils generally induced the most severe water repellency in the 0-1.0 cm surface layer, but burning dry soils caused the repellency to be most severe in the underlying 0.5-2.0 cm layer. Fire-related water repellency has also been reported from Europe. Mallik and Rahmann (1985) highlighted the effects of the repeated burning of vegetation as the principal land management practice in areas of Scotland, although similar effects are observed in areas where forest fires have occurred. Imeson *et al.* (1992) also reported fire-related water repellency in Spain. In contrast to many studies, Doerr *et al.* (1996) found that water repellency in soils from eucalyptus and pine forests in northern Portugal was not enhanced by fire and not confined to near-surface layers.

Long term post-fire monitoring is rare and therefore comparatively little is known about the longevity of these high temperature effects on water repellency (Doerr *et al.* 2000a). Existing results vary widely; in coniferous forests in the U.S.A., fire-induced repellency was found to persist for as long as six years (Dyrness 1976) or as little as a few months (DeBano 1976).

Controlled laboratory studies have attempted to mimic the phenomena described in field studies. It has been established in such studies that water repellency is generally intensified at temperatures of 175-200 °C, but destroyed above *ca.* 270-300 °C (DeBano 1981, Doerr *et al.* 2000a). A study on Portuguese water repellent soils by

Evans (personal communication) found that, in addition to temperature, duration of heating directly influenced the degree of water repellency and the temperature threshold for its destruction. The longer a soil was exposed to heating, the lower the temperature required to induce maximum water repellency.

Until recently, soil water repellency researchers were not aware of the influence of drying temperature on the severity of soil water repellency for initially moist soils. Dekker *et al.* (1998) found the severity of water repellency in some Dutch soils increased as a result of high drying temperatures. It is therefore now common practice for water repellency measurements to be made on air-dried (*ca.* 20 °C) and oven-dried (*e.g.* 105 °C) samples to assess the 'actual' as well as the 'potential' water repellency of a sample (as defined by Dekker and Ritsema 1994a; see also Chapter 3).

1.5.2 Soil moisture content

Soil water repellency is temporally variable. An important factor in these variations is soil moisture. Water repellency is generally considered to be more severe in dry soil and to decline as soil moisture increases (Doerr *et al.* 2000a) until a 'critical soil water content' is reached, above which a soil becomes wettable (Dekker and Ritsema 1994a). Critical soil water content varies considerably between soils. For example, values ranged from 4.75 - 1.75 vol. % in layers of a sandy soil investigated by Ritsema and Dekker (1994a), 20 - 24% in a silt loam assessed by Dekker and Ritsema (1995) and 34 - 38% in peat soils assessed by Dekker and Ritsema (1996). Many authors have reported that soil water repellency is seasonal, increasing in severity during the dry season and decreasing in severity, or becoming completely absent, under prolonged wet conditions (Roberts and Carbon 1971, Crockford *et al.* 1991, Imeson *et al.* 1992, Shakesby *et al.* 1993, Dekker *et al.* 2001).

In theory a soil will remain water repellent as long as the repellent organic layer covering the surface of individual particles remains unaltered during contact with water and the surface tension of the water remains constant. For repellency to break down the following mechanisms have been suggested. It has been suggested that where water repellency is caused by a coating of amphiphilic molecules (*i.e.* molecules which possess both hydrophobic and hydrophilic components), the attraction of water to the polar end groups of the molecules would weaken the 'soil-molecule bond', eventually leading to the displacement of the organic compounds from the soil particles, resulting in a wettable soil (Tschapek 1984, Ma'shum and Farmer 1985). This model is shown in Figure 1.5. Water repellency may also be overcome if the surface tension of the water is reduced. If surface-active substances (such as humic and fulvic acids) migrated from the soil into the water the surface tension of the water may decrease sufficiently to allow infiltration (Barrett and Slaymaker 1989, Chen and Schnitzer 1978). It is generally accepted that water repellency becomes re-established upon drying. As the soil water content decreases it is thought that a molecular reorientation would occur, in which the polar end groups of the amphiphilic molecules would re-adopt the position in which they were originally attached to the mineral surface, thus leaving the non-polar ends orientated outwards and re-establishing water repellency (Tschapek 1984, Ma'shum and Farmer 1985, Valat *et al.* 1991).

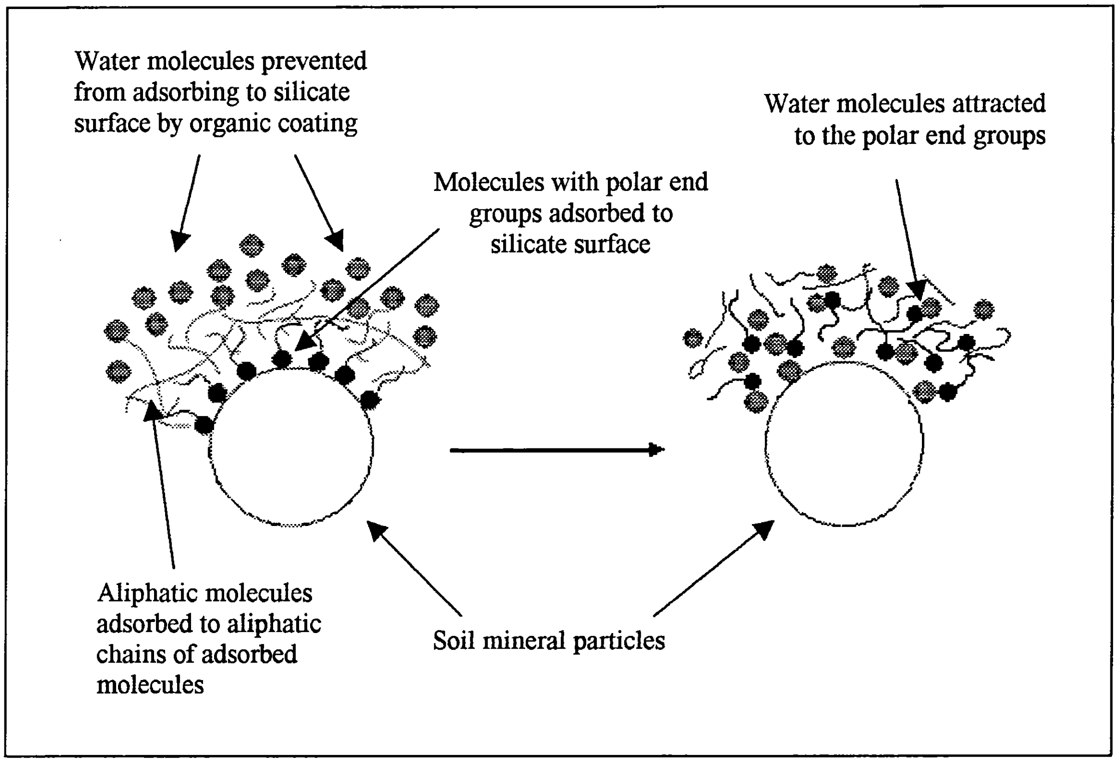

Figure 1.5: The change in soil particle surface as a water repellent soil becomes wettable.

As the degree of water repellency under field conditions can be strongly influenced by weather conditions, measurements are often made on dried samples. However, the heating temperature during drying influences the severity of water repellency measured on dried samples (Evans (personal communication), Franco *et al.* 1995). Generally, for samples dried at higher temperatures an increase in water repellency was observed. Therefore, as discussed in Section 1.5.1, Dekker and Ritsema (1994a) referred to water repellency measured on field-moist samples as "actual water repellency" and that measured on dried samples as "potential water repellency". Doerr and Thomas (2000) challenged the two-way soil moisture/water repellency relationship. They accepted that water repellency can be expected to remain absent as long as the soil moisture content remains above a critical level but argued that it cannot be assumed that repellency will be restored when soil moisture falls below that threshold.

1.5.3 Soil texture or particle size distribution

According to DeBano (1981), soil texture along with organic matter content are the most important factors affecting water repellency in soils. Water repellency is generally associated with coarse textured sandy soils (Bond 1969, Roberts and Carbon 1971, McGhie and Posner 1980, DeBano *et al.* 1970, 1976, Karnok and Tucker 2002). It is thought that given a limited supply of hydrophobic substances to coat soil particles, coarser soils would be more water repellent as their surface area per unit weight or volume is small compared to finer textured soils (Blackwell 1993). Coarser soils could therefore acquire a thicker and more intensely water repellent layer than finer textured soils (DeBano 1976). In addition, it has been demonstrated that incorporating clays into water repellent soils reduces the severity of water repellency by covering the repellent coatings (Ma'shum *et al.* 1989, Blackwell 1993). Methods of amelioration are discussed further in Section 1.7.

Although coarser soils seem to be more susceptible to developing water repellency, it has also been observed in soils of fine texture and even severe repellency is not uncommon in soils with considerable clay content (Doerr *et al.* 2000a). It has been proposed that in such cases the clay particles form aggregates, thus reducing the surface area to be covered (Wallis *et al.* 1991, Bisdom *et al.* 1993). However, this does not explain the occurrence of water repellency in all cases; scanning electron microscopy (SEM) studies on a fine-textured water repellent soil revealed no aggregation of fine particles (Doerr 1997). It was suggested that in such cases, the supply of hydrophobic material might be sufficiently high to cover the fine particles as well as the coarser fraction. A fine textured soil could therefore be more water repellent than a coarser one due to its larger total area of hydrophobic surface (Doerr *et al.* 2000a).

1.5.4 Soil pH

Water repellency is generally confined to acidic soils and does not develop under alkaline conditions (Roberts and Carbon 1971). A simple explanation for the reduction in water repellency above pH 7 is discussed by Chen and Schnitzer (1978), Tschapek (1984) and Karnok *et al.* (1993). Certain alkali-soluble compounds in humic substances (the fraction of substances in a soil which are only water-soluble at pH > 6.5) are thought to be responsible for water repellency. Therefore, under alkaline conditions the water repellent soils could effectively be washed of these compounds during periods of sufficient precipitation. In a study on localized dry spots (LDS) on golf course putting greens, Karnok *et al.* (1993) have shown that the application of sodium hydroxide can render the originally acidic water repellent soil wettable. For acidic conditions, however, Wallis *et al.* (1993) found no strong relationship between pH and water repellency.

1.6 The chemistry of soil water repellency

In this section soil particle surface chemistry and the types of compounds and mechanisms thought to be associated with soil water repellency are summarised as well as the methods by which such compounds have been isolated and characterized.

1.6.1 Soil particle surface chemistry

As soil water repellency is most commonly found in sandy soils (Roberts and Carbon 1971, De Bano 1981) the soils used in this study are of sandy texture (silica based sandy soils). This section therefore focuses on silica (or quartz) particles and the interactions between such mineral surfaces and organic compounds.

According to Greenwood and Earnshaw (1997), the earth's crustal rocks and their breakdown products such as soils are composed almost entirely (*ca.* 95%) of silicate materials and silica. Invariably silicon is coordinated tetrahedrally to 4 oxygen atoms, creating SiO_4 units which can combine to form a lattice by the sharing of oxygen atoms. Silica surfaces are hydrophilic as the hydrogen atoms in water molecules are able to form weak bonds with the oxygen atoms of the mineral particles, *i.e.* hydrogen bonding (Brady and Weil 1999). In the same way, organic compounds which contain polar functional groups (such as –COOH) are able to adsorb to the mineral surfaces. However, when such compounds also contain non-polar aliphatic chains (*i.e.* amphiphilic molecules) a hydrophobic organic coating will protrude from the mineral surface, thus repelling water (Doerr *et al.* 2000a), as shown in Fig. 1.5. Organic compounds are therefore required to coat mineral surfaces such as silica for water repellency to occur.

1.6.2 Types of organic compound associated with soil water repellency

Some researchers have claimed that humic materials or substances are responsible for causing soil water repellency (DeBano 1981). However, Wershaw *et al.* (1986) stated that humic materials have been 'the subject of research for 200 years, and still we have no clear fundamental chemical structure(s) of these materials'. Humic substances are 'those organic compounds found in the environment that cannot be classified as any other class of compounds (*e.g.* polysaccharides, proteins *etc.*)' (Gaffney *et al.* 1996). They are traditionally defined according to their solubilities. When extracting humic materials, they are generally fractionated into two fractions by reducing the pH to 1; the fraction that precipitates at pH 1 is termed humic acid, whilst the fraction that remains in solution is fulvic acid. The fraction that remains in the soil after extraction with a basic solution is called humin (Wershaw 2000). It has been proposed that humin materials expose a hydrophobic face and may have an important role in the binding of non-polar hydrophobic compounds (Hayes and Graham 2000). This may be relevant to soil water repellency. However, a claim that these materials are responsible for causing water repellency would be somewhat unspecific and not be particularly informative as humic materials are complex mixtures of organic compounds.

In the last 20 years, more detailed studies have been carried out of the precise chemical composition of water repellent soils. However, Roy *et al.* (1999) and Doerr *et al.* (2000a) have argued that despite advances made in previous studies, sufficient separation and exact chemical characterisation of these compounds has yet to be achieved. Consequently, the molecular basis of water repellency is still poorly understood.

Ma'shum *et al.* (1988) studied the components of extracts of water repellent soils and reported the presence of both free and esterified long-chain, C_{16}-C_{32} fatty acids. McIntosh and Horne (1994) and Horne and McIntosh (2000) identified alkanes (C_{23}-C_{33}) and (to a lesser extent) fatty acids as key components of the soil lipid (or chloroform-soluble) fraction, which are believed to be important in the development of repellency. The fatty acids extracted were those commonly found in animals and plants. Both saturated and unsaturated acids in the C_{10}-C_{18} range were detected. In a related study it was suggested that the nature of the compounds on the outer surface of the soil particles and not the total lipid (chloroform-soluble) content was the important factor in the development of water repellency (Horne and McIntosh 1994). It was found that if the compounds at the surface of the soil particles were lipid then the soil was repellent but if the outer layer was comprised of polar material then the soil was wettable. The lipid compounds alone were unable to bind to the soil particles but required the prior adsorption of fulvic acids.

Franco *et al.* (1994, 2000a) analysed waxes from water repellent soils and detected alkanes and fatty acids as well as esters, alcohols, phytanols, phytanes, aromatics, steroids and sterols. The major components were straight chain and branched in the C_{16}-C_{36} range and a strong similarity between compounds found in the soil and those from plant waxes was observed.

In western Australia, Spadek *et al.* (1994) also detected alkanes and fatty acids in water repellent soils. In this study quantification of these compound types was also achieved. Total amounts of alkanes and fatty acids in the water repellent soils studied were *ca.* 500 – 3700 $\mu g\ kg^{-1}$ and *ca.* 3500 – 14000 $\mu g\ kg^{-1}$ respectively.

In related studies Morley *et al.* (in press) and Mainwaring *et al.* (2004) have carried out detailed chemical analysis of water repellent soils from the Netherlands and the UK. Compounds identified were predominantly of aliphatic character and included long chain carboxylic acids (C_{16}-C_{24}), where even chain acids predominated. A similar distribution of mostly even-numbered long chain fatty acids was also noted by Ma'shum *et al.* (1988). A similar chain length distribution of amides (C_{14}-C_{24}) was also observed. Alkanes were detected in a slightly higher chain length distribution (C_{25}-C_{31}) with a predominance of odd number chain lengths. This observation suggested that a high proportion of the alkanes detected was of plant origin (Eglinton *et al.* (1962) reported that most plant hydrocarbons are straight chain, saturated compounds with an odd number of carbon atoms). Aldehydes or ketones (C_{25}-C_{29}) as well as more complex ring-containing structures were detected. Morley *et al.* (in press) and Mainwaring *et al.* (2004) also analysed a wettable sample; the relative abundances of alkanes were similar between the wettable and repellent samples. However, the extract from the wettable sample contained smaller amounts of the larger polar compounds (containing oxygen-based functional groups) compared to the extracts from the repellent samples. It was speculated that the inherently lower water solubility of these compounds (compared to lower molecular mass polar compounds) would result in relatively slow diffusion into water. They would therefore remain on the soil surface for longer, together with hydrophobic and lower molecular weight compounds, thus maintaining the barrier to water penetration for longer.

1.6.3 Extraction and isolation of compounds

In determining the types of compounds associated with soil water repellency, material from soil samples is normally removed by some extraction procedure to isolate a particular fraction of compounds or the compounds thought to be of interest. Extraction of material from the soil into a solvent (by dissolution) is the most common method. The most widely used extraction method is the Soxhlet technique whereby solvent is refluxed over a period of time and effectively washes the soil sample, although other methods such as extraction by stirring/shaking, column and supercritical liquid/gas have been used. The resulting extract solution can then be analysed by various techniques to determine specific compounds or types of compound present. The extraction solvent is normally removed to obtain a dry extract which can then be dissolved in or partitioned between other solvents to separate fractions of compounds, *e.g.* in a mixture of chloroform and water to partition the extract between organic and aqueous phases (Morley *et al.* in press). Many different extraction solvents and solvent mixtures have been used in various studies on soil water repellency (Table 1.1).

Ma'shum *et al.* (1988) and various other researchers since (listed in Table 1.1) have found an isopropanol: aqueous ammonia (7:3, v/v) solvent mixture appropriate as it often successfully removes organic material and renders previously water repellent soil wettable. Use of harsher extractants such as aqueous NaOH (Roberts and Carbon 1972, Litvina *et al.* 2003) and H_2O_2 (Bisdom *et al.* 1993) has also been found to eliminate water repellency. However, Roy *et al.* (1999) deemed these inappropriate for use in analytical work because they extract organic material non-selectively and/or destroy the extracted material. Various organic solvents have also been used but with little success. Most extract very little material and can even increase the severity of water repellency. Hudson *et al.* (1994) used hexane as an extraction solvent and observed an increase in repellency. It was proposed that the retention of non-polar solvent molecules by the soil may be the cause.

Table 1.1: Summary of extraction solvents used to remove and isolate compounds associated with soil water repellency.

Extraction solvent	**Author(s)**
Isopropanol: aq. ammonia (7:3, v/v)	Ma'shum *et al.* (1988), Franco *et al.* (1994, 2000a), Horne and McIntosh (1994, 2000), McIntosh and Horne (1994), Spadek *et al.* (1994), Roy *et al.* (1999), Litvina *et al.* (2003), Llewellyn *et al.* (2004), Mainwaring *et al.* (2004), Morley *et al.* (in press), Doerr *et al.* (in press (a)), Doerr *et al.* (in press (b))
Isopropanol: water (7:3)	Ma'shum *et al.* (1988), Roy *et al.* (1999)
Isopropanol: acetic acid (7:3)	Roy *et al.* (1999)
Chloroform:methanol:aq. ammonia (10:10:1)	Horne and McIntosh (1994, 2000)
Chloroform:methanol:water (9:1:1)	Horne and McIntosh (1994, 2000)
Chloroform:methanol:1M HCl (9:9:1)	Horne and McIntosh (1994, 2000)
Toluene: ethanol (2:1)	Horne and McIntosh (2000)
Benzene: ethanol (2:1)	Ma'shum and Farmer (1985), Ma'shum *et al.* (1988)
Acetylacetone: benzene	Giovannini *et al.* (1983)
Acetone	Roberts and Carbon (1972), McGhie and Posner (1980)
Benzene	Roberts and Carbon (1972), McGhie and Posner (1980), Giovannini *et al.* (1983)
Chloroform	Roberts and Carbon (1972), McGhie and Posner (1980), Ma'shum *et al.* (1988), Franco *et al.* (1994, 2000a), Litvina *et al.* (2003), Llewellyn *et al.* (2004), Doerr *et al.* (in press (b))
Cyclohexane	Roy *et al.* (1999)
Dichloromethane	Roy *et al.* (1999), Litvina *et al.* (2003), Doerr *et al.* (in press (a))
Ethanol	Roberts and Carbon (1972), McGhie and Posner (1980)
Ether	Ma'shum *et al.* (1988)
Hexane	Hudson *et al.* (1994), Doerr *et al.* (in press (a))
Hydrochoric acid (0.1 M)	McGhie and Posner (1980)
Hydrogen peroxide	Bisdom *et al.* 1993
Isopropanol	Roy *et al.* (1999), Doerr *et al.* (in press (a)), Doerr *et al.* (in press (b))
Methanol	Ma'shum *et al.* (1988), Roy *et al.* (1999)
Propanol	Ma'shum *et al.* (1988), Roy *et al.* (1999)
Sodium hydroxide (aqueous, 0.01 - 2.5 M)	Roberts and Carbon (1972), McGhie and Posner (1980), Doerr *et al.* (in press (a))
Tetrachloroethylene	Ma'shum *et al.* (1988)
Tetrahydrofuran	Llewellyn *et al.* (2004)
Toluene	McGhie and Posner (1980), Doerr *et al.* (in press (a))
Water	Roberts and Carbon (1972), McGhie and Posner (1980), Horne and McIntosh (1994), Doerr *et al.* (in press (a)), Doerr *et al.* (in press(b))

When using weakly polar or non-polar solvents (dichloromethane and cyclohexane), in a study of oil contaminated soils, Roy *et al.* (1999) argued that: (i) extraction increased the repellency of oil-contaminated wettable soils but did not affect the wettability of un-contaminated (or pristine) wettable soils; (ii) non-polar solvent molecules retained on the soil should have volatilised during the drying treatment preceding water repellency assessment; (iii) the relevant solvent peaks were never detected by GC. These observations suggest that organic matter coatings and/or surface chemistry of the contaminated soils differ from those found in the uncontaminated soils, and are therefore affected differently by non-polar solvents. Increase in water repellency after using weakly polar extractants was also observed by Ma'shum *et al.* (1988) (diethyl ether, tetrachloroethylene and chloroform) and Litvina *et al.* (2003) (dichloromethane). McGhie and Posner (1980) used a number of organic extraction solvents and, again, observed increased water repellency when using non-polar solvents. They suggested that changes in soil water repellency may be due to changes in the molecular configuration/orientation of organic compounds on the soil surface rather than removal of compounds. Ma'shum and Farmer (1985) observed that considerable changes in soil water repellency can be induced without removal of compounds from soil.

Ma'shum *et al.* (1988) and Roy *et al.* (1999) found that the extraction of water repellent substances and elimination of soil water repellency were strongly dependent on the polarity of the extractant. A significant decrease in extraction efficiency was observed in the order: amphiphilic to polar to non-polar solvents.

It is therefore thought that the success of the isopropanol: aqueous ammonia mixture is due to the combination of organic and polar solvents, *i.e.* the amphiphilicity of the solvent mixture rather than the alkalinity which only slightly improves extraction efficiency (Roy *et al.* 1999). As substances associated with water repellency are more soluble in polar and amphiphilic solvents than in non-polar solvents, it is therefore probable that they consist of amphiphilic rather than strictly non-polar water repellent compounds. In relation to this, Horne and McIntosh (2000) suggested that a subtle mechanism is required to explain soil water repellency as there was nothing unique about the compounds extracted from water repellent soils. They proposed that repellency is determined by the properties of the outer surface of the organic matter coating on soil particles (of which amphiphilic compounds are key constituents) and how functional groups (*e.g.* carboxylic groups) behave according to the degree of hydration. The following possible mechanism for repellency development and expression was suggested. Amphiphilic compounds may change orientation. When soils are wet these compounds are likely to have their polar end group pointing outwards interacting with water molecules (*i.e.* screening the water repellent ends), but when dehydration occurs there is a reconfiguration/reorientation. Polar groups interact with each other and these compounds present their non-polar water repellent ends at the surface (Ma'shum *et al.* 1985).

1.6.4 Separation and characterization of compounds

Compound types and specific compounds associated with soil water repellency have been identified and discussed in section 1.6.2. This section summarizes the main analytical techniques used to isolate and characterize the compounds of interest. Table 1.2 summarizes the techniques used in similar studies. As water repellency is caused by organic matter both nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy have been used to characterize the main types of organic compounds present in water repellent soils (as summarized in Table 1.2). Both techniques, in the form of cross polarization – magic angle spinning (CP-MAS) ^{13}C NMR (Capriel *et al.* 1990, Roy *et al.* 1999, Franco *et al.* 2000a, Litvina *et al.* 2003) and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy (Capriel *et al.* 1995, Franco *et al.* 1995, Capriel 1997, McKissock *et al.* 2003), have also been used to analyse solid samples (*i.e.* raw soil samples) which allow a direct non-destructive method of analysis.

The techniques discussed so far only determine the groups of organic compounds present in either raw soil or soil extracts. To obtain more detailed information, specific compounds need to be separated and then analysed to determine exact chemical structures of individual compounds. Thin layer chromatography (TLC) has been used to separate soil extracts into groups of similar compounds (Ma'shum *et al.* 1988, McIntosh and Horne 1994, Horne and McIntosh 2000, Doerr *et al.* in press (a)), whilst gas chromatography (GC) has been used to separate individual compounds (McIntosh and Horne 1994, Spadek *et al.* 1994, Horne and McIntosh 2000). The most common method of detection for GC is mass spectrometry (MS) and therefore gas chromatography - mass spectrometry (GC-MS) has been used to identify specific compounds associated with soil water repellency (Ma'shum *et al.* 1988, Franco *et al.* 1994 and 2000a, Roy *et al.* 1999, Litvina *et al.* 2003, Mainwaring *et al.* 2004, Morley *et al.* in press). GC-FID uses flame ionisation detection and has also been used in related studies. Other techniques which do not require extracts to be soluble in particular solvents have been used. Thermal desorption was used by Roy et al. (1999) whilst pyrolysis GC-MS was used by Nierop and Buurman (1998).

Table 1.2: Summary of analytical techniques used to characterize compounds associated with soil water repellency.

Analytical technique	Author(s)
Infrared (IR) spectroscopy	Ma'shum *et al.* (1988), Capriel *et al.* (1990), Horne and McIntosh (2000), Litvina *et al.* (2003), Doerr *et al.* (in press (a))
Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy	Hudson *et al.* (1994), Capriel *et al.* (1995), Franco *et al.* (1995), Capriel (1997), McKissock *et al.* (2003), Doerr *et al.* (in press (b))
Ultraviolet-visible (UV-Vis) spectroscopy	Ma'shum *et al.* (1988), Horne and McIntosh (2000)
Nuclear magnetic resonance (NMR) spectroscopy	Ma'shum *et al.* (1988), Capriel et al. (1990), Hudson *et al.* (1994), Litvina *et al.* (2003), Todoruk *et al.* (2003), Morley *et al.* (in press), Doerr *et al.* (in press (a))
Solid state (CP-MAS) NMR spectroscopy	Capriel *et al.* (1990), Roy *et al.* (1999), Franco *et al.* (2000a), Litvina *et al.* (2003)
Gas chromatography (GC)	McIntosh and Horne (1994), Spadek et al. (1994), Horne and McIntosh (2000), Litvina *et al.* (2003), Morley *et al.* (in press)
Gas chromatography - mass spectrometry (GC-MS)	Ma'shum *et al.* (1988), Franco *et al.* (1994, 2000a), Roy *et al.* (1999), Litvina *et al.* (2003) Llewellyn *et al.* (2004), Mainwaring *et al.* (2004), Morley *et al.* (in press)
Thin layer chromatography (TLC)	Ma'shum *et al.* (1988), McIntosh and Horne (1994), Horne and McIntosh (2000), Doerr *et al.* (in press (a))
Pyrolysis / GC-MS	Nierop and Buurman (1998)
Thermal desorption - MS	Roy *et al.* (1999)
Thermal analysis	Mallik and Rahman (1985), Evans (personal communication)

1.7 Amelioration strategies

In many cases water repellency in soils is undesirable and special management action is required to counteract their detrimental effects (DeBano 1981). According to Blackwell (1993) there are four principles on which to base better management of water repellent soils: (i) increase the 'wetting power' of water by increasing water pressure at the surface (*e.g.* at the base of water-filled depressions or furrows), or by reducing the surface tension of water by treating the soil with surfactants; (ii) cover the 'waxy skins' (water repellent coatings) on the soil particles with a thin layer of clay; (iii) avoid (by furrowing) or remove the repellent surface soil; (iv) minimise soil drying by, for example, accumulation of crop residues and not cultivating the soil.

A common treatment for water repellent soils is the application of chemical wetting agents containing surface-active compounds such as surfactants (Wallis *et al.* 1990b, Wallis and Horne 1992, Blackwell 1993 and 2000, Kostka 2000, Feng *et al.* 2002, Karnok and Tucker 2002). Adding wetting agents to water lowers the surface tension of the solution allowing initial infiltration. Amphiphilic wetting agent molecules can then adsorb onto the repellent soil particles creating a wettable surface, allowing further infiltration of subsequent rain or irrigation water (Wallis *et al.* 1990b). When water repellent soils are treated with wetting agents, runoff and soil erosion (section 1.4.2.3) are usually significantly reduced due to more rapid infiltration (DeBano 1981). A problem with using wetting agents is that on large areas such treatments are expensive and difficult to apply (Blackwell 1993). For this reason their use has principally been confined to turf management (Wallis and Horne 1992). Abadi Ghadim (2000) assessed whether amelioration of water repellency was a viable option for farmers in Western Australia. A large increase in crop yield would be necessary to justify the expenditure. It was found that farms with proportionately large areas of water repellent soils were more likely to benefit.

The addition of clays to water repellent soils has also been investigated as a method to reduce water repellency (Ma'shum *et al.* 1989, Ward and Oades 1993, McKissock *et al.* 2002). It was found that the intermixing of dispersible clays with water repellent soils was particularly effective in alleviating water repellency. Ma'shum *et al.* (1989) found that the dispersibility of clays was the major factor influencing the efficiency of clays in reducing water repellency, as clays which easily disperse expose a greater available surface area for the adsorption of water. Ward and Oades (1993) suggested possible mechanisms by which clays may improve wettability of water repellent soils: (i) dilution of hydrophobic compounds; (ii) preferential adsorption of hydrophobic materials, leaving the soil particles wettable; (iii) masking the repellent particle surfaces and exposing a wettable clay surface. In South and Western Australia experiments have shown that incorporation of about 100 tonnes/hectare of sodic, kaolinitic clays can reduce water repellency to near zero, improve germination and increase the storage of water available to plants (Blackwell 1993).

Other strategies to improve agricultural production and water infiltration in water repellent soils include high-pH treatments with the application of sodium hydroxide to golf greens (Karnok *et al.* 1993) and wax degradation by the stimulation of microorganisms with the addition of slow-release fertilisers (Franco *et al.* 2000b). By establishing microorganisms as a component in the resident flora, they would function continuously and prevent the development or persistence of water repellency (McKenna *et al.* 2002). Roper (2004) isolated and characterised wax-degrading bacteria from soils and other sources. Inoculation of water repellent soils with such bacteria under controlled conditions was found to improve soil wettability.

Blackwell (2000) highlighted the fact that there are risks involved with all management methods. Applying clays seems to be least risky whilst furrowing has the highest risk of encouraging preferential flow and thus leaching of pesticides and nutrients through water repellent soils, leading to groundwater contamination (as described in section 1.4.2.1).

1.8 Research aims

As evident from the preceding evaluation of currently published work, and from previous reviews, despite significant advances made in previous studies, sufficient isolation and characterisation of the key compounds responsible for water repellency has yet to be achieved (Roy *et al.* 1999, Doerr *et al.* 2000a). As a result of this, water repellency at a molecular level is still not fully understood. This research addresses this research gap through the analysis and characterisation of both water repellent soils and wettable control soils in order to determine the compounds or compound types and/or mechanism(s) responsible for causing soil water repellency. In contrast to other studies, the soils used in this work were sampled from a range of locations worldwide (Australia, Greece, Portugal, The Netherlands, U.K.) rather than just one location in order to gain a broader understanding of soil water repellency.

Generally, the first step in analysing compounds associated with soil water repellency is to isolate the compounds by some extraction procedure. The efficiency and selectivity of a chosen extraction procedure is therefore very important when considering the compounds associated with soil water repellency. The main aims of this work are therefore focussed on filling these gaps in current knowledge by the following methods:

1 Assess the properties of water repellent soils (and wettable control soils) in terms of severity of water repellency exhibited, total organic carbon (TOC) content and aliphatic C-H content.

2 Soxhlet extract a range of water repellent soils (and wettable control soils) using isopropanol: aqueous ammonia (7:3, v:v) as the extraction solvent and assess its efficiency in terms of the removal of water repellency, mass of material extracted, total organic carbon (TOC) content and aliphatic C-H content.

3 Assess the ability of soil extracts to induce water repellency in wettable acid washed sand (AWS).

4 Monitor the extraction procedure (Soxhlet extraction using isopropanol: aqueous ammonia (7:3, v:v)) over a 24 h period (by varying extraction duration) in terms of the removal of water repellency, mass of material extracted, organic material removed and the types of compounds extracted.

5 Compare the extraction efficiency of isopropanol: aqueous ammonia (7:3, v:v) with other solvents (chloroform, THF, isopropanol, water, aqueous ammonia).

1.9 Thesis outline

This thesis is divided into six chapters. Following this introductory chapter, Chapter 2 describes the materials and chemicals used as well as the techniques and specific conditions employed. Chapters 3, 4 and 5 present the main results of the thesis and are divided primarily by the techniques used to assess the water repellency of samples and the efficiency of the extraction procedures used. Chapter 3 describes how a range of water repellent soils were characterised by various methods including particle size analysis, water repellency assessments and Soxhlet extraction. Chapter 4 reports on an investigation into the organic matter (both aliphatic and total organic carbon (TOC) content) present in the range of water repellent soils (using TOC and

DRIFT analysis). Chapter 5 focuses on the kinetics of the Soxhlet extraction procedure used to isolate compounds associated with soil water repellency. The kinetics and selectivity of the extraction procedure were investigated for a single water repellent soil by varying extraction duration and solvent and measuring the effects using GC-MS. Finally, Chapter 6 presents the conclusions and implications of this research.

Chapter 2

Experimental

2.1 Introduction

In this chapter details of the chemicals, materials and soil samples used are given, and the methodologies used in sample characterization and instrumentation are discussed.

2.2 Resources

2.2.1 Chemicals and materials

Table 2.1 gives details of all chemicals and materials used in this research.

2.2.2 Soil samples

Soils of sandy texture known to exhibit water repellency were sampled in five countries comprising a range of locations with differing climates and vegetation cover. Wettable soils were also sampled from each location to carry out control experiments. Soils were confirmed as predominantly silica based by microscopy (carried out by Dr. Peter Douglas). The sample sites in the Netherlands (NL) and Wales (UK) have an oceanic humid-temperate climate with rainfall occurring throughout the year. The sites in Greece (GK) are also temperate, but with a summer dry season, whereas sites in Portugal (PT) and Australia (AU) exhibit a warmer Mediterranean type climate with prolonged dry periods during the summer months. Samples were oven-dried at 20 °C and passed through a 2 mm sieve prior to further analysis. All soils are of medium sand texture, with a clay content of < 0.1 %. Site locations and sample characteristics are summarized in Table 2.2.

2.2.3 Sampling

All soils were selected and sampled by other researchers as part of a larger research project called 'Water Repellent Soils' (EU grant FAIR-CT98-4027) and were made accessible for this work. The aim of the larger project was to develop amelioration strategies to reduce environmental deterioration and agricultural production losses in water repellent regions by combining the complimentary knowledge of scientists in institutes and universities around the world. The project objectives were:

1. Determination of the severity of soil water repellency in various representative soil types around the world according to uniform measurement protocol.
2. Characterization of the organic substances responsible for soil water repellency.
3. Execution of infiltration experiments on soils with varying degrees of water repellency.
4. Extension of flow and transport models to make them applicable to water repellent soils.
5. Execution of field trials to test varying amelioration strategies to reduce runoff and leaching, and optimize crop and pasture production.
6. Formulation of guidelines for optimal, (*i.e.* environmentally friendly and cost-effective) soil and water management practices on water repellent land.

The research described in this thesis contributes to the second objective, *i.e.* 'Characterization of the organic substances responsible for soil water repellency'.

The selection criteria for the soils chosen by the project research team were:

1. Sample three sandy soils from each country which (i) were from a region known to suffer from problems caused by water repellency, (ii) were typical of the particular region and (iii) exhibited varying degrees of water repellency.
2. Sample a wettable control soil from each country which was as similar as possible to the repellent samples selected.

Replicate soil samples were not taken spatially.

Table 2.1: Chemicals and materials used.

Chemical / Material	Grade	Supplier
Air	-	BOC Gases
Aqueous ammonia	Laboratory grade (35%, 0.88 SG)	Fisher Chemicals
Chloroform	Analytical grade	Fisher Chemicals
Dichloromethane	Analytical grade	Fisher Chemicals
Helium	-	BOC Gases
Hydrogen	High purity (> 99.995 %)	BOC Gases
Nitrogen	Oxygen free	BOC Gases
Oxalic acid	-	Merck
Potassium bromide	-	Fisher Chemicals
Isopropanol (propan-2-ol)	Laboratory grade	Fisher Chemicals
Sand (silicon dioxide)	Acid washed	Riedel-de Haën
Soxhlet thimbles	Cellulose	Whatman
Soxhlet thimbles	Glass microfibre	Whatman
Tetrahydrofuran	Analytical grade	Aldrich
Triacontane	99 %	Aldrich
Water	HPLC grade	Fisher Chemicals

Table 2.2: Sample codes and sampling location details. Samples codes represent an abbreviation for each soil's country of origin: PT=Portugal, NL=The Netherlands, UK=United Kingdom, AU=Australia and GK=Greece. Samples with the letter C denote wettable control soils. [†] Samples UK1a, UK1b and UK1c were taken from the same location but sampled at 14/10/99, 24/11/99 and 06/08/02 respectively.

Sample	**Region**	**Site Location**	**Latitude/Longitude**	**Vegetation**	**Depth (cm)**
PT1	Aveiro	Gafanha do Areão	40°32' N, 8°46' W	Cabbage	0-10
PT2	Aveiro	Caldeiras	40°19' N, 8°46' W	*Eucalyptus globulus*	0-10
PT3	Aveiro	Berlingas	40°20' N, 8°47' W	*Pinus pinaster*	0-10
PTC	Aveiro	Berlingas	40°20' N, 8°47' W	*Pinus pinaster*	0-10
NL1	Zuid Holland	Ouddorp	51°48' N, 3°54' E	Grass & moss	0-10
NL2	Zuid Holland	Ouddorp	51°48' N, 3°54' E	Grass & moss	10-20
NL3	Zuid Holland	Ouddorp	51°48' N, 3°54' E	Grass & moss	20-30
NLC	Zuid Holland	Ouddorp	51°48' N, 3°54' E	Grass & moss	30-40
UK1a[†]	Gower	Nicholaston dunes	51°35' N, 4°06' W	Dune grasses & herbs	0-5
UK1b[†]	Gower	Nicholaston dunes	51°35' N, 4°06' W	Dune grasses & herbs	0-5
UK1c[†]	Gower	Nicholaston dunes	51°35' N, 4°06' W	Dune grasses & herbs	0-5
UK2	Gower	Pennard Golf Course	51°35' N, 4°06' W	Turfgrass	0-5
UKC	Gower	Nicholaston dunes	51°35' N, 4°06' W	Bare	0-5
AU1	Naracoorte	Pine Views	36°26' S, 140°40' E	Paddock	0-10
AU2	Naracoorte	Pine Views	36°26' S, 140°40' E	Paddock	0-10
AU3	Naracoorte	Pine Views	36°26' S, 140°41' E	Paddock	0-10
AUC	Naracoorte	Myome	36°30' S, 140°42' E	Paddock	0-10
GK1	Thrace	Dialambi, Rodopi	41°07' N, 25°07' E	Permanent pasture	0-12
GK2	Thrace	Mitriko, Rodopi	40°57' N, 20°19' E	Permanent pasture	0-5
GK3	Thrace	Abdera, Xanthi	40°56' N, 24°59' E	Dune grasses & herbs	0-19
GKC	Thrace	Maggana, Xanthi	40°55' N, 24°53' E	Winter wheat	0-26

2.3 Sub-sampling method

Sub-sampling has long been recognised as an important procedure due to the non-uniform nature of many soils. The principal cause for variation between two sub-samples is the separation of the gross soil sample according to particle size, *i.e.* larger particles remain on top while smaller particles accumulate at the bottom of the holding container. It is therefore necessary to use an effective sub-sampling method before any procedure is carried out upon a particular soil to ensure that the results obtained are a true reflection of the gross soil sample taken from the field and not just a reflection of a selected sub-sample. Various sub-sampling methods have been investigated previously and their relative merits assessed (Jackson 1958, Reeve 1994). The most effective sub-sampling method was found to be 'cone and quartering' (Jackson 1958). This method was therefore used to sub-sample each soil before extraction or analysis. The gross sample (*ca.* 2 kg) was formed into a cone with a large funnel and the top flattened. The cone was then divided into four equal quarters and two opposite segments were removed. These segments were combined and formed into a second cone using a smaller funnel. The resulting cone was then coned and quartered further until each sub-sample was of the size required for experimental work to be carried out. A schematic representation of this technique is given in Figure 2.1.

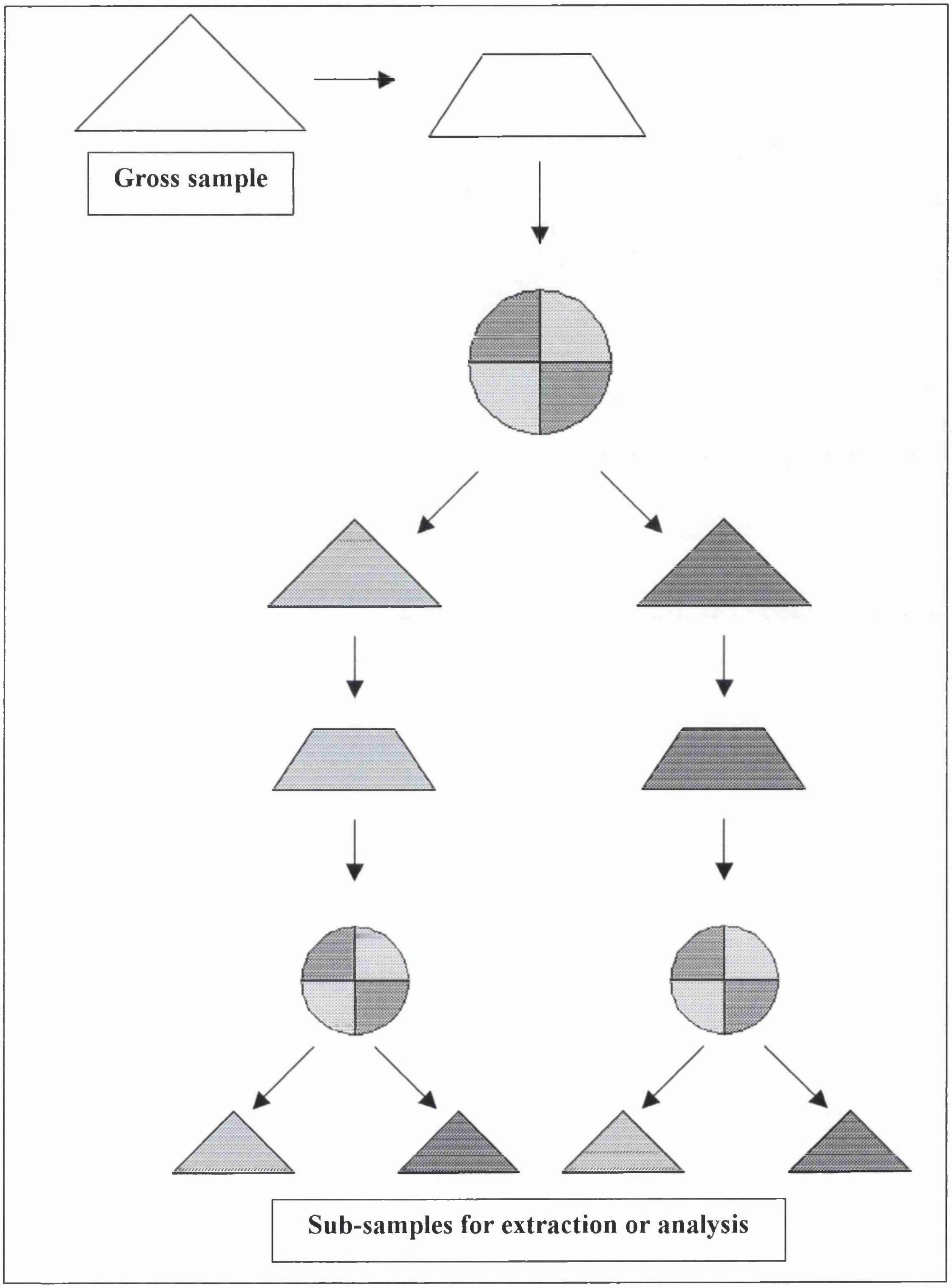

Figure 2.1: Schematic representation of the cone and quartering technique.

2.4 Sample characterization

2.4.1 Water repellency assessments

After equilibrating the samples in a controlled atmosphere of 20 °C and 45-55 % relative humidity (in a controlled temperature and humidity room) for 24 hours in order to avoid any influence of changing atmospheric conditions on measurement results (Doerr *et al.* 2002), water repellency was assessed using the Water Drop Penetration Time (WDPT) method. Approximately 10 g of sample was placed in a plastic dish (*ca.* 5 cm diam. x 1 cm depth) so as to form a layer *ca.* 0.5 cm deep. The sample surface was flattened by gently tapping the dish on a surface. Five drops of distilled water (*ca.* 80 µl at 20 °C) were then placed onto the sample surface (from a low height) using a dropper and the time for complete drop penetration noted (Letey 1969). Repellency values were recorded according to distinct repellency classes and are based on the median class of the 5 drops (Bisdom *et al.* 1993). Due to the WDPT repellency class interval sizes varying considerably, 'log mid-point WDPT' was used as a measure of repellency level for the purpose of plotting repellency versus other variables (Table 2.3). For example, a water drop penetrating a soil sample between 30 and 60 s would normally be given the 60 s WDPT class. To calculate the log mid-point value for this class, the mid-point between 30 and 60 s was taken as 45 s and the log mid-point value of 1.65 obtained.

Additional WDPT tests were carried out after drying another set of samples at 105 °C for 24 hours and then equilibrating them as described above. This procedure was included since previous studies have shown that some soil samples, either taken directly from the field or after extraction, which were wettable after drying at 20 °C developed water repellency after heating to 105 °C (Ma'shum and Farmer 1985, Dekker *et al.* 1998).

Table 2.3: WDPT class increments used in this study, log mid-point WDPT values for each class and corresponding descriptive repellency rating. Numbers denote the upper time limits (in seconds) for individual repellency classes.
† after Bisdom et al. (1993)
‡ arbitrarily taken as 2 × lower limit

WDPT classes	≤5	10	30	60	180	300	600	900	3600	18000	>18000
log mid-point WDPT	0.40	0.88	1.30	1.65	2.08	2.38	2.65	2.88	3.35	4.03	4.56‡
Repellency rating†	wettable	slight			strong			Severe		extreme	

2.4.2 Extraction procedure

Unless stated otherwise, extractions were carried out using a Soxhlet apparatus for 24 hours with 80 g of soil and 800 ml of solvent using Whatman cellulose thimbles (*ca.* 115 mm length × 30 mm diameter) with a 100 ml Soxhlet extractor. For the work reported in Chapter 5, extraction times were varied to assess the kinetics of the extraction procedure and extractions were carried out using Whatman glass microfibre thimbles (100 mm external length × 25 mm internal diameter) rather than the cellulose variety as an extra precaution in avoiding the potential risk of extract contamination by material extracted from cellulose thimbles. (Although glass microfibre thimbles were used for work reported in Chapter 5 it is worth noting that extraction of a cellulose thimble alone resulted in the removal of < 25 mg of solid (Mainwaring, personal communication)). When using isopropanol: aqueous ammonia (0.88 SG) (7:3, v:v) as extraction solvent the sample was pre-wetted with the solvent mixture for 15 minutes prior to refluxing. This was done as ammonia is lost to the atmosphere during the extraction. The extraction procedure was also carried out with the other extraction solvents used (chloroform, tetrahydrofuran, isopropanol, aqueous ammonia and water). After extraction, the solution was filtered and the liquid concentrated by rotary evaporation under reduced pressure. A fraction of the extract was retained as liquid for later use, and the remainder taken to dryness on a hot water bath. For the GC-MS analysis reported in Chapter 5 the whole extract solution was taken to dryness to maximise the amount of sample available for analysis.

2.5 Assessment of extracts

2.5.1 Extract re-applications following isopropanol: aqueous ammonia extraction

Following the procedures of Ma'shum *et al.* (1988), extracted material was filtered, heated gently on a water bath until a dry extract was obtained (*i.e.* of constant mass), re-dissolved in chloroform ($CHCl_3$), and reapplied to 5 g of wettable (WDPT <5 s) acid-washed sand (AWS) (to assess the ability of the extracts to induce water repellency). Laser particle size analysis (procedure described in Section 2.6.3.) shows the acid washed sand used has a mean particle diameter of 270 μm and distribution width of ±70 μm, which are intermediate values with respect to the soils investigated in this study (see Chapter 3). Since dried extracted material did not always fully re-dissolve, extract that had not been taken to dryness was also applied directly to AWS as an additional exploratory procedure. Note that this is effectively application from an isopropanol/water (*ca.* 7:3, v:v) mixture, because by this stage in the process there is little, if any, ammonia left in the extraction mixture. The ratio of sand to extract was chosen so that the extract was reapplied at the same mass ratio as it was extracted. As for the un-extracted soils, all samples were equilibrated for 24 hours in a controlled relative humidity of 45-55 % at 20 °C before WDPT tests were carried out. As control experiments, tests were also carried out on AWS samples after the application and evaporation of solvents alone. This procedure was found to have no effect on the wettability of the AWS.

2.5.2 Separation of extracted material

The dried extract was dissolved in a 200 ml chloroform and water mixture (1:1, v:v). The phases were separated and washed with 2 x 100 ml aliquots of the other solvent. Both phases were taken to dryness on a hot water bath. This allowed

2.6 Instrumentation

2.6.1 Scanning electron microscopy (SEM)

The surfaces of the soil samples' particles were investigated using SEM primarily to evaluate whether there were any distinguishing characteristics between water repellent and wettable soil samples. SEM images of soils pre- and post-extraction as well as acid washed sand samples with extracts reapplied were obtained using a *Philips FEI XL 30 CP* scanning electron microscope at the Department of Materials Engineering, University of Wales Swansea. The samples were analysed directly without any additional preparation.

2.6.2 Soil pH measurements

pH measurements were carried out on all soil samples to assess the influence acidic compounds may have in causing water repellency and whether any correlation existed between pH and water repellency. Measurements were made using a *Jenway 3010* pH meter calibrated at pH 4 and pH 10 using buffer solutions. Samples were prepared for measurement by placing in distilled water (2:1 w/w, water: soil), and allowing to equilibrate for 20 minutes before taking measurements. Typically, 10 g soil samples were used with 20 cm^3 aliquots of distilled water. Three independent measurements were made for each soil sample.

2.6.3 Particle size analysis

Particle size distribution and surface area analysis was carried out using a *Beckmann Coulter LS 230 Particle Size Analyzer (Dry Powder Module).* Specific surface area and mean particle diameter values were determined for all soil samples to determine whether correlations existed between these parameters and water repellency. Measurements were made assuming particles were spherical and non-porous. For each soil, three sub-samples were each analysed three times.

2.6.4 Thermogravimetric analysis and Differential scanning calorimetry

A *PL Thermal Sciences Ltd. (PL-STA 1500H)* instrument was used to analyse samples by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) to assess the change in mass of a sample and the changes in energy of a system respectively as a soil was heated. A water repellent and wettable soil were compared to establish if any there were any clear differences. *Ca.* 20 mg soil samples (oven-dried at 20 °C prior to analysis) were placed in platinum crucibles and heated to 1000 °C at a rate of 10 °C min^{-1} in a N_2 atmosphere.

2.6.5 Total organic carbon (TOC) analysis

Total organic carbon (TOC) measurements were made on all soils pre- and post-extraction to establish whether a relationship existed between the TOC content and water repellency and to assess extraction efficiency (in terms of the organic carbon removed). A *Skalar Primacs^{SC} TOC Analyzer* was used to make these measurements. As no calcium carbonate was detected (no CO_2 gas was produced on addition of acid to the soils), the inorganic carbon content in the samples analysed was assumed to be negligible and the total carbon (TC) content was used as a measure of the total organic carbon content. (Note: the test for calcium carbonate was carried out by other researchers (EU project partners) prior to receiving the soil samples for this study). The determination of total carbon content was based on the empty tube combustion method. A quartz crucible with typically a 300 – 350 mg sample (weighed with an external balance) was introduced into the combustion zone at a temperature of 1050 °C. In the presence of a catalyst (cobalt oxide) carbon in the sample is oxidized to carbon dioxide in a flow of oxygen. The flow of oxygen transports the carbon dioxide to the detector. The carbon dioxide is measured at 4.2 μm by IR detection and then recalculated to the total carbon content according to the calibration by a standard. Oxalic acid was used as a standard for the calibration of the instrument. At least three independent measurements were made for each soil sample. Depending upon the reproducibility of the results obtained more measurements were made in some cases. Runs were repeated as necessary in order to obtain, if reasonably possible, a standard deviation of $< 20\%$. Specific carbon based compounds were evaluated using approaches described in sections 2.6.6 – 2.6.8.

2.6.6 Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopic analysis

DRIFT spectroscopy was used in order to investigate the aliphatic fraction of the organic carbon present rather than simply the total amount. As with TOC analysis, measurements were made to evaluate whether a relationship existed between the aliphatic C-H content and water repellency and to assess extraction efficiency (in terms of the aliphatic compounds removed).

Two different FTIR spectrometers with diffuse reflectance attachments were employed in this work:

(a) *Mattson Satellite FTIR Spectrometer* equipped with a *Spectra Tech Diffuse Reflectance Unit* (0030-033) used to record DRIFT spectra of:

(i) All soil samples pre- and post-extraction. For each sample, 1024 scans were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Depending upon sample-to-sample reproducibility up to twelve independent samples were measured per soil. Runs were repeated as necessary in order to obtain, if reasonably possible, a standard deviation of < 20%.

(ii) Acid washed sand samples with soil extracts reapplied. For each sample, 16 scans were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}. Three independent sub-samples were measured per sample.

For the analyses carried out using this set-up, samples were placed in sample cups of 2.5 mm diameter and 2 mm depth and flattened using a glass microscope slide.

(b) *Perkin Elmer Spectrum One FTIR spectrometer* with *Perkin Elmer diffuse reflectance sampling accessory* used to record DRIFT spectra to assess the kinetics of Soxhlet extraction in terms of removing aliphatic hydrocarbons (as reported in Chapter 5). For each sample, 8 scans were recorded from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

For the analyses carried out using the *Perkin Elmer Spectrum One FTIR spectrometer* samples were placed in sample cups of 5 mm diameter and 3 mm depth and again flattened using a glass microscope slide.

In all sections of DRIFT work dried, ground potassium bromide was used to obtain a background spectrum before running samples.

2.6.7 Gas chromatography – flame ionisation detection (GC-FID) analysis

GC-FID was used to separate individual compounds present in the chloroform-soluble fractions of soil extracts. Gas chromatograms were obtained using a *Hewlett Packard 5890 series II* gas chromatograph equipped with a flame ionisation detector (FID) and a ZB5 5 % phenyl polysiloxane coated capillary column (30 m, 0.32 mm i.d., 1.0 μm df). 2 μl samples were injected splitlessly (0.6 min) and helium was used as the carrier gas. The temperature program used was 210 °C to 280 °C at 2 °C min^{-1}, held for 2.5 minutes, followed by ramping at 15 °C min^{-1} to a final temperature of 310 °C and held for 60 minutes, as shown in Figure 2.2. Both the injection port and the detector were set at 250 °C.

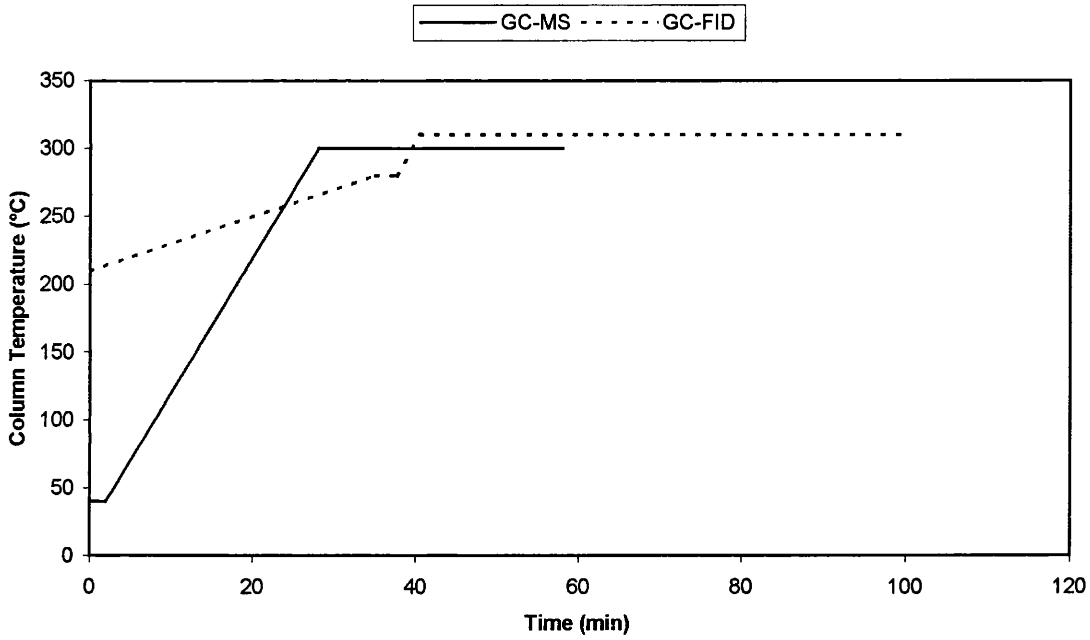

Figure 2.2: Temperature programs used for GC-MS and GC-FID analysis.

To quantify the amounts of alkanes present in soil extract UK1c (Chapter 5, Section 5.2.8) the chloroform-soluble fraction of the isopropanol: aqueous ammonia 24 h extract was analysed using a C_{30} linear alkane, triacontane ($C_{30}H_{64}$) as an internal standard. The calibration curve is shown in Fig. 2.3. A linear relationship between GC peak area and the mass of triacontane injected was obtained.

Response factors (Rf) for alkanes in the range C_{18}-C_{30} for this apparatus were previously determined by Mainwaring (personal communication) using tetradecane ($C_{14}H_{30}$) as an internal standard (Table 2.4). A calibration plot using C_{18}, C_{26}, C_{28} and C_{30} alkanes is shown in Fig. 2.4. Response factors for each alkane of interest (C_{27}, C_{29}, C_{31}, C_{33}) and the internal standard (C_{30}) were determined from this plot. Using the ratio of alkane response factor: internal standard response factor (Table 2.4) it was possible to calculate the mass of each alkane (C_{27}, C_{29}, C_{31}, C_{33}) injected onto the GC column and therefore estimate the mass of each alkane per kg of soil.

Example of calculation:

Each alkane peak area was multiplied by the calculated ratio value and converted into a mass value. For example: 8×10^{-7} g of internal standard was added to a sample of soil extract and injected onto the column. The area of the peak corresponding to the standard was 1.73×10^{7} (arbitrary units), whilst the area of the peak corresponding to the C_{31} alkane was 7.16×10^{6}. The ratio of C_{31} alkane Rf: internal standard Rf was 0.74. This ratio value was multiplied by the peak area for C_{31} alkane giving an adjusted peak area value of 5.37×10^{6}. Dividing this value by the internal standard peak area (5.37×10^{6} / 1.73×10^{7}) and then multiplying by the mass of internal standard injected (8×10^{-7} g) gives a mass of 2.48×10^{-7} g for the C_{31} alkane. This was the mass present in 2 μl of extract solution and corresponds to 307 μg kg^{-1} of soil.

Note: Two other amounts of internal standard (4×10^{-7} g and 2.4×10^{-7} g) were also added to extract samples. The same calculations were made and average μg kg^{-1} values were obtained for the results discussed in Chapter 5 (see Table 5.2).

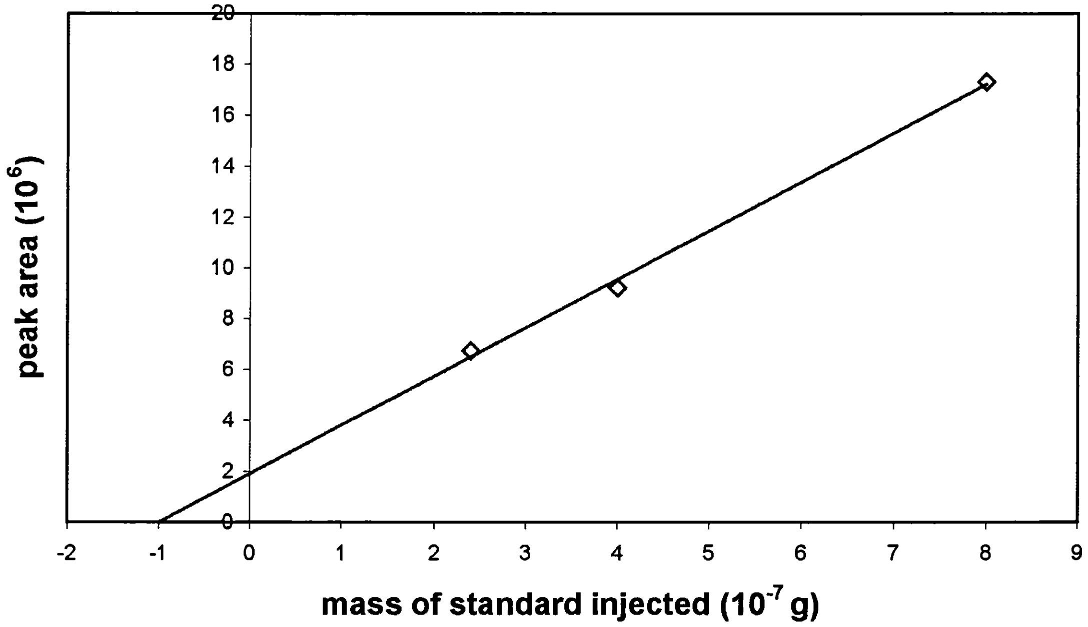

Figure 2.3: Relationship between peak area according to GC-FID and the mass of standard injected. $r^2 = 0.997$; slope = 1.91×10^{13} (unit area per gram); y-intercept = 1.91×10^6; x-intercept = -1.0×10^{-7}.

Table 2.4: Alkane Rf values and ratios of alkane Rf: internal standard Rf (internal standard Rf = 0.27). *Rf values determined by Mainwaring (personal communication).

Alkane	Response factor (Rf)*	Ratio of alkane Rf: internal standard Rf
$C_{27}H_{56}$ (heptacosane)	0.42	1.56
$C_{29}H_{60}$ (nonacosane)	0.31	1.15
$C_{31}H_{64}$ (hentriacontane)	0.20	0.74
$C_{33}H_{68}$ (tritriacontane)	0.09	0.33

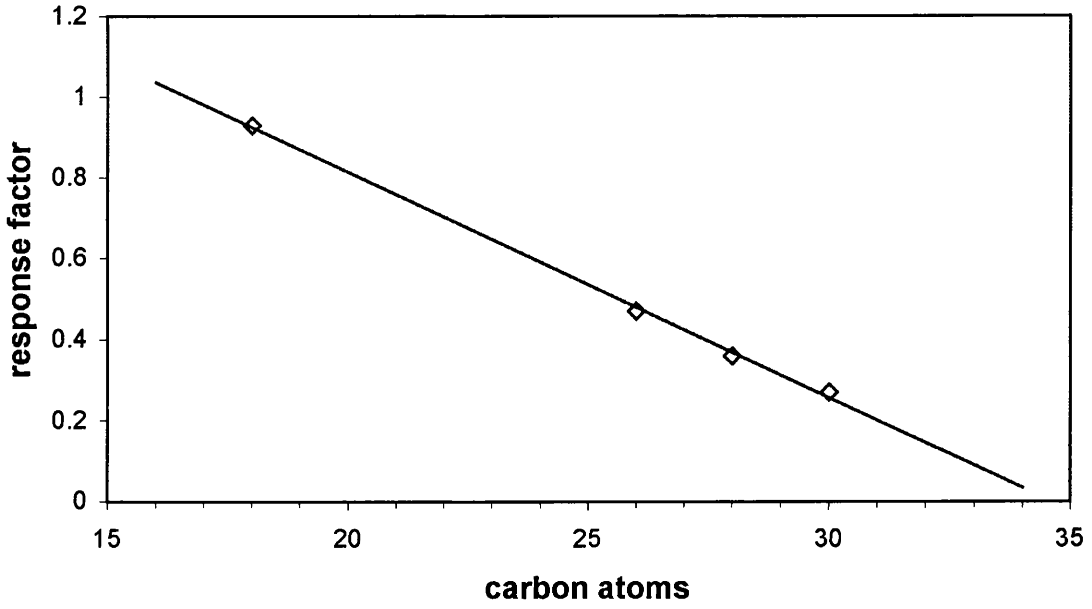

Figure 2.4: *Mainwaring (personal communication)*: Calibration plot for alkanes in the range C_{18}-C_{30}. $r^2 = 0.9986$; slope = -0.0557; y-intercept = 1.9284; x-intercept = 34.54.

2.6.8 Gas chromatography – mass spectrometry (GC-MS) analysis

GC-MS was used to separate and identify specific compounds associated with soil water repellency. A *Fisons GC8000* gas chromatograph interfaced directly with a *Fisons Masslab MD800* low-resolution GC-MS instrument was used to obtain electron impact (EI) mass spectra. The Fisons GC8000 gas chromatograph also contained a ZB5 5 % phenyl polysiloxane capillary column (15 m, 0.32 mm i.d., 1.0 µm df). 1 µl samples were injected splitlessly and hydrogen used as the carrier gas. The temperature program used was 40 °C isothermal for 2 minutes, then ramped at 10 °C min^{-1} to 300 °C and held for 30 minutes as shown in Figure 2.2. The injection port was set at 250 °C. Compounds were identified based on retention times, mass spectral interpretation, use of the NIST mass spectral search program and

NIST/EPA/NIH mass spectral library v.2.0, and comparison with authentic compounds.

2.6.9 Statistical analysis of data

Chatfield (1983) and Tebbutt (1998) were the texts used throughout for the statistical analysis of data. In all cases throughout the thesis the error estimates quoted are ± one standard deviation (*s*). Standard deviation (*s*) is the square root of the sample variance (s^2) of *n* observations, $x_1, x_2, \ldots, x_n$, and is given by

$$s = \sqrt{\left(\sum_{i=1}^{n} \frac{(x_i - \bar{x})^2}{n-1}\right)}$$

where $\bar{x}$ = mean value.

The standard deviation is expressed in the same units as the individual measurements. It can also be useful to measure the spread in relative terms by dividing the standard deviation by the sample mean. This ratio is called the coefficient of variation.

In some cases, for example, calculating the proportion of aliphatic C-H extracted from a soil involves the division of two values (the difference between pre- and post extraction values divided by the pre-extraction value) both of which have errors associated with them. It was therefore necessary to calculate the propagated error values using:

$$\frac{y}{Y} = \sqrt{\left(\frac{a}{A}\right)^2 + \left(\frac{b}{B}\right)^2}$$

where the ratio y/Y is the relative error in Y (*e.g.* the proportion of aliphatic C-H extracted), a and b are the errors of the variables A (*e.g.* pre-extraction value) and B (*e.g.* post-extraction value) respectively. The error in Y can then be calculated by multiplying by y/Y *by* Y.

Chapter 3

Characterization of water repellent soils and assessment of extraction procedures

3.1 Introduction

Different soils may exhibit different levels of water repellency, however, the reasons for this are not fully understood. Work presented in this chapter aims to find trends between general soil properties (*e.g.* particle size, surface area, pH) and water repellency. The general techniques and procedures used to characterize soil samples prior to chemical analysis are described, as well as an assessment of procedures used to extract material from soil samples.

Initially the surfaces of the samples' particles were investigated to evaluate whether there were any distinguishing characteristics between water repellent and wettable soil samples. Particle size analysis was used to measure mean particle diameter and surface area of soil samples and scanning electron microscopy (SEM) was used to image particle surfaces at high magnifications to assess whether any clear differences between particles from wettable and water repellent soils existed (such as a difference in the homogeneity of a particle coating). As all of the soils studied were of sandy texture (but varying widely in the severity of water repellency exhibited) it was not anticipated that these methods of evaluation would reveal particularly significant information regarding the causes of water repellency. However, it was essential to carry out such experiments to rule out: (i) potential relationships between water repellency and particle size/surface area and (ii) differences between particles from wettable and water repellent soils

Based on a range of previous studies it has been argued that water repellency is most commonly found in coarse, sandy textured soils (Roberts and Carbon 1971, De Bano 1981, Karnok 2002), although McGhie and Posner (1980) found that fine, clayey soils could also exhibit water repellency. Doerr *et al.* (1996) also demonstrated in a study on Portuguese soils that severe repellency occurred in all samples tested regardless of particle size. As water repellency is commonly found in sandy soils, all soil samples assessed in this study were of sandy texture to provide a comparable sample pool. It was speculated that the particle size (and therefore surface area) of a sample would influence how organic material might coat particles, which could in turn have an effect on the severity of water repellency. A given amount of organic material would be expected to coat a given amount of coarse sand (relatively low surface area) more thickly than it would coat fine sand (relatively high surface area). Doerr *et al.* (1996) speculated that if only a limited supply of hydrophobic substances is available then coarser particles would become most repellent. Conversely, if supply were ample then all particles would become similarly repellent. A relatively dense coating or multi-layer of organic compounds may be required to cause water repellency, although it has been suggested that only a thin or partial layer (possibly only a monolayer) is sufficient (Horne and McIntosh 2000, Karnok 2002).

Bisdom *et al.* (1993) identified differences between water repellent and wettable soils using scanning electron microscopy (SEM) to analyse different sieve fractions of soils. With increasing water repellency samples were found to contain more 'soil structures' and components that contained water repellent organic remains such as macro-aggregates, plant fragments and coatings on sand grains. However, it was noted by Doerr *et al.* (2000a) that since organic coatings can be as thin as a molecular monolayer they may remain undetected by SEM.

Once the particle surfaces had been investigated the next step was to assess each sample by chemical analysis. Soil water repellency is particularly common in coarse-textured sandy soils (Roberts and Carbon 1971, Karnok 2002), which consist primarily of quartz mineral (SiO_2) particles or other primary silicates (Brady and Weil 1999). Silicate particles themselves are wettable and the main cause of water repellency has been attributed to organic compounds coating the silicate mineral surfaces (Bisdom *et al.* 1993, Doerr *et al.* 2000a), although additional organic material may be present as interstitial matter (Franco *et al.* 2000a). To assess the amounts of material and the types of compounds present as coatings or interstitial matter, it is necessary to extract the material. In previous studies a number of extraction procedures and their relative extraction efficiencies have been assessed (Roberts and Carbon 1971, Ma'shum *et al.* 1988, Horne and McIntosh 1994, Hudson *et al.* 1994, Franco *et al.* 1995, Roy *et al.* 1999, Franco *et al.* 2000a, Doerr *et al.* in press (a)).

A range of solvents was also employed in previous studies and their relative extraction efficiencies assessed (in terms of the removal of both material and water repellency). Soxhlet extraction using isopropanol: aqueous ammonia (0.88 SG) (7:3, v:v) as extraction solvent was found to be effective in many previous studies (Ma'shum *et al.* 1988, Franco *et al.* 1994, 2000a, Horne and McIntosh 1994, 2000 and others summarised in Table 1.1). This was therefore selected as the standard procedure throughout this work, although other extraction solvents were used for specific investigations.

Water repellency assessments were performed on each soil sample pre-extraction using the water drop penetration time (WDPT) method. Repellency assessments were also carried out post-extraction as an initial assessment of extraction efficiencies in terms of the change in repellency level as a consequence of extraction. Extraction efficiencies were also assessed in terms of the masses of material extracted from each soil. Following the procedures of Ma'shum *et al.* (1988), the reapplication of the soil extracts obtained to acid washed sand (AWS) was also used to assess extraction efficiencies in terms of the ability of extracts to induce water repellency as measured by the WDPT method.

Exploratory thermal analysis experiments were also carried out, primarily to assess whether any noticeable differences existed between water repellent and wettable soils. Thermogravimetric analysis (TGA) was used to assess the change in mass of a sample as a result of the thermal degradation of the organic material present on the silicate particles. The use of differential scanning calorimetry (DSC) was also investigated to assess the changes in energy of a system by measuring the heat required to maintain the same temperature in a soil sample versus an empty sample crucible in the furnace. Finally, as carboxylic acids have been identified as one of the predominant types of compound found in water repellent soils (Hudson *et al.* 1994, Franco *et al.* 2000a, Ma'shum *et al.* 1998, McIntosh and Horne 1994, Morley *et al.* in press), pH measurements for each soil were obtained to assess the influence acidic compounds may have in causing water repellency.

3.2 Results and discussion

3.2.1 Particle size analysis

Particle size analysis was carried out on all soil samples. The surface area and mean particle diameter (with standard deviation) were obtained for each sample (Table 3.1).

Mean particle diameter values range from *ca.* 0.2 to 0.7 mm and specific surface area values from *ca.* 120 to 400 $cm^2 ml^{-1}$. Note the specific surface area and mean particle diameter of the acid washed sand used in reapplication of soil extract experiments (Section 3.2.5) are 235 $cm^2 ml^{-1}$ and 0.27 mm respectively and are intermediate values with respect to the soils investigated here. Figs. 3.1 and 3.2 show there is no correlation between specific surface area and water repellency level of sample (r^2 = 0.08) and mean particle diameter and repellency level (r^2 = 0.1) respectively (note: water repellency is represented by 'log mid-point WDPT' as described in section 2.4.1). However, this may not be surprising as the particle size range is relatively narrow across the soils investigated here. All samples are of a coarse, sandy texture as a result of their origin. Aeolian transport of the particles (transportation by the wind) has caused a sorting in terms of particle size.

Particle size distribution was also assessed for each sample. Table 3.2 shows the particle size distribution of each sample by indicating the percentage of sample volume in each particle diameter class. For example, 99.7 % by volume of soil GK3 consists of particles less than 1.00 mm, 87 % less than 0.50 mm diameter and 23 % less than 0.25 mm. Note that 100 % of all samples consist of particles of diameters less than 2.00 mm as all samples were sieved to less than this diameter to remove plant debris prior to analysis. It should also be noted the classification system used here is that used by the United States Department of Agriculture (USDA) and the International Soil Science Society (Brady 1999, Foth 1990). Each classification corresponds to a soil *separate,* i.e. a size group of particle diameters less than 2 mm. Sand is defined as '*material containing at least 85% sand, provided that the percentage of silt plus 1.5 times the percentage of clay shall not exceed 15*'

(Townsend 1974). It is the 2.00 to 0.05 mm fraction that can be subdivided into very coarse (< 2.00 mm), coarse (< 1.00 mm), medium (< 0.50 mm), fine (< 0.25 mm) and very fine sand (< 0.125 mm). Particles of even smaller diameter are classed as silt (< 0.05 mm and < 0.02 mm) and clay (< 0.002 mm).

Table 3.1: Particle size measurements. Samples with the letter C denote wettable control soils.

Sample code	Specific surface area ($cm^2\ ml^{-1}$)	Mean particle diameter (mm)	Standard deviation (mm)
PT1	122	0.57	0.23
PT2	148	0.46	0.16
PT3	144	0.47	0.16
PTC	133	0.50	0.17
NL1	407	0.27	0.22
NL2	338	0.23	0.10
NL3	294	0.22	0.08
NLC	294	0.22	0.07
UK1b	193	0.33	0.08
UK2	240	0.30	0.08
UKC	168	0.39	0.12
AU1	410	0.25	0.16
AU2	396	0.29	0.23
AU3	351	0.23	0.11
AUC	346	0.24	0.14
GK1	365	0.45	0.32
GK2	213	0.47	0.24
GK3	195	0.35	0.14
GKC	162	0.70	0.36
AWS	235	0.27	0.07

Examples of particle size distribution curves are shown in Fig. 3.3, which represent samples UK1b and GK1. The two samples were selected to demonstrate the extremes in sample homogeneity of the sample pool used here. Sample UK1b is relatively homogenous in terms of particle size, reflected by the relatively small coefficient of variation of 0.24 (*i.e.* standard deviation: mean value ratio). Sample

GK1 is an example of a relatively non-homogenous soil in terms of particle size, reflected by the relatively large coefficient of variation (0.71).

Table 3.2: Particle size distribution. Tabulated values correspond to the percentage of sample volume smaller than each particle diameter class.

	Particle diameter (mm)							
Sample code	**< 0.002**	**< 0.02**	**< 0.05**	**< 0.125**	**< 0.25**	**< 0.50**	**< 1.00**	**< 2.00**
PT1	0	0	0	0.065	0.94	44.7	94.7	100
PT2	0	0	0	0	5.44	66.5	99.8	100
PT3	0	0	0	0.029	3.86	65.3	99.4	100
PTC	0	0	0	0.00082	1.66	57.1	98.7	100
NL1	0.072	0.53	2.41	11	64.8	92.1	97.3	100
NL2	0.049	0.22	0.51	3.25	68.9	97.9	99.9	100
NL3	0	0	0	2.38	72.2	98.8	99.99	100
NLC	0	0	0	2.01	72.3	99.7	100	100
UK1b	0	0	0	0	15.9	96.9	99.99	100
UK2	0.0065	0.23	0.78	2.28	24.2	98.5	100	100
UKC	0	0	0	0	6.93	86.5	99.6	100
AU1	0.041	0.56	2.79	13.8	64.3	93.4	99.6	100
AU2	0.039	0.77	2.77	12.7	58.9	88.1	97.6	100
AU3	0.011	0.26	1.46	9.21	66.8	96.7	99.6	100
AUC	0.045	0.27	0.73	6.54	66.4	97.9	99.8	100
GK1	0.07	1.07	3.39	11.4	31.7	65.8	93.3	100
GK2	0.000022	0.51	1.68	3.86	12.5	62.9	96	100
GK3	0	0	0	0.3	23	87	99.7	100
GKC	0.027	0.37	0.75	1.26	5.9	32.5	80.2	100
AWS	0	0	0	0.0067	42.2	99.4	100	100

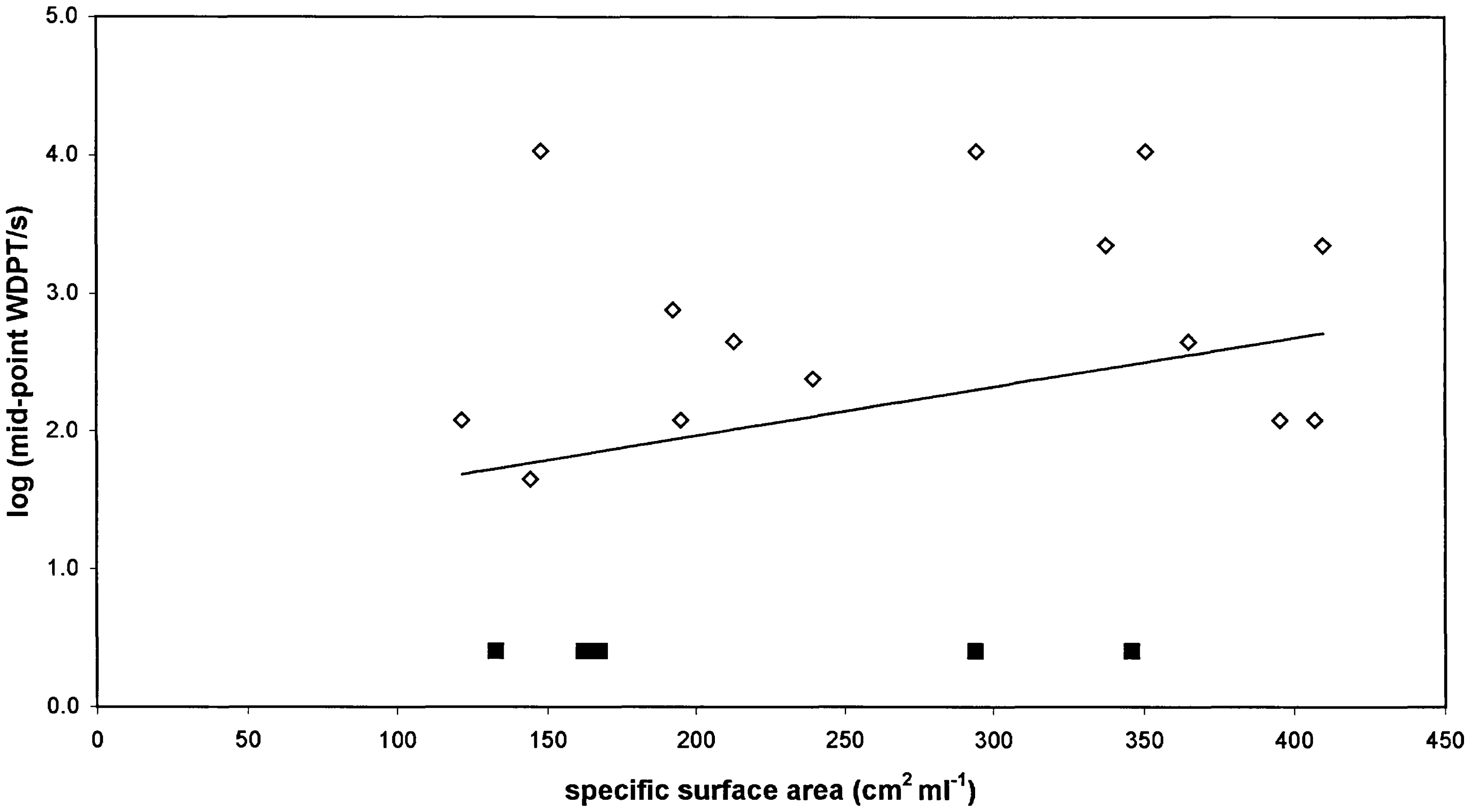

Figure 3.1: Specific surface area of soil samples *vs.* log mid-point WDPT. ◇= repellent samples; ■= wettable control samples. $r^2 = 0.08$; slope = 0.0036 (±0.0029); intercept = 1.25 (±0.82).

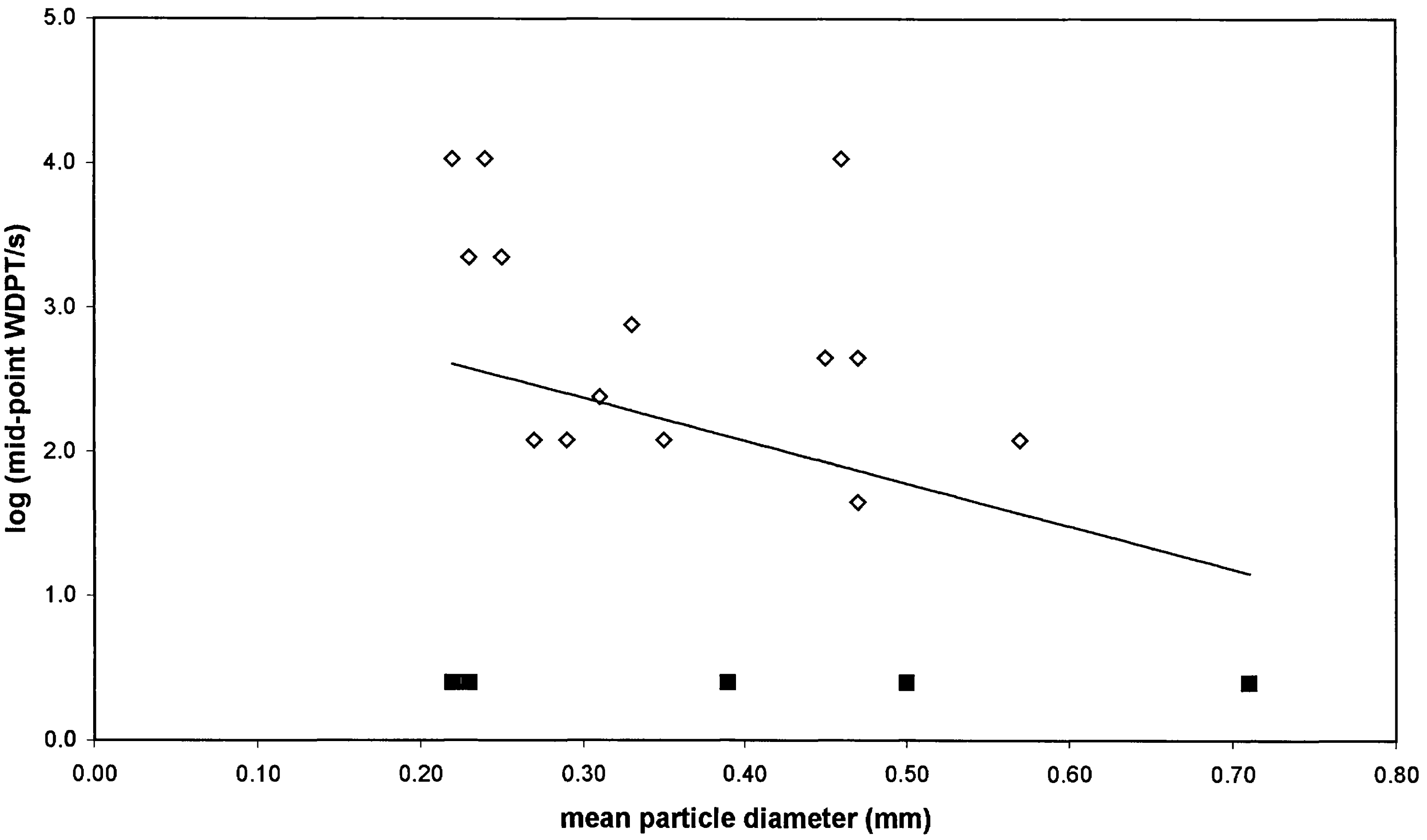

Figure 3.2: Mean particle diameters of soil particles *vs.* log mid-point WDPT. ◇= repellent samples; ■= wettable control samples. $r^2 = 0.1$; slope = -2.96 (±2.15); intercept = 3.26 (±0.84).

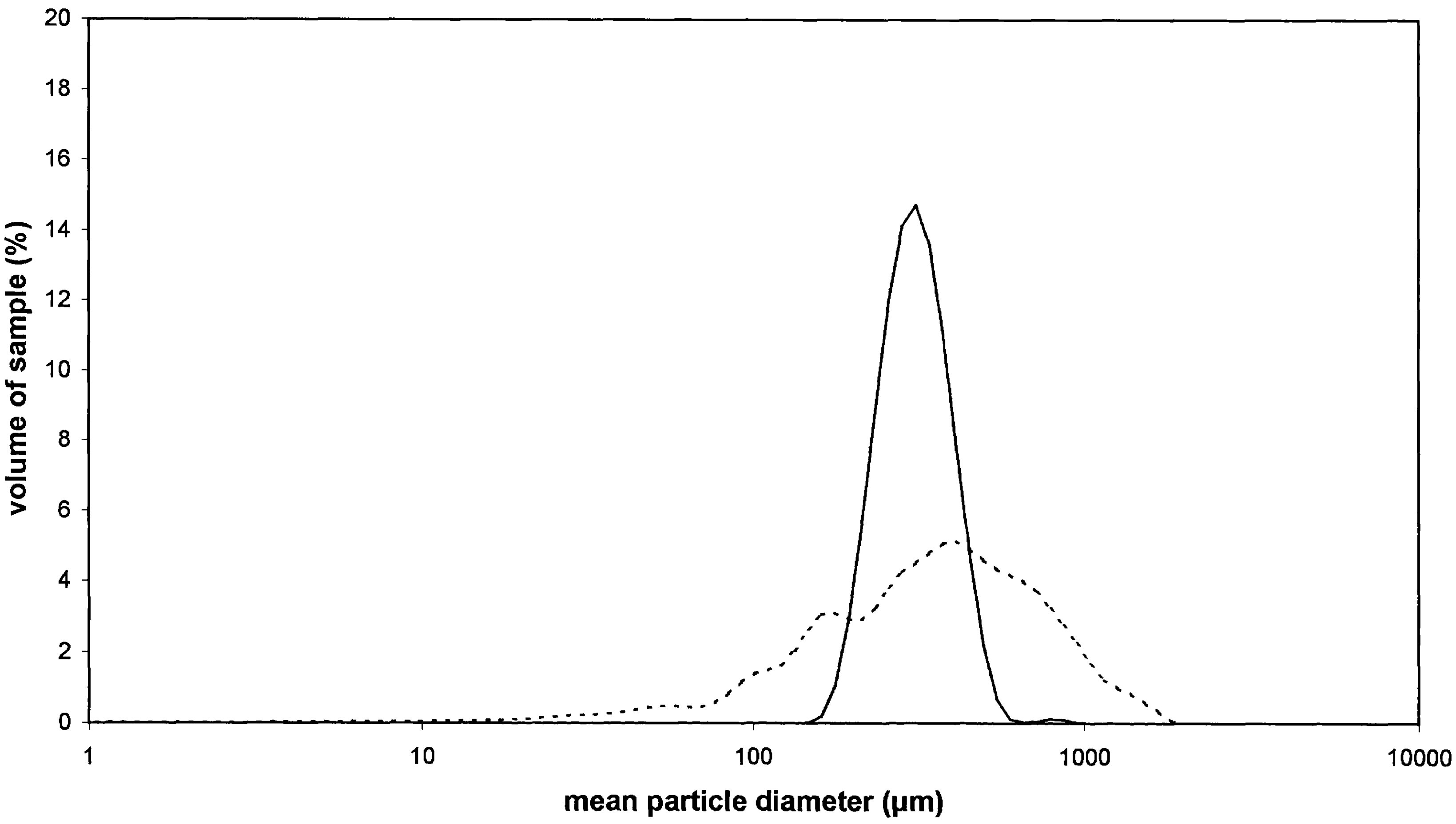

Figure 3.3: Particle size distributions for soil samples UK1b (full line) and GK1 (dashed line).

3.2.2 Scanning electron microscopy (SEM)

As an exploratory study, analysis of samples by SEM was carried out to examine the surfaces of soil particles, primarily to evaluate whether there were any distinguishing characteristics between water repellent and wettable soil samples at the level of magnification afforded by SEM. Scanning electron micrographs of the following samples were assessed and compared (Figures 3.4 - 3.14):

1. Water repellent and wettable soil samples dried at 20 °C (pre-extraction);
2. Water repellent sample dried at 105 °C (pre-extraction);
3. Water repellent sample dried at 20 °C (post-extraction);
4. Water repellent samples of varying homogeneity in terms of particle size and shape (pre-extraction);
5. Acid washed sand samples reapplied with soil extract from a water repellent soil, dried at both 20 °C and 105 °C.

A few particles of each soil sample were examined and one or two particles which were typical of each sample are shown in Figures 3.4 – 3.14. The soil material sampled in the UK (repellent samples UK1b, UK2 and wettable sample UKC) was chosen to assess any differences between water repellent and wettable soils (Figs. 3.4–3.6). There did not appear to be any features that distinguished repellent soils from wettable ones. All three micrographs are similar although UK1b and UKC show more resemblance to each other, in terms of the evenness of the particle surface and attached smaller particulate matter, than to UK2. The particles of soil UK2 have a relatively uneven surface compared to those of UK1b and UKC. There is also more smaller particulate matter attached to the larger particles present in the UK2 sample.

Although sample UK1b is water repellent and UKC is wettable both are dune soils sampled from the same location (Table 2.2). They are soils of the same type and origin, having been exposed to the same natural processes such as aeolian transport, abrasion and in situ weathering. It is therefore not surprising that the size and shape of the particles are very similar.

Soil UK2 was sampled from a golf course, and may well have been subjected to non-natural chemical processes, such as the application of fertilizers and pesticides to promote the growth of a high quality sports turf whilst minimising unwanted weed growth. In addition to this, whilst the golf course is built on the same dune sand complex as samples UK1b and UKC the soil will have been supplemented by 'topdressing', which involves adding sandy material of various origins to the top of the thatch layer. These factors may be an explanation for the difference in surface characteristics observed here.

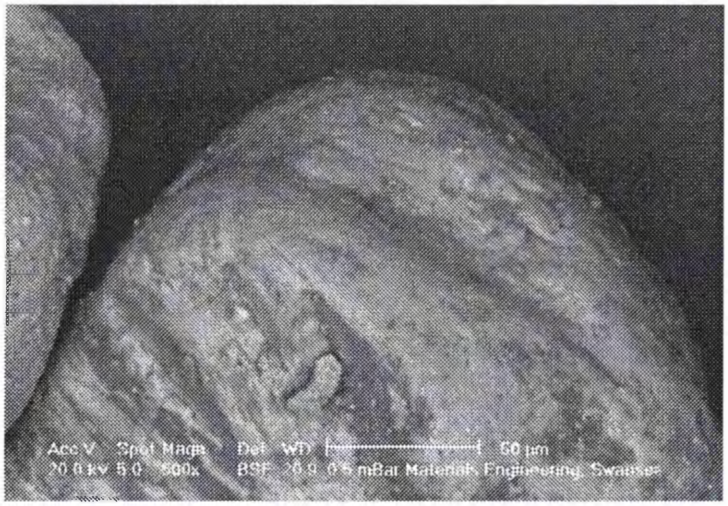

Figure 3.4: SEM of a water repellent soil sample (UK1b).

Figure 3.5: SEM of a water repellent soil sample (UK2).

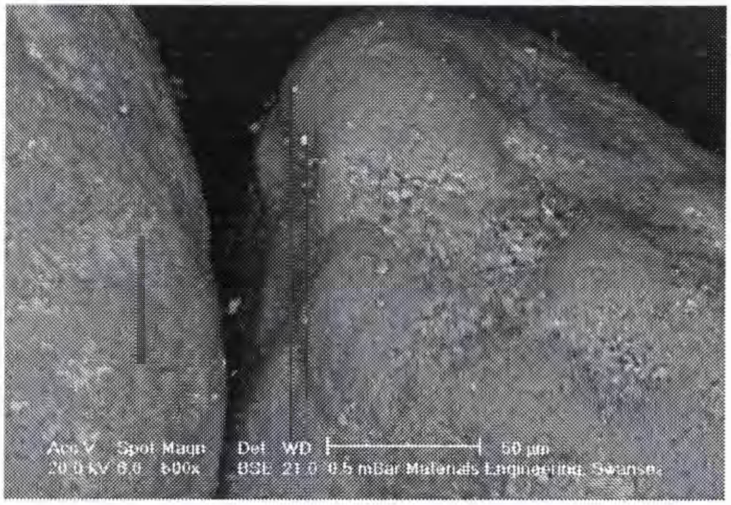

Figure 3.6: SEM of a wettable soil sample (UKC).

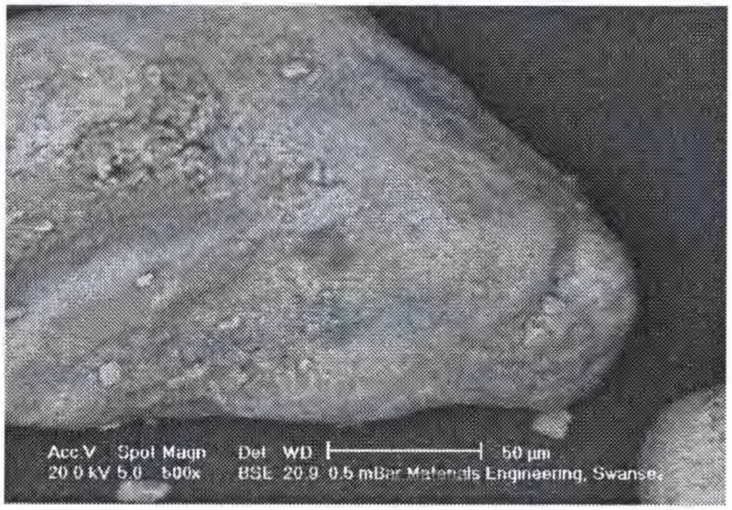

Figure 3.7: SEM of water repellent soil sample NL3 pre-extraction.

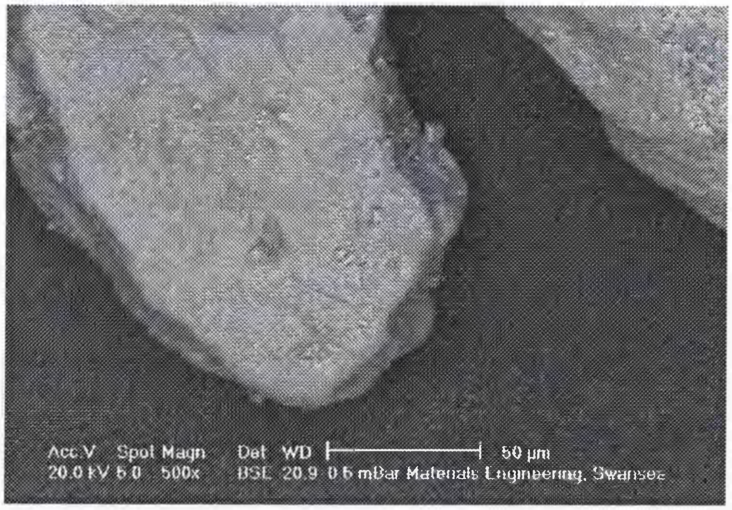

Figure 3.8: SEM of water repellent soil sample NL3 post-extraction.

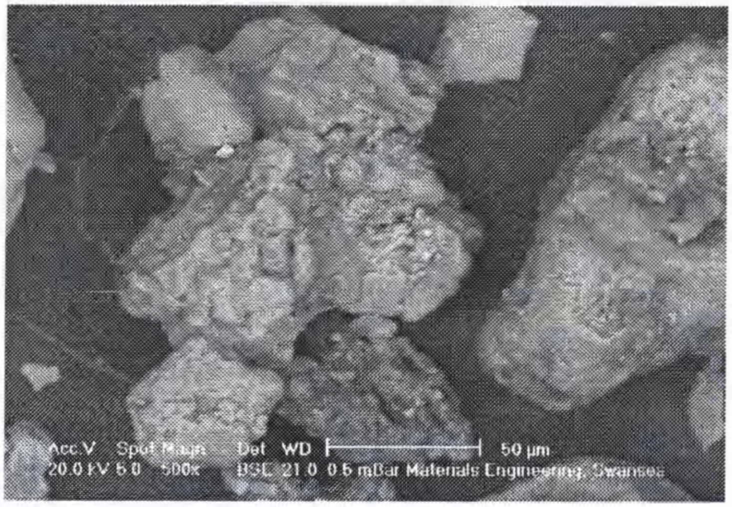

Figure 3.9: SEM of soil sample AU1 dried at 20°C.

Figure 3.10: SEM of soil sample AU1 dried at 105°C.

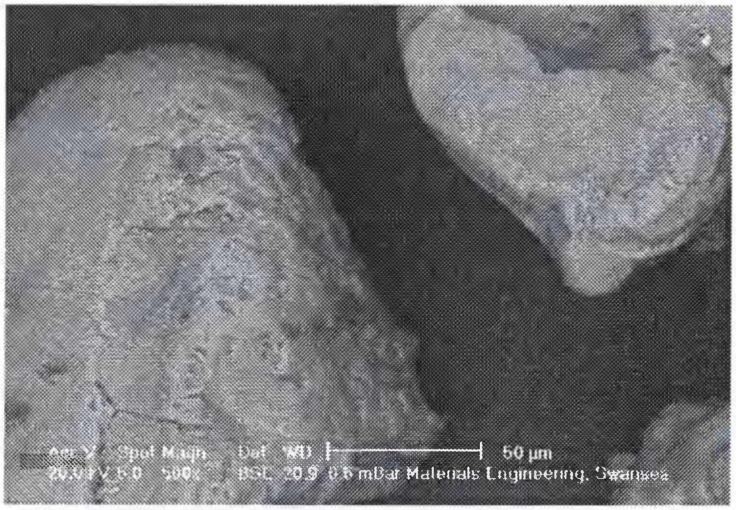

Figure 3.11: SEM of soil sample AU3.

Figure 3.12: SEM of soil sample GK2.

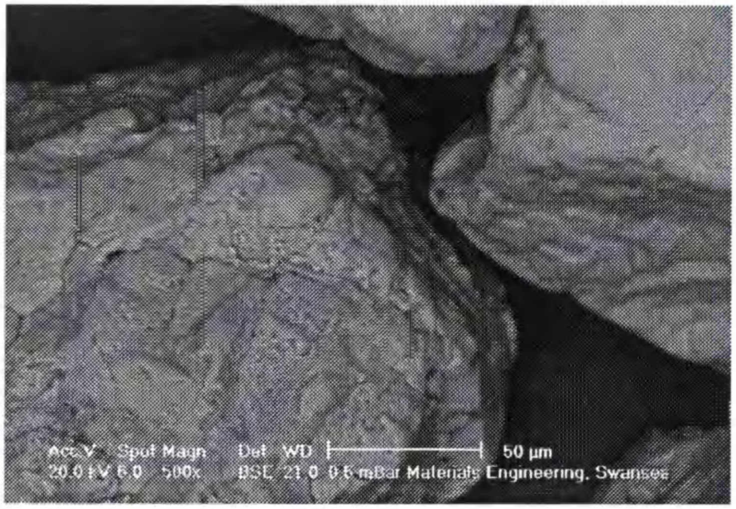

Figure 3.13: SEM of AWS after application of AU3 soil extract (dried at 20°C).

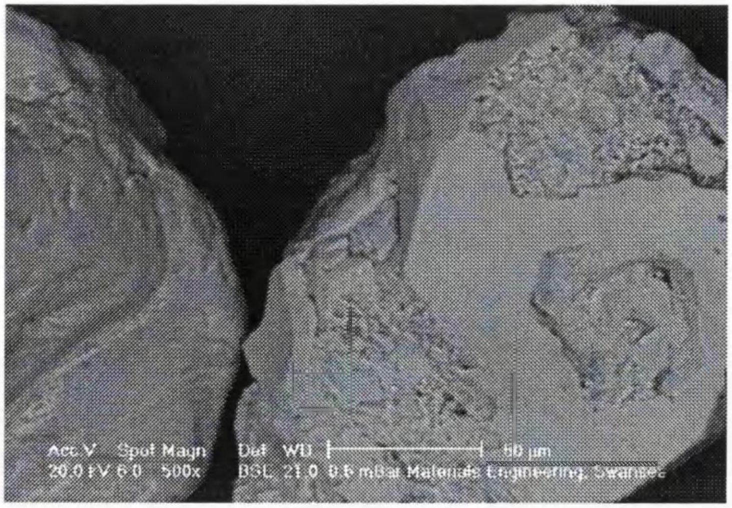

Figure 3.14: SEM of AWS after application of AU3 soil extract (dried at 105°C).

Figs. 3.7 and 3.8 show particles of a water repellent soil (NL3) pre- and post-extraction respectively. Pre-extraction the soil was extremely repellent but the extraction procedure rendered it wettable (Table 3.6). Once again, the difference between the particles in the two micrographs is negligible although the particle surface of the extracted soil does appear smoother. This suggests that the extraction procedure used (Section 3.2.3) has removed some of the particulate matter and effectively 'washed' the surface of the smaller particles, although some particulates still remain on the surface. This observation complements the mass extracted results (Table 3.4), water repellency assessments (Section 3.2.4) and DRIFT results (Chapter 4). The mass of material removed during extraction is small (Table 3.4), therefore the difference between the particles pre- and post-extraction would not be easily visible on this scale.

In many pedological studies soil samples taken from the field are dried at 20 °C or 105 °C for at least 24 hours prior to further analysis. In previous studies (Dekker and Ritsema 1994a, Roy *et al.* 1999, Franco *et al.* 2000a) and in this work (Section 3.2.4) it has been demonstrated that, in some cases, drying water repellent soil samples at an elevated temperature of 105 °C can cause the severity of water repellency in a sample to increase. To assess any change in surface characteristics caused by this elevated drying temperature scanning electron micrographs of sample AU1 dried at both 20 and 105 °C were obtained (Figs. 3.9 and 3.10 respectively). For soil AU1 repellency increased from 'severe' to 'extreme' using the repellency rating shown in Table 2.3 (Bisdom *et al.* 1993). Assessing the particles in the two micrographs does not reveal any information regarding the effect of drying the sample at an elevated temperature, although heating at 105 °C is unlikely to visibly alter the surface to the extent that it would be detectable at the magnification used here (500×). Removal of adsorbed water molecules and/or a re-arrangement or re-ordering of organic material at a molecular level is likely to be responsible for the increased severity in water repellency.

Soil samples of different homogeneity were also assessed. The two soils examined were AU3 (extremely repellent) and GK2 (strongly repellent) (Figs. 3.11 and 3.12 respectively). These were selected as they demonstrate the extremes in homogeneity of the sample pool used in this work. Soil AU3 was extremely homogenous in terms of particle size, shape and colour, whilst GK2 was less homogenous, containing large amounts of particulate matter of varying shape, size and colour. Soil GK2 was one of two samples that were not rendered wettable as a result of extraction (Section 3.2.4).

To assess the ability of soil extracts to induce water repellency, extracts were reapplied to wettable acid washed sand (AWS) (followed by drying at 20 and 105 °C as for the original soil samples) and water repellency assessments were performed

(Section 3.2.5). This is similar to the method used to assess extracted material by Ma'shum *et al.* (1988). Scanning electron micrographs of acid washed sand samples treated with soil extract were obtained to assess the reapplication procedure by comparing the particle surfaces with those of original soil particles. Figs. 3.13 and 3.14 show acid washed sand after reapplication of soil extracts and drying at 20 and 105 °C respectively. For the sample dried at 20 °C (Fig. 3.13) the extract coated the sand particle evenly and there was very little difference between its surface and that of actual soil samples. After drying the sample at 105 °C the extract did not coat the particle shown as evenly (Fig 3.14). Certain parts of the particle shown were coated more generously than others, though this may not have been a result of the higher drying temperature but rather the particle shape initially.

In conclusion, at the level of magnification afforded by SEM it was not possible to distinguish water repellent soil samples from wettable ones. (Note: the SEM analysis was provided as a service by the Department of Materials Engineering, University of Wales Swansea and therefore a more detailed investigation at different levels of magnification was not carried out). Similarly, any difference between an initially repellent sample pre-extraction and the same sample rendered wettable post-extraction was negligible. Comparison of the particle surface characteristics (i.e. size and shape) of the sandy soils assessed here did not therefore indicate any specific relationship with water repellency. This emphasises the need to assess the differences between repellent and wettable samples at a molecular level by chemical analysis.

3.2.3 Extraction procedure

An exploratory evaluation of a range of solvents employed in previous studies by others such as Ma'shum *et al.* (1988), Horne and McIntosh (1994), Franco *et al.* (1995) was carried out by others in our group (reported in Doerr *et al.* in press (a)) using the strongly water repellent sample UK1a (WDPT 600 s) and the wettable sample UKC (WDPT <5 s) as a control. 100 g of dry soil and 500 ml of solvent using Soxhlet apparatus were used for these experiments. Solvents, in order of increasing polarity, included hexane, toluene, dichloromethane, isopropanol, and isopropanol: aqueous ammonia (0.88 SG) (7:3, v:v). After extraction the soils were air-dried at 20 °C and tested for repellency, and the masses of material extracted were determined. Their results are shown in Table 3.3. Isopropanol: aqueous ammonia (0.88 SG) (7:3, v:v) was found to be the most effective extraction solvent in terms of the mass of material extracted and removal of water repellency. Other studies also found isopropanol: aqueous ammonia to be an efficient/best extraction solvent (Ma'shum *et al.* 1988, Franco *et al.* 1994, 2000a, Horne and McIntosh 1994, 2000 and others summarised in Table 1.1). Extraction with the less polar, organic solvents, dichloromethane, hexane, isopropanol and toluene was considerably less effective. The four organic solvents rendered the soil more water repellent (pre-extraction WDPT 600 s; post-extraction WDPT 18000 s) despite removing some material (although considerably less was removed compared to extraction with isopropanol: aqueous ammonia). These observations were in agreement with other studies where a wider range of solvents was evaluated in extracting Australian (Ma'shum *et al.* 1988, McGhie and Posner 1980) and Canadian soils (Roy *et al.* 1999).

Table 3.3: *Doerr et al. (in press (a))*: Efficiency of Soxhlet extractions with different solvents on sample UK1a (bold; WDPT class 600 s) and the wettable control sample UKC (italics; WDPT <5 s).

Solvent	Hexane[†]	Dichloromethane[†]	Toluene[†]	Isopropanol[†]	Isopropanol:ammonia
Mass extracted	**368**	**418**	**881**	**1240**	**2024**[‡]
(mg kg^{-1})	*54*	*18*	*46*	*590*	*226*[¶]
WDPT class (s)	**18000**	**18000**	**18000**	**18000**	**< 5**
(post-extraction)	*< 5*	*< 5*	*< 5*	*< 5*	*< 5*

[†] Extraction duration: 60-67 hours [‡] Extraction duration: 48 hours [¶] Extraction duration: 24 hours

In many previous studies the efficiency of extraction procedures has been assessed in terms of the mass of material extracted (Franco *et al.* 1995, Horne and McIntosh 1994, Ma'shum *et al.* 1988, McIntosh and Horne 1994, Roy *et al.* 1999). In the work presented in this thesis, to obtain results comparable to other studies, the mass of material extracted from each soil sample was therefore measured as an initial method of assessing extraction efficiency. For each extraction the soil to be extracted was weighed prior to extraction and the mass of extract obtained was recorded. The mass of extract from each sample was then converted to mass of extract obtained per kilogram of soil extracted (g kg^{-1} values are therefore used throughout). In this study, unless stated otherwise, the isopropanol: aqueous ammonia (0.88 SG) (7:3, v:v) solvent mixture was used to extract all soil samples as described in Section 2.4.2. In addition, chloroform, tetrahydrofuran, isopropanol, aqueous ammonia and water were also used to extract a single soil sample (UK1c) in order to assess the extraction efficiency when using different solvents (Table 3.5).

Results of isopropanol: aqueous ammonia extractions with respect to masses of material extracted for all samples are given in Table 3.4. On average, each sample was extracted five times to estimate the errors involved. Masses extracted ranged from *ca.* 0.25 to 9.8 g kg^{-1} of soil. The lowest value derived from a wettable dune sand with a low organic matter content (UKC), while the highest value was from the top layer of an organic-rich, grass-covered water repellent sand (NL1). Since it is generally accepted that compounds causing water repellency are of organic origin it was thought this finding might suggest a relationship between sample repellency and the mass extracted.

Table 3.4: Mean masses of material extracted by Soxhlet extraction with isopropanol: aqueous ammonia (7:3, v:v) (g kg^{-1}). Error estimates are typically based on 1 standard deviation of 5 independent measurements. Samples with the letter C denote wettable control soils.

Sample code	Mass extracted (g kg^{-1})
PT1	1.55 (±0.31)
PT2	3.28 (±0.40)
PT3	1.22 (±0.55)
PTC	1.28 (±0.44)
NL1	9.76 (±1.50)
NL2	2.64 (±0.33)
NL3	1.10 (±0.06)
NLC	0.55 (±0.23)
UK1b	1.17 (±0.52)
UK2	2.41 (±0.28)
UKC	0.23 (±0.03)
AU1	2.64 (±0.57)
AU2	3.67 (±1.26)
AU3	0.83 (±0.47)
AUC	0.86 (±0.61)
GK1	2.62 (±0.79)
GK2	3.02 (±1.90)
GK3	0.41 (±0.18)
GKC	2.32 (±0.54)

There was a very general 'correlation' between sample repellency and mass extracted, in that there were no soils which showed both a high extraction efficiency in terms of mass extracted and low WDPT results (Table 3.6) and few soils which showed a low extraction efficiency and high WDPT results, but in the general region of moderate extraction efficiency and moderate WDPT results the correlation between mass extracted and WDPT time was very poor (Fig. 3.15). These observations applied regardless of whether only samples of similar origin, type or vegetation (Table 2.2), or the complete sample pool was considered.

The effect of varying the extraction solvent was also assessed by determining the mass of material extracted and post-extraction water repellency level for a single soil sample, UK1c (Table 3.5).

Table 3.5: Efficiency of Soxhlet extractions with different solvents on sample UK1c (WDPT class 18000 s).

Solvent	Isopropanol: aq. ammonia	Chloroform	Tetrahydrofuran	Isopropanol	Aq. ammonia	Water
Mass extracted (mg kg^{-1})	1491	250	117	344	10554	3660
WDPT class (s) post-extraction	< 5	> 18000	> 18000	> 18000	< 5	< 5

The use of lower polarity organic solvents (chloroform, tetrahydrofuran and isopropanol) resulted in poor extraction efficiency in terms of both mass of material extracted and post-extraction repellency. The masses extracted were between *ca.* 5% and 25% of that extracted with the standard isopropanol: aqueous ammonia solvent mixture whilst post-extraction repellency level increased from WDPT class 18000 s to > 18000 s in all cases. These observations are in agreement with previous studies (Ma'shum *et al.* 1988; Roy *et al.* 1999). Although extraction efficiency was low after extraction with low polarity solvents, soils contained less non-polar organic material and could, therefore, be expected to be less repellent as a result. However, the fact that treatment with these solvents caused increases in repellency suggests that water repellency is not simply related to the amount of non-polar organic material present

(Roy *et al.* 1999, Litvina *et al.* 2003). Using highly polar, aqueous solvents such as water and aqueous ammonia resulted in much higher extraction efficiency in terms of masses extracted as well as rendering the samples wettable. Water extracted more than double the amount extracted by isopropanol: aqueous ammonia whilst using aqueous ammonia alone resulted in more than a six-fold increase in extraction efficiency. The isopropanol: aqueous ammonia solvent mixture, being amphiphilic in nature, was therefore an intermediate extraction solvent with respect to polarity as well as mass of material extracted, although the soil was rendered wettable (WDPT: < 5 s). However, it is shown by TOC analysis (Chapter 4) that the material extracted by water must be predominantly inorganic as no organic carbon is removed and although both water and aqueous ammonia alone extract large amounts of material it is shown by DRIFT analysis (Chapter 4) that they remove less aliphatic carbon than isopropanol: aqueous ammonia.

The different effects exhibited after extraction with either low polarity or aqueous solvents were also observed by McGhie and Posner (1980). In their study sequential extractions were performed with a range of low polarity and aqueous solvents. It was found that repetition of sequential treatment with hot water and chloroform produced the same effects on soil water repellency. The soil was always wettable after treatment with the hot water and repellent after treatment with chloroform. It was speculated that the use of highly polar solvents caused a dispersion of the material on the soil particles leading to the presentation of a greater proportion of wettable surfaces in the soil on drying. An explanation for the observations when using less polar solvents was that the water repellent organic matter probably remains in suspension, tending to concentrate on the external surfaces of particles on evaporation of the solvent. Wallis and Horne (1992) also ascribed observations of this nature to either molecular re-orientation of organic matter or re-distribution of repellent material on exposed wettable surfaces. Similar 'reversible' water repellency was observed by Ma'shum and Farmer (1985) when wetting and drying soil samples and was described as being likely to be due to changes in molecular conformation of the organic matter. It was suggested that polar (*i.e.* hydrophilic) groups such as hydroxyl, carboxylic acid, carboxylate and amide would be exposed on surfaces of the organic matter and therefore interact with water molecules when a soil was wet. When dried, the re-orientation of polar groups so as to interact with each other (as water is lost) would cause the organic matter to largely present non-polar groups at the surface, such as methyl and methylene, which would not interact with water molecules and thus exhibit water repellency.

Based on the results given in Table 3.5, the polarity of the extraction solvent is evidently an important factor in determining the efficiency of extraction (both in terms of mass extracted and post-extraction repellency level). The effect of alkalinity is also relevant in the case of aqueous ammonia. In a study on oil-contaminated water repellent soils by Roy *et al.* (1999), a range of solvents was assessed including low polarity organic solvents and three amphiphilic mixtures; isopropanol: aqueous ammonia, isopropanol: acetic acid and isopropanol: water. These amphiphilic mixtures were selected to assess whether acid-base properties enhanced extraction efficiencies. The low-polarity organic solvents were the least efficient in terms of the removal of repellency and the masses of material removed, whilst extraction with the amphiphilic mixtures extracted the largest amounts of material, rendering the soils wettable. Results therefore suggested that it is the amphiphilicity of a solvent that is the most important property contributing to the removal of repellency and that alkalinity only slightly improves extraction efficiency.

As mentioned previously, carboxylic acids make up an important group of the extracted compounds and the role of an extraction solvent such as ammonia may well be two-fold: to provide a transient base for neutralisation of insoluble acids to give soluble salts; and to provide OH^- ions which can compete with $RCOO^-$ for cations on and around the silica surface. In the early stages of an isopropanol: aqueous ammonia extraction the mixture is rich in ammonia and is alkaline. This alkalinity is expected to assist in the extraction of compounds such as acids by bringing them out as ammonium salts. As the extraction proceeds, and also in the subsequent concentration of the extract by evaporation, ammonia is lost to the atmosphere and the equilibrium between the protonated form and the ammonium salts of these weak acids will shift to favour the former, to give, as is found, the organic acids rather than ammonium salts in the extraction mixture.

As the standard isopropanol: aqueous ammonia mixture contains only 30% aqueous ammonia by volume, during extraction the ammonia would all be lost sooner than if 100% aqueous ammonia was used. This would explain the higher extraction efficiency in terms of mass extracted when using aqueous ammonia as opposed to isopropanol: aqueous ammonia (7:3, v:v) mixture. After a 24 h extraction with aqueous ammonia the resulting extraction mixture still had a strong smell of ammonia, suggesting some of the initial ammonia remained. Extraction with the isopropanol: aqueous ammonia mixture revealed that after 4 – 8 h of extraction most of the ammonia had been lost to the atmosphere, as there was very little or no smell of ammonia in the extraction mixture (experiments reported in Chapter 5). The mass of material extracted after the initial 4 – 8 h of extraction was therefore significantly less than during the first few hours (Fig. 5.1). As a result, the overall mass of material extracted compared to using 100% aqueous ammonia was also significantly less. It should be noted that although using aqueous ammonia was more efficient in terms of mass extracted, soil samples were rendered wettable as a result of extraction by both isopropanol: aqueous ammonia mixture and aqueous ammonia alone. The isopropanol component of the isopropanol: aqueous ammonia mixture may have aided the extraction of compound types that aqueous ammonia may not have been able to extract alone, though the composition of the aqueous ammonia extract was not analysed to test this.

3.2.4 Water repellency assessments

Water repellency assessments of all soils pre- and post-extraction were carried out using the WDPT method (results given in Table 3.6). Pre-extraction WDPT results (after drying at 20 °C) indicated that fourteen soils were water repellent (WDPT values ranging from 60 s to 18000 s) and five were wettable (WDPT < 5 s). To assess correlations with other parameters, 'log mid-point WDPT' values were plotted to represent water repellency (described in Section 2.4.1).

3.2.4.1 Effect of extraction on water repellency

Of the 14 repellent samples investigated, all but two were rendered wettable after the extraction and drying (at both 20 and 105 °C), and all four control samples remained wettable (results given in Table 3.6). For samples UK1b and GK2, water repellency was reduced from a severe and strong repellency respectively, to a slight repellency after extraction and drying at 20 °C. Drying at 105 °C caused a slight increase in repellency for GK2 (WDPT from 30 to 60 s) and a large increase in repellency for UK1b (WDPT from 30 to 3600 s). Soxhlet extraction using isopropanol: aqueous ammonia was therefore an effective method of removing water repellency and had no unwanted effects on the wettability of the wettable control samples. Furthermore, the fact that this extraction procedure proved to be successful at removing repellency from such a geographically wide range of soils is a significant and useful observation for future work in the field (in contrast to other studies which have only generally focussed on relatively narrow ranges of soils).

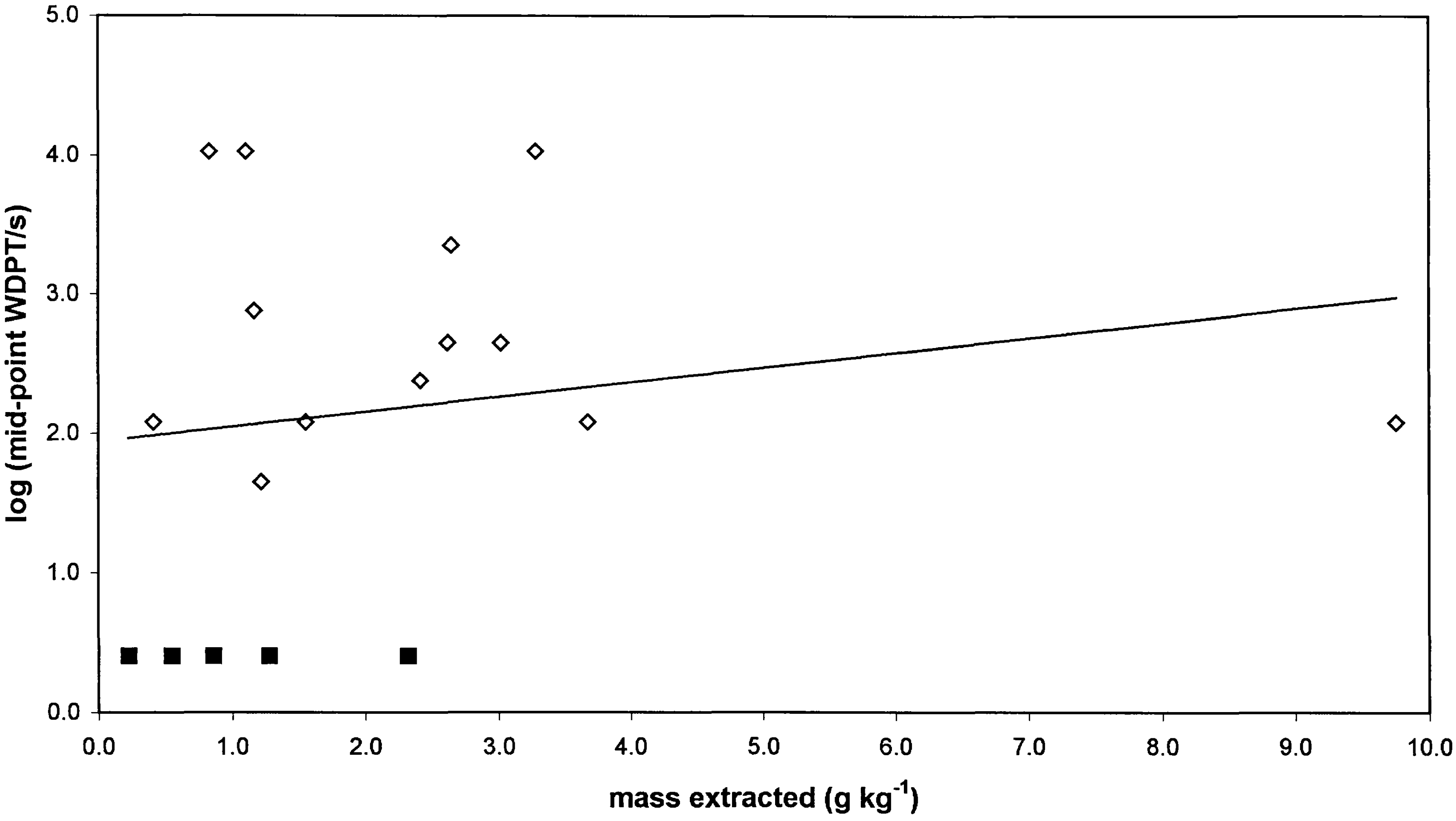

Figure 3.15: Mass of material extracted per kg of soil *vs.* log mid-point WDPT for soil pre-extraction dried at 20 °C. ◇ = repellent samples; ■ = wettable control samples. $r^2 = 0.03$; slope = 0.11 (±0.15); intercept = 1.94 (±0.44).

3.2.4.2 Effect of drying temperature on water repellency

Drying of soil samples at 105 °C prior to extraction did not consistently increase water repellency levels of samples compared to drying at 20 °C. Repellency increased for four of the fifteen repellent samples and decreased for three, which agreed with the inconsistent patterns reported by Ziogas *et al.* (in press). However, only for sample NL1 did this change exceed more than one WDPT class and therefore only for this sample could the change be regarded as significant. All control samples retained their wettability after drying at 105 °C. Since WDPT classes were consistent for the five water drops applied it was concluded that WDPT measurement of samples dried at 105°C was an unnecessary step for soils prior to extraction. In a study on repellent soils in New Zealand, Horne and McIntosh (2000) came to a similar conclusion. In contrast, measurements taken after drying at 105 °C for soils after extraction provide a useful additional assessment of soil water repellency characteristics.

Table 3.6: WDPT classes (s) of samples pre- and post-Soxhlet isopropanol/ammonia (IPA/NH_3) extraction. WDPT tests were carried out on sub-samples after drying at 20 °C and 105 °C. Samples with the letter C denote wettable control soils.

Sample Code	Pre-extraction (20 °C)	Post-extraction (20 °C)	Pre-extraction (105 °C)	Post-extraction (105 °C)
PT1	180	< 5	180	< 5
PT2	18000	< 5	> 18000	< 5
PT3	60	< 5	180	< 5
PTC	< 5	< 5	< 5	< 5
NL1	180	< 5	18000	< 5
NL2	3600	< 5	18000	< 5
NL3	18000	< 5	3600	< 5
NLC	< 5	< 5	< 5	< 5
UK1b	900	30	900	3600
UK2	300	< 5	180	< 5
UKC	< 5	< 5	<5	< 5
AU1	3600	< 5	18000	< 5
AU2	180	< 5	180	< 5
AU3	18000	< 5	18000	< 5
AUC	< 5	< 5	< 5	< 5
GK1	600	< 5	600	< 5
GK2	600	30	3600	60
GK3	180	< 5	60	< 5
GKC	< 5	< 5	30	< 5

3.2.5 Assessment of soil extracts

To examine whether the compounds extracted from the soils were capable of inducing water repellency in wettable substrates, extracts were reapplied onto acid washed sand (AWS) following procedures used by Ma'shum *et al.* (1988), as described in Section 2.5. Sub-samples were dried at 20 °C and 105 °C (as for the original soil samples), and their water repellencies assessed by the WDPT method (results given in Table 3.7). Control experiments in which chloroform or isopropanol: aqueous ammonia was applied to AWS showed that these solvents did not affect the wettable nature of AWS.

Table 3.7: WDPT classes (s) after reapplying extracts directly (IPA/NH_3), or after drying and re-dissolving in $CHCl_3$, to wettable acid-washed sand (AWS). WDPT tests were carried out on sub-samples after drying at 20 °C and at 105 °C. Samples with the letter C denote wettable control soils.

Sample code	$CHCl_3$ extract on AWS (20 °C)	$CHCl_3$ extract on AWS (105 °C)	IPA/NH_3 extract on AWS (20 °C)	IPA/NH_3 extract on AWS (105 °C)
PT1	10	600	10	60
PT2	900	18000	< 5	10
PT3	180	600	30	60
PTC	30	3600	10	60
NL1	3600	> 18000	< 5	3600
NL2	18000	> 18000	< 5	180
NL3	18000	> 18000	< 5	60
NLC	3600	18000	< 5	10
UK1b	600	18000	10	180
UK2	18000	>18000	10	60
UKC	10	180	10	30
AU1	3600	18000	< 5	900
AU2	3600	18000	< 5	300
AU3	3600	> 18000	180	900
AUC	600	300	30	180
GK1	900	3600	10	300
GK2	300	3600	30	600
GK3	180	600	60	300
GKC	3600	> 18000	180	3600

Extracted material from water repellent soils (applied in chloroform) induced water repellency on AWS in all cases, even though it did not always fully re-dissolve in chloroform. Drying AWS samples at 105 °C consistently resulted in higher WDPT classes than both the AWS samples dried at 20 °C as well as the original soil samples dried at 105 °C (Fig. 3.18). Extracts from each of the wettable control samples also induced water repellency, with levels being in the range of those induced by extracts from repellent soils for both drying temperatures. Ignoring the wettable control samples, the repellency of AWS samples treated with extracts re-dissolved in chloroform (dried at 20 °C) correlated best with the repellency of the original soil samples as shown in Fig. 3.16 and 3.20.

Extracted material applied directly from the extraction solvent without reduction to dryness and re-dissolution (i.e. from the residual isopropanol/water mixture as a result of loss of ammonia (Section 2.5)) induced no, or only comparatively low levels of repellency after drying at 20 °C (Fig. 3.17). However, after drying at 105 °C all of these extracts, including those from wettable control samples, also induced repellency in AWS closer to that found in the original soil samples (Fig. 3.19), with the WDPT classes generally being lower than those attained after applying extracts in chloroform for both drying temperatures.

The fact that all extracts contained material capable of inducing repellency in AWS suggested that the extraction procedure had removed at least some of the material that caused water repellency in the soils investigated, and that these substances retained their ability to bond to silicate particle surfaces and impart water repellency after being subjected to the extraction procedure. The procedure was therefore considered suitable for the extraction of organic compounds from water repellent soils for the subsequent further separation and characterization (Chapters 4 and 5).

Extract reapplication and drying procedures provided a valuable assessment of whether extracts contained compounds capable of causing water repellency. However, induced levels of repellency were not always consistent with the repellency levels of the original samples. Most notably, extracts from all wettable control soils re-dissolved in chloroform induced repellency levels comparable to those induced by extracts from repellent soils. This demonstrated that these soils also contained compounds capable of inducing water repellency, suggesting that either: these compounds were in too low a concentration in these soils to induce water repellency;

other compounds present conferred wettablity even in the presence of the repellent materials; or the particular molecular adsorption at the soil surface was such as to mask their water repellent nature. Also, some extracts re-dissolved in chloroform induced a higher level of repellency compared to that of the original soil sample and that following extract reapplication directly from the extraction solvent mixture. This was surprising since chloroform did not always fully re-dissolve the extracted material. Differences in repellency levels between the original soils and AWS after reapplication could also have been due to differences in the respective surface areas of the acid-washed sand and the original soils (Table 3.1), resulting in thicker or less thick organic coatings on the acid washed sand samples. An additional factor could also have been that the bonding of the organic compounds to AWS was not identical to that in the original soil. The same adsorption situation may not have been reached immediately and some relaxation from an initial 'kinetic' position may have been necessary to reach the same 'pseudo-equilibrium' situation as is found in soils which have been exposed to organic compounds over a long period of time.

The observations that reapplication of similar materials from chloroform and isopropanol/water gave sands with very different water repellencies, and that heating to 105 °C increased sample repellency markedly, are compelling evidence that the simple presence or absence of specific organic compounds is not enough alone to determine water repellency. Hydration effects and the intermolecular arrangement of material are probably important contributing factors.

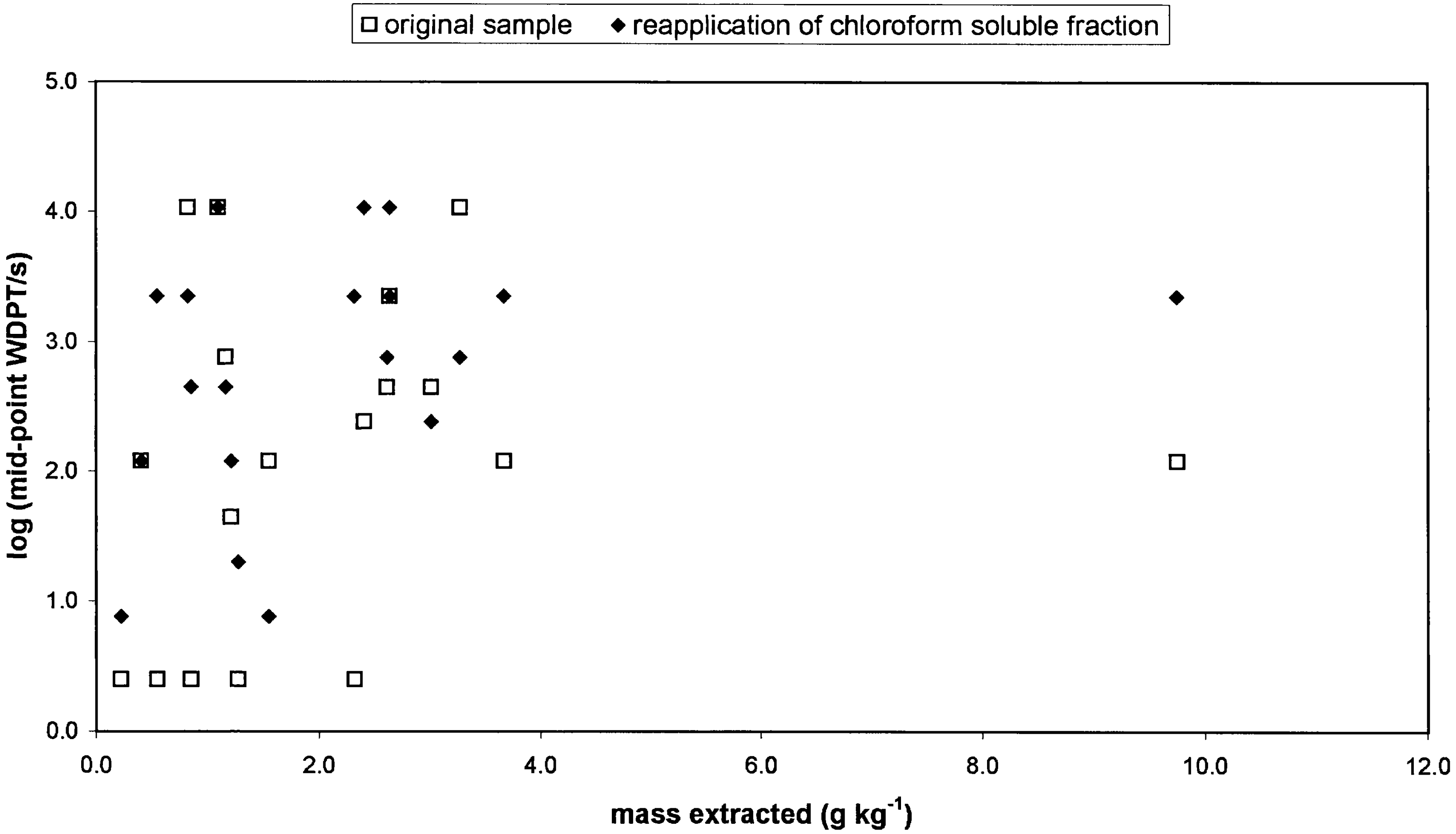

Fig 3.16: Comparison between WDPT values for soil pre-extraction and AWS after reapplication of chloroform soluble fraction and drying at 20 °C.

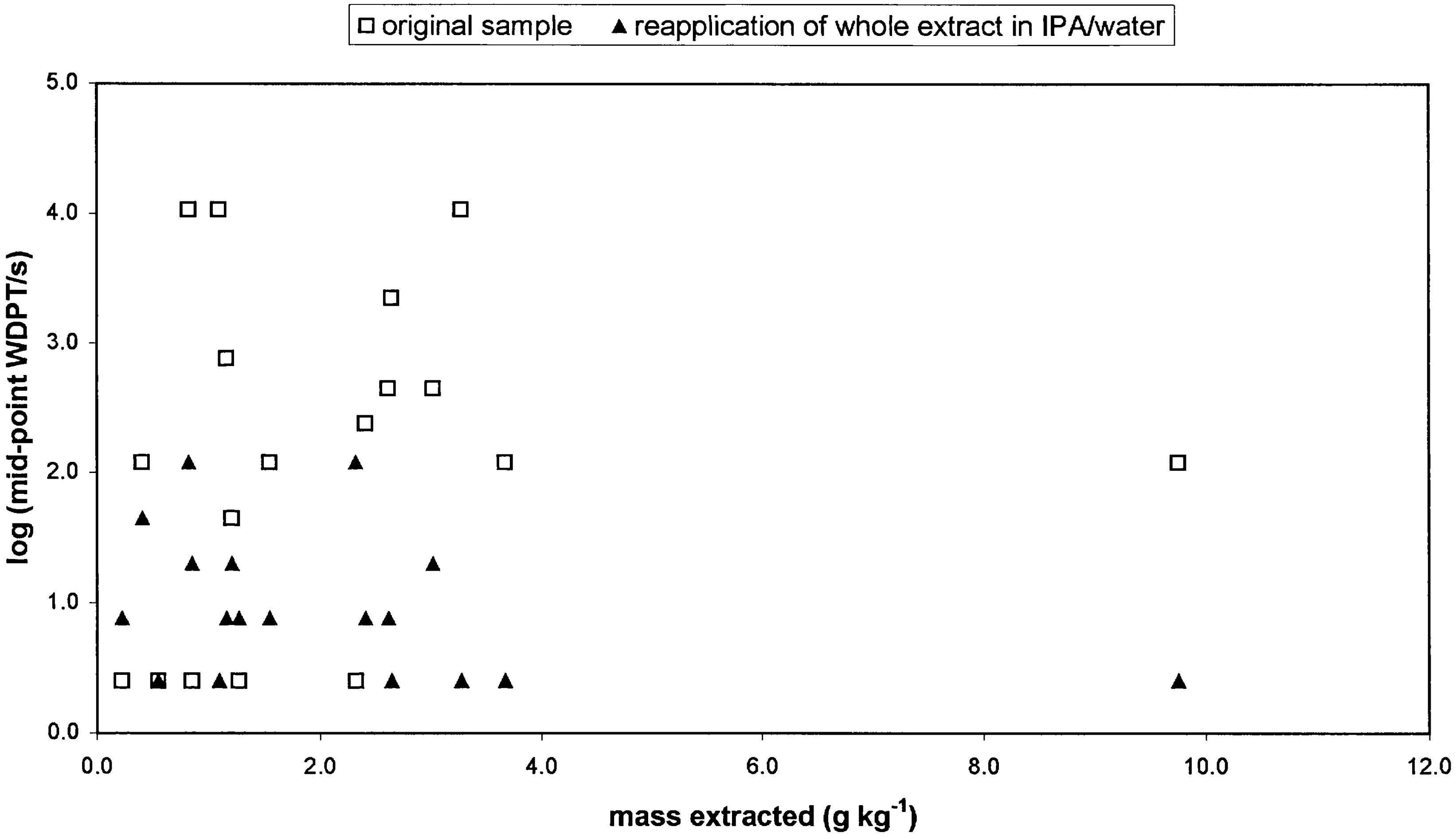

Fig 3.17: Comparison between WDPT values for soil pre-extraction and AWS after reapplication of whole extract in IPA/H_2O and drying at 20 °C.

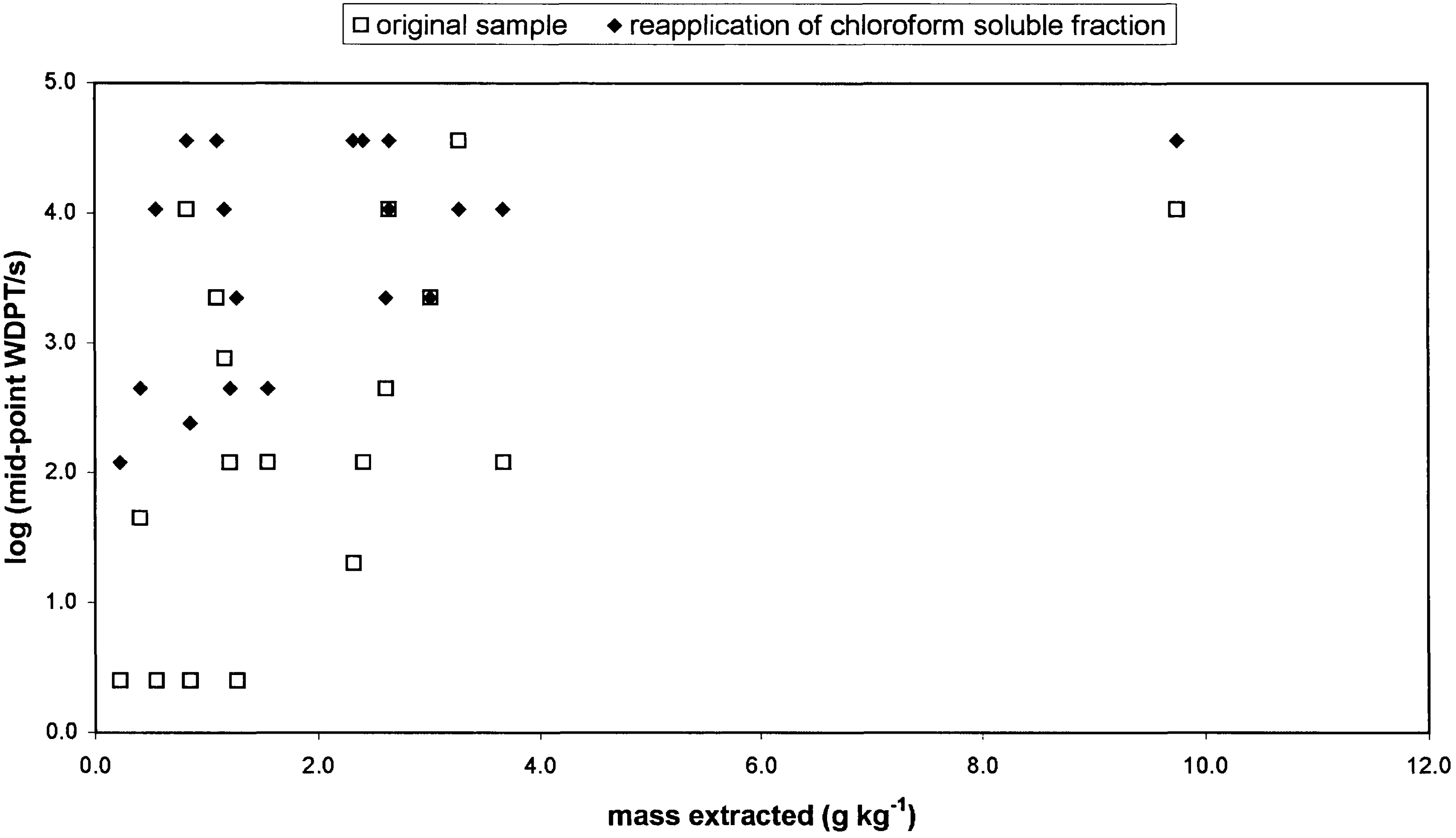

Fig 3.18: Comparison between WDPT values for soil pre-extraction and AWS after reapplication of chloroform soluble fraction and drying at 105 °C.

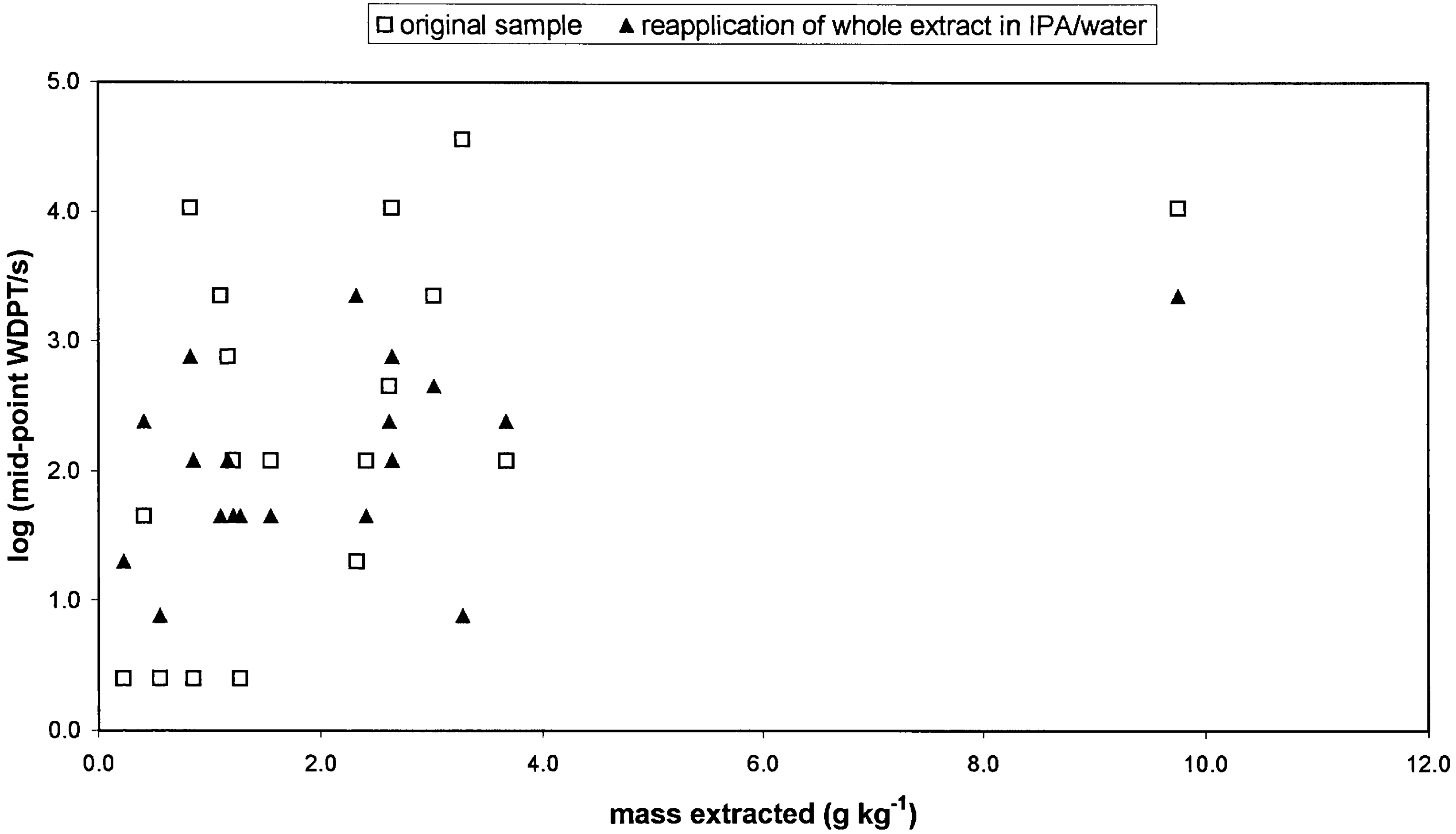

Fig 3.19: Comparison between WDPT values for soil pre-extraction and AWS after reapplication of whole extract in IPA/H_2O and drying at 105 °C.

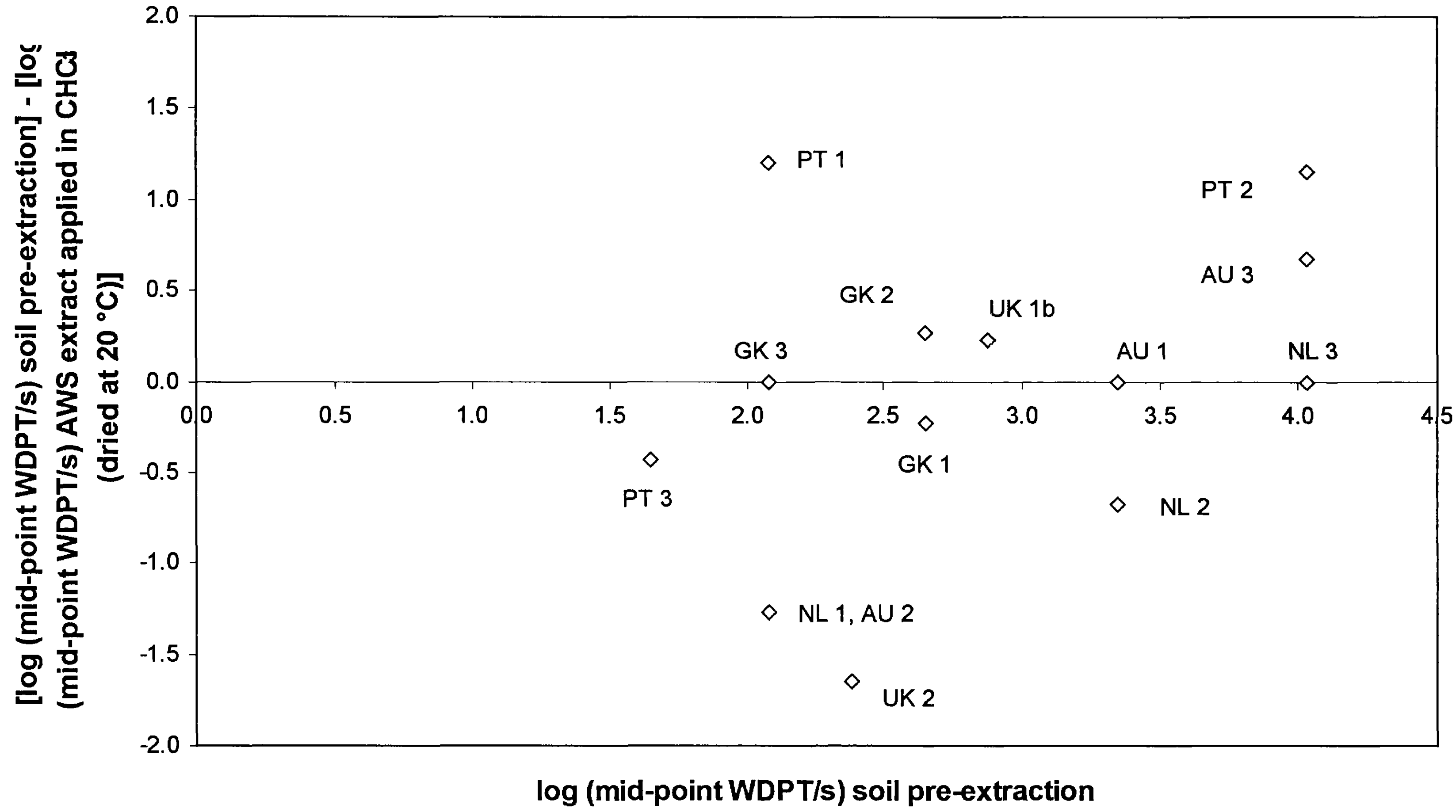

Fig 3.20: The difference between log mid-point WDPT for water repellent soils (control samples removed from set) pre-extraction, and AWS after reapplication of chloroform soluble fraction and drying at 20 °C *vs.* log mid-point WDPT soil pre-extraction.

3.2.6 Thermal analysis

An exploratory investigation using thermal analysis was carried out on a water repellent (PT2) and a wettable soil sample (PTC). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out simultaneously on each sample under a nitrogen atmosphere (samples were oven-dried at 20 °C prior to analysis). The resulting TGA and DSC curves for PT2 are shown in Fig. 3.21. The first stage in mass loss is observed between 20 and 100 °C as a result of the removal of water from the sample. This accounts for *ca.* 0.5% sample mass by TGA and is accompanied by a large endothermic DSC peak in the same temperature region with a maximum at *ca.* 55 °C. Between *ca.* 100 and 250 °C the rate of mass loss decreases significantly, followed by an increase between *ca.* 250 and 500 °C probably corresponding to the loss of easily decomposed or more volatile organic matter and/or the transformations in structural conformation of the organic matter. Mallik and Rahman (1985) also observed loss of organic matter in this temperature region whilst analysing burned heathland soils from north-east Scotland. A small endothermic trough (i.e. heat transfer to the sample) is observed in the DSC curve in this temperature region. Between 570 and 580 °C a large endothermic peak occurs. This corresponds to a SiO_2 phase transition, between α-quartz (the most thermodynamically stable form at room temperature) and β-quartz (Greenwood and Earnshaw 1997). In addition, a rapid mass loss of about 0.3% occurs. Between 600 and 1000 °C the rate of mass loss remains relatively constant with the overall mass loss at 1000 °C being *ca.* 4.2 %. This value is significantly greater than the % total organic carbon value of *ca.* 1 % (*i.e.* 10.3 g kg^{-1} as shown in Table 4.2), suggesting that components other than organic compounds were removed (although the TOC measurement was obtained by combustion in oxygen at 1050 °C for *ca.* 3-4 minutes rather than a 10 °C min^{-1} temperature ramp in an atmosphere of nitrogen for the thermal analysis). In addition, it could be expected that a significant proportion of the mass loss would be due to the loss of water from the sample. Mallik and Rahman (1985) speculated that the dissociation of mineral oxides could contribute to sample mass loss.

The results obtained for the wettable sample (PTC) were very similar to those obtained for the repellent sample (PT2). The only noticeable difference was that the overall mass loss in the wettable sample was about half that of the repellent sample (*ca.* 2%). This is not surprising since sample PTC contained virtually no detectable organic carbon (Table 4.3) and considerably less material was extracted (Table 3.4) compared to sample PT2. Potential future work would be to carry out an in-depth study of a larger sample pool using thermal analysis.

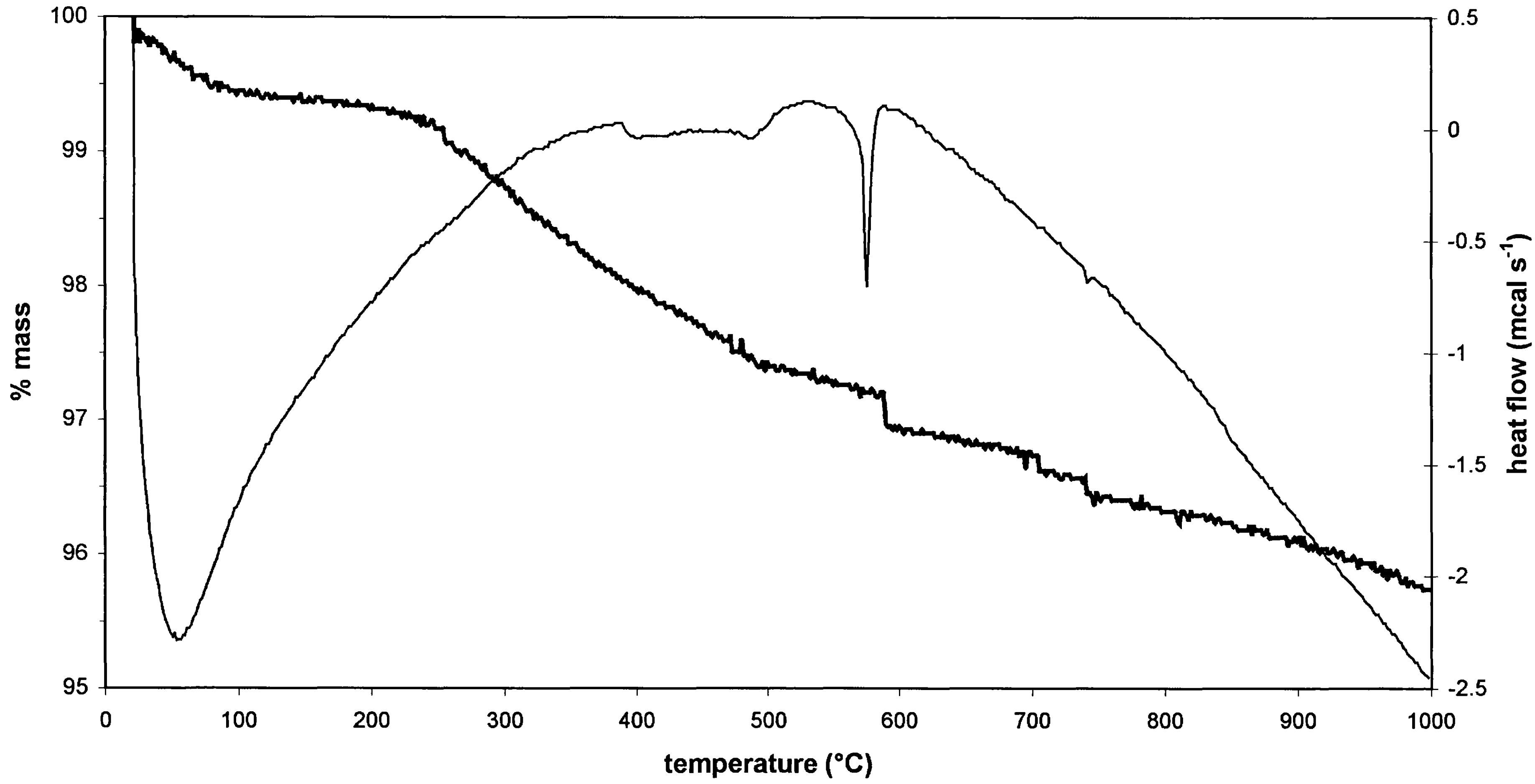

Figure 3.21: Thermogravimetric analysis (bold line) and differential scanning calorimetry (normal line) curves for sample PT2 under a nitrogen atmosphere.

3.2.7 Soil pH

As discussed previously, carboxylic acids have been identified as one of the predominant types of compound found in water repellent soils (Ma'shum *et al.* 1988, Franco *et al.* 1994, McIntosh and Horne 1994, Horne and McIntosh 2000, Morley *et al.* in press, Llewellyn *et al.* 2004). Being acidic, it was speculated that they could play a significant role in determining the pH of a soil. In previous studies it has been suggested that water repellency does not develop under alkaline conditions generally (Roberts and Carbon 1971), and for acidic conditions no high correlations between pH and water repellency have been reported (Wallis *et al.* 1993). Karnok et al. (1993) also demonstrated that treating acidic water repellent soils on golf greens with alkali was a successful method of removing water repellency.

The pH values obtained from this sample pool (for both water repellent and wettable samples) ranged from *ca.* 4 – 7, corresponding to mildly/moderately acidic soils (see Table 3.8). These are consistent with those typically found in forest and humid region arable soils (Brady and Weil 1999). There was virtually zero correlation between water repellency levels and soil pH (Fig. 3.22), which is in agreement with the observations made by Roberts and Carbon (1971) and Wallis *et al.* (1993). The observation that carboxylic acids are one of the predominant compound types found in water repellent soils is complemented by these results.

Table 3.8: pH measurements. Error estimates based on 3 independent measurements. Samples with the letter C denote wettable control soils.

Sample code	pH
PT1	6.33 (±0.54)
PT2	4.37 (±0.70)
PT3	4.68 (±0.78)
PTC	4.24 (±0.40)
NL1	4.44 (±0.38)
NL2	5.36 (±0.39)
NL3	4.75 (±0.58)
NLC	4.06 (±0.24)
UK1b	5.35 (±0.41)
UK2	4.40 (±0.60)
UKC	5.96 (±0.67)
AU1	5.24 (±0.67)
AU2	5.13 (±0.58)
AU3	5.37 (±0.82)
AUC	6.79 (±1.47)
GK1	5.42 (±0.68)
GK2	4.83 (±0.39)
GK3	6.95 (±1.34)
GKC	4.07 (±0.27)

3.3 Chapter summary

An initial exploratory comparison of particle surface characteristics (i.e. size and shape) of a range of soils (water repellent and wettable soil samples, both pre- and post-extraction) by SEM did not indicate any specific relationship with water repellency. Particle size distribution was also investigated. Poor correlations were observed between both the specific surface area and mean particle diameter of the soil samples, and water repellency level. However, as the particle size range is relatively narrow across the soils investigated in this study this is not necessarily surprising.

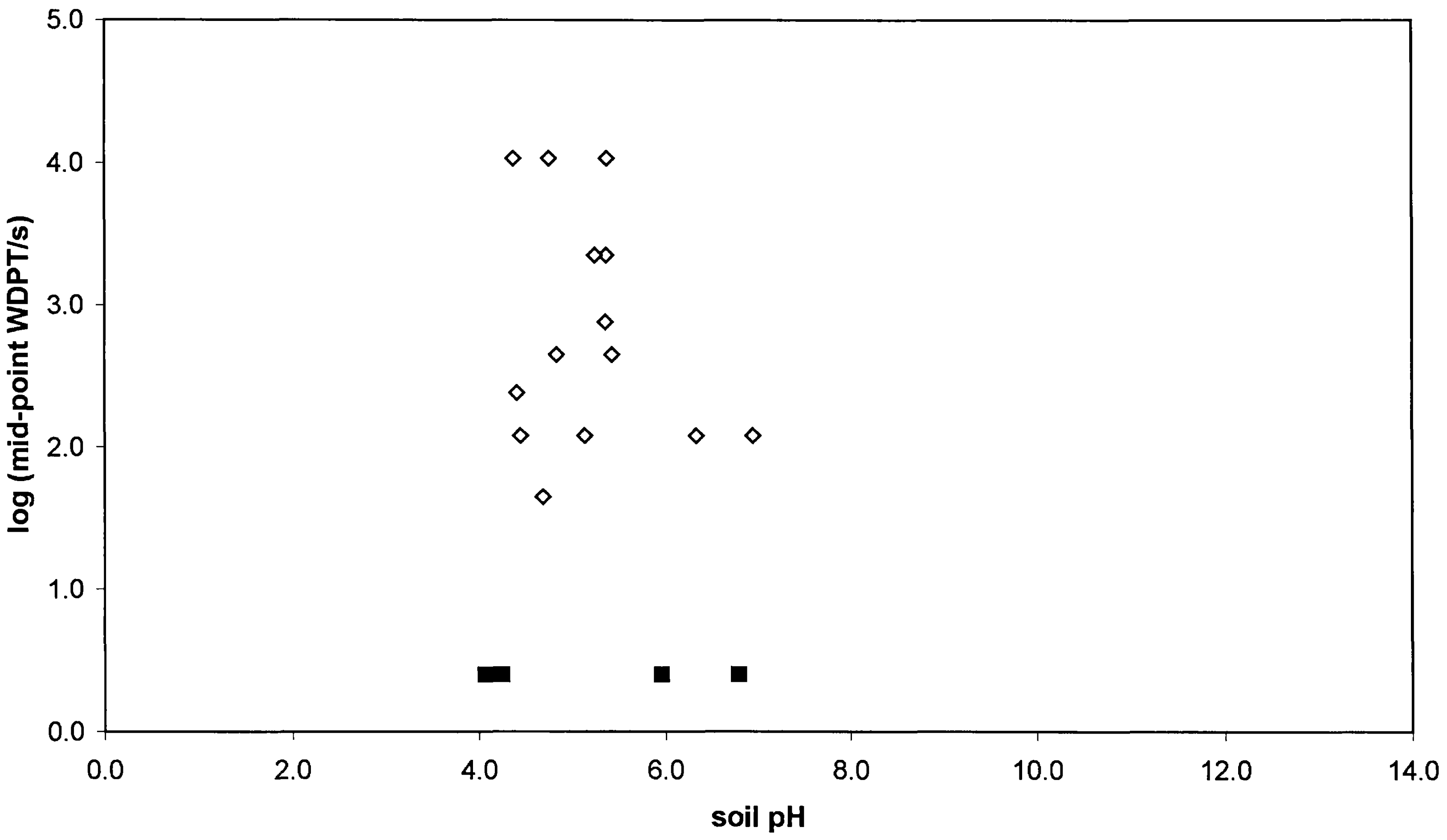

Figure 3.22: Soil pH *vs.* log (mid-point WDPT/s). ◇ = repellent samples; ■ = wettable control samples.

Isopropanol: aqueous ammonia (0.88 SG) (7:3, v:v) solvent mixture was used to Soxhlet extract all soil samples. This was an effective method of removing water repellency and had no unwanted effects on the wettability of wettable control samples. Furthermore, as stated previously, the fact that this extraction procedure proved to be successful at removing repellency (and had no unwanted effects on wettable samples) from such a geographically wide range of soils is a significant and useful observation for future work in the field (in contrast to other studies which have only generally focussed on relatively narrow ranges of soils). Soxhlet extraction with lower polarity solvents such as chloroform, tetrahydrofuran and isopropanol was also carried out on one sample as an exploratory procedure. This resulted in poor extraction efficiency in terms of the amount of material extracted and the post-extraction water repellency level. Extraction with these solvents actually increased the level of water repellency. Highly polar solvents (aqueous ammonia and water) had a much higher extraction efficiency in terms of the mass of material extracted and successfully removed water repellency. However, it will be shown by TOC analysis (Chapter 4) that the material extracted by water must be predominantly inorganic as no organic carbon was removed and although both aqueous polar solvents extracted large amounts of material it will be shown by DRIFT analysis (Chapter 4) that they removed less aliphatic carbon than isopropanol: aqueous ammonia. Hence, isopropanol: aqueous ammonia was selected as the extraction solvent of choice.

Drying soil samples at 105 °C both pre- and post-extraction was also carried out to assess the effect on sample repellency (compared to drying at 20 °C). For unextracted soils, water repellency increased in some cases but decreased in others, with many samples remaining the same. In only one case was the change in repellency regarded as significant (sample NL1, for which the change exceeded more than one WDPT class). It was therefore concluded that WDPT measurement of samples dried at 105 °C was an unnecessary step for soils prior to extraction. However, measuring WDPT after drying at 105 °C for soils after extraction provides a useful additional assessment of soil water repellency characteristics.

Soil extracts were reapplied onto acid washed sand to examine whether compounds extracted from the soils were capable of inducing water repellency. Extracted material from water repellent soils induced water repellency on AWS in all cases (including wettable control samples). The fact that all extracts contained material capable of inducing repellency in AWS suggests that the extraction procedure had removed at least some of the material responsible for causing water repellency and that these substances retained their ability to bond to silicate particle surfaces and impart water repellency after being subjected to the extraction procedure.

These observations are compelling evidence that the simple presence or absence of specific organic compounds is not enough alone to determine water repellency. Hydration effects and the intermolecular arrangement of material are probably important factors.

Chapter 4

DRIFT and TOC analysis of water repellent and wettable soils

4.1 Introduction

Since it is generally acknowledged that organic compounds cause water repellency, it may seem reasonable to assume that the amount of organic material in a sample is related to its repellency. Some previous studies have indeed found a positive relationship between the total organic matter content in soils and water repellency (Wallis *et al.* 1990a, Berglund *et al.* 1996, McKissock *et al.* 2003), although others have found no such relationship (Jungerius *et al.* 1989, De Bano 1991). As not all carbon-containing compounds are water repellent it seemed likely that closer relationships between water repellency and organic carbon may be obtained by considering the type of organic carbon present rather than simply the total amount (McKissock *et al.* 2003). Capriel *et al.* (1995) specifically identified the aliphatic fraction of organic matter in soil as a key factor in causing water repellency. It was thought that the hydrophobicity of organic matter in soil was related to the amount of methyl, methylene and methyne groups present in both aliphatic and aromatic compounds (Capriel *et al.* 1995).

Two of the most common ways of investigating the aliphatic fraction of organic compounds are nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. Conventional NMR spectroscopy can only be applied to samples in solution and therefore only the soluble fraction of organic compounds in soils would be available for analysis. Due to the complex mixture of organic compounds present in soils, depending upon the solvent used, the soluble fraction may be small and any analysis would therefore not be representative of the sample as a whole. An alternative is solid-state cross-polarization magic angle spinning or CPMAS ^{13}C NMR, allowing the direct, non-destructive investigation of solids (whole soil samples in this case), although several limitations have been identified. The low carbon content of mineral soils coupled with the low natural abundance of ^{13}C nuclei of 1.1% causes difficulties in obtaining spectra with favourable signal-to-noise ratios as large numbers of scans are necessary. In addition to this, reduced efficiency of the cross-polarization process can occur due to paramagnetic species (such as Fe^{3+}, Cu^{2+} and organic free radicals) in proximity rendering ^{13}C nuclei 'invisible' in terms of the NMR analysis (Capriel *et al.* 1995).

Analysis of aliphatic material using IR spectroscopy is possible due to stretching vibrations of the aliphatic C-H bonds in methyl, methylene and methyne groups typically absorbing in the 3000-2800 cm^{-1} region of the electromagnetic spectrum (*ca.* 2930 cm^{-1} for asymmetrical CH_2 stretching and 2860 cm^{-1} for symmetrical CH_2 stretching). These are usually superimposed on the shoulder of the broad O-H stretching band. Transmission IR spectroscopy has been used in studies to characterize organic molecules such as those in humic substances (Niemeyer *et al.* 1992) but obtaining spectra of solids using transmission techniques has disadvantages such as: improper sample dispersion in a potassium bromide disk causing background scattering and poor line shape; interferences caused by water bands leading to poor resolution; time consuming sample preparation (Capriel *et al.* 1997). Many of these disadvantages have been overcome by a technique known as Diffuse Reflectance Infrared Fourier Transform spectroscopy or DRIFT (see also Section 2.6.6). The technique is well established (Fuller and Griffiths 1978) and peak assignments are the same as in transmission IR spectroscopy. It has been used in previous studies to analyse solid samples such as humic and fulvic acids, composts and peats (Baes and Bloom 1989, Niemeyer *et al.* 1992). To analyse soils by DRIFT minimal sample preparation is required. It is therefore a direct and non-destructive method of investigating aliphatic C-H present in whole soil samples (Nguyen *et al.* 1992).

One of the most comprehensive studies to date is by Capriel *et al.* (1995) in which a large number of German arable soils with widely differing textures was selected and their organic C contents investigated by DRIFT. Results indicated that the soil texture influenced the composition of the soil organic matter. It was found that the organic matter of sandy soils contained more alkyl C (aliphatic C-H) and less carbohydrates and proteins compared to clayey soils, and therefore sandy soils may be expected to be more hydrophobic. It was suggested that the aliphatic C-H to C_{org} ratio could serve to characterize the degree of repellency of the soil organic matter. In a more recent study, McKissock *et al.* (2003) carried out measurements of both aliphatic C-H (by DRIFT) and TOC content on a set of water repellent soils from Western Australia. They found that aliphatic C-H gave a better prediction of soil water repellency than TOC content, suggesting that aliphatic C-H contributes more to water repellency than other types of organic carbon.

The main objective of the first part of the research described in this chapter was to further assess DRIFT spectroscopy as a means of analysing aliphatic carbon in water repellent soils, and to identify any relationship between the amount of aliphatic C-H units present in the wide range of soils selected (Table 2.2) and their water repellency by DRIFT analysis and water drop penetration time (WDPT) results. Solvent-extracted soils were also included to assess the efficiency of the extraction procedure at removing aliphatic compounds.

Infrared absorption by soil mineral matter masks much of the spectral region that would be of help in identifying the functional groups of the organic compounds present. However bands arising from C-H stretching in aliphatic compounds can be observed. Capriel *et al.* (1995) found that the absorption efficiency (as measured by the area beneath the peaks in the 2800-3000 cm^{-1} region) is quantitatively related to the amount of aliphatic C-H present in a sample. Absorption due to aromatic C-H occurs at a slightly higher wavenumber, *ca.* 3010 – 3040 cm^{-1}, and is generally weaker than that due to aliphatic C-H (Williams and Fleming 1997). The nature of the quantitative relationship between the DRIFT signal and mass % C-H depends upon: mode of measurement (i.e. transmittance, absorbance, application of Kubelka-Munk correction); instrument optics; and sample characteristics and preparation. Capriel *et al.* (1995) have shown that the amount of aliphatic material added to a finely ground (<40 μm) soil substrate (concentration range: 0.5 to 3.5 mg g^{-1}) can be related by a linear equation to the DRIFT absorbance of the sample when diluted 1:9 with KBr. However, none of the DRIFT measurement modes available can necessarily be expected to give a wide-ranging linear relationship between mass % C-H and DRIFT signal for organic coatings non-uniformly adsorbed onto non-uniform, relatively coarse grain granular samples such as soils. For this reason, in this study, measurements were made on soil samples directly without any intermediate preparation such as grinding or dilution with KBr. Absorbance mode was used directly without the Kubelka-Munk correction, and the data, and correlations between DRIFT and other parameters, such as TOC, are treated empirically.

The second part of this chapter focuses on the total organic carbon (TOC) content of the soils. Measurements were carried out as described in Section 2.6.5. The objective was to identify any relationship between TOC content and water repellency, as well as measuring solvent-extracted soils to assess the efficiency of the extraction procedure at removing organic carbon. In addition to this, the relationship between the aliphatic fraction of organic carbon and total organic carbon was assessed.

4.2 Results and discussion

4.2.1 DRIFT spectroscopy of soils

DRIFT spectra were obtained for all soils both pre- and post-extraction as described in Section 2.6.6. A typical DRIFT spectrum of a sandy soil is given in Fig. 4.1. The example shown is a spectrum of sample UK2 pre-extraction. Fig. 4.2 focuses on the C-H band. The area between the solid line of the spectrum and the dashed line was calculated, thus providing an assessment of the relative amounts of aliphatic C-H units present in each sample analysed. Results are shown in Table 4.1.

For the broad range of soil samples analysed the comparison of amount of aliphatic C-H units detected in the un-extracted soil samples by DRIFT and water repellency reveals no close relationship between the two parameters (Fig. 4.3) although there is some correlation in that there are no samples that show both a severe level of water repellency and low C-H absorption and *vice versa*. The coefficient of determination (r^2) of 0.23 indicates a low positive correlation between the two variables. Chatfield (1983) suggests that, for a sample size of 15 or 20, the critical correlation coefficient (r) values required to show significant correlation are 0.51 and 0.44 respectively. The corresponding r^2 values are therefore 0.26 and 0.19 respectively. In this study a sample size of 19 soils with an r^2 value of 0.23 corresponds to an *r-value* of 0.48, indicating the correlation is statistically significant at the 95% level (*i.e.* there is a 95% chance of the correlation being true). However, whether the correlation is strong enough to make one parameter a practically useful predictor of the other is doubtful. McKissock *et al.* (2003) obtained $r^2 = 0.45$ for a plot of 'log WDPT (s)' *vs.* 'log aliphatic C' (from DRIFT measurements), which is a considerably stronger correlation than that observed here (Fig. 4.3). However, the sample range investigated was relatively narrow as all soils were sampled from the same region (Western Australia), and it may be that the relatively strong correlation is therefore only applicable to that region.

The comparison of aliphatic C-H units detected by DRIFT and the mass of material extracted from samples was also assessed. Fig. 4.4 shows a relatively high positive correlation between the two variables, provided sample NL1 is excluded from the data set (explanation given in Section 4.2.1.1). The coefficient of determination (r^2) was calculated as 0.53, corresponding to a correlation coefficient (r) of 0.73. The correlation was therefore significant at the 95% level.

From the mean area values pre- and post-extraction the proportion of the initial aliphatic C-H units extracted was calculated for each soil (Table 4.1). Comparison of the mean area values suggests that in no case did extraction remove all aliphatic material from the soil. The proportional reduction in DRIFT signal ranges from 21 to 85%, with an average of *ca.* 45%. However, for sample UKC, which initially has very little aliphatic organic matter present, there is little change in the C-H absorption band intensity (*ca.* 10%) as a consequence of extraction. Positive linear correlations were observed between the change in DRIFT signal (or the proportion of aliphatic C-

H extracted) as a consequence of extraction and: (i) the initial amount of C-H present (Fig. 4.5); (ii) the mass of material extracted (Fig. 4.6). The coefficients of determination (r^2) are 0.61 (r = 0.78) and 0.51 (r = 0.71) respectively and are thus significant at the 95% level. The relationship shown in Fig. 4.5 suggests that, after a small amount of perhaps inorganic material is removed, a similar proportion of aliphatic C-H is removed from all samples, regardless of the initial amount present. Calculating the slope value reveals that 29 (±6) % of the initial aliphatic C-H is removed as a consequence of extraction. The relationship in Fig. 4.6 reveals that 0.86 (±0.21) g kg^{-1} of material is extracted per unit of change in C-H band area.

Table 4.1: Relative amounts of aliphatic C-H extracted by IPA/NH_3 as measured by DRIFT analysis. Values in brackets are error estimates based on 1 standard deviation.

Sample code	Relative area under C-H peak		% of total C-H extracted
	Pre-extraction	Post-extraction	
PT1	3.5 (±1.6)	2.0 (±0.6)	43 (±24)
PT2	6.8 (±2.1)	4.0 (±1.2)	41 (±17)
PT3	2.1 (±0.4)	0.61 (±0.30)	71 (±37)
PTC	2.7 (±1.0)	0.64 (±0.39)	76 (±55)
NL1	7.7 (±1.6)	3.2 (±1.0)	58 (±21)
NL2	6.3 (±0.8)	3.3 (±1.1)	48 (±17)
NL3	3.6 (±0.4)	1.1 (±0.4)	69 (±29)
NLC	1.2 (±0.3)	0.18 (±0.05)	85 (±37)
UK1$_b$	5.0 (±1.2)	3.6 (±2.0)	28 (±17)
UK2	4.1 (±0.8)	2.0 (±1.1)	51 (±31)
UKC	0.29 (±0.08)	0.26 (±0.16)	10 (±7)
AU1	5.7 (±1.1)	3.5 (±1.0)	39 (±13)
AU2	5.1 (±0.6)	3.1 (±1.0)	39 (±14)
AU3	6.2 (±0.5)	4.0 (±0.5)	35 (±6)
AUC	2.4 (±0.6)	1.07 (±0.14)	55 (±16)
GK1	7.9 (±3.6)	5.9 (±2.3)	25 (±15)
GK2	12.1 (±2.7)	8.4 (±2.3)	31 (±11)
GK3	1.9 (±0.5)	1.5 (±1.1)	21 (±17)
GKC	7.0 (±1.7)	5.1 (±0.9)	27 (±9)

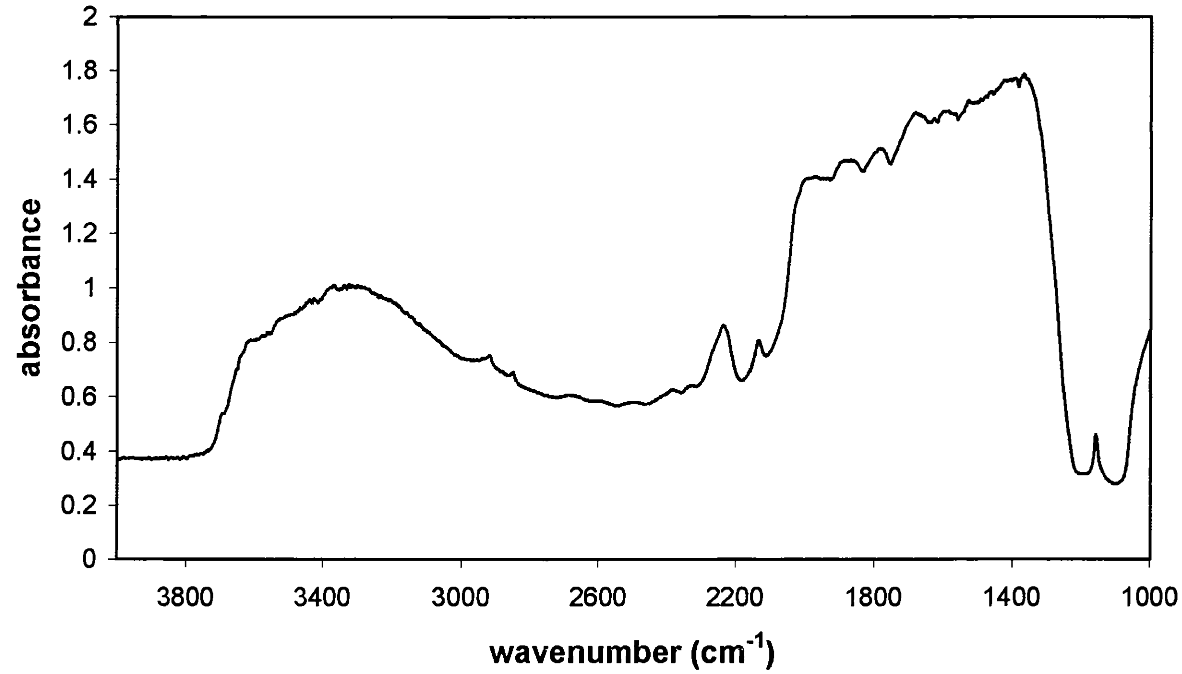

Figure 4.1: DRIFT spectrum of the water repellent soil sample UK2.

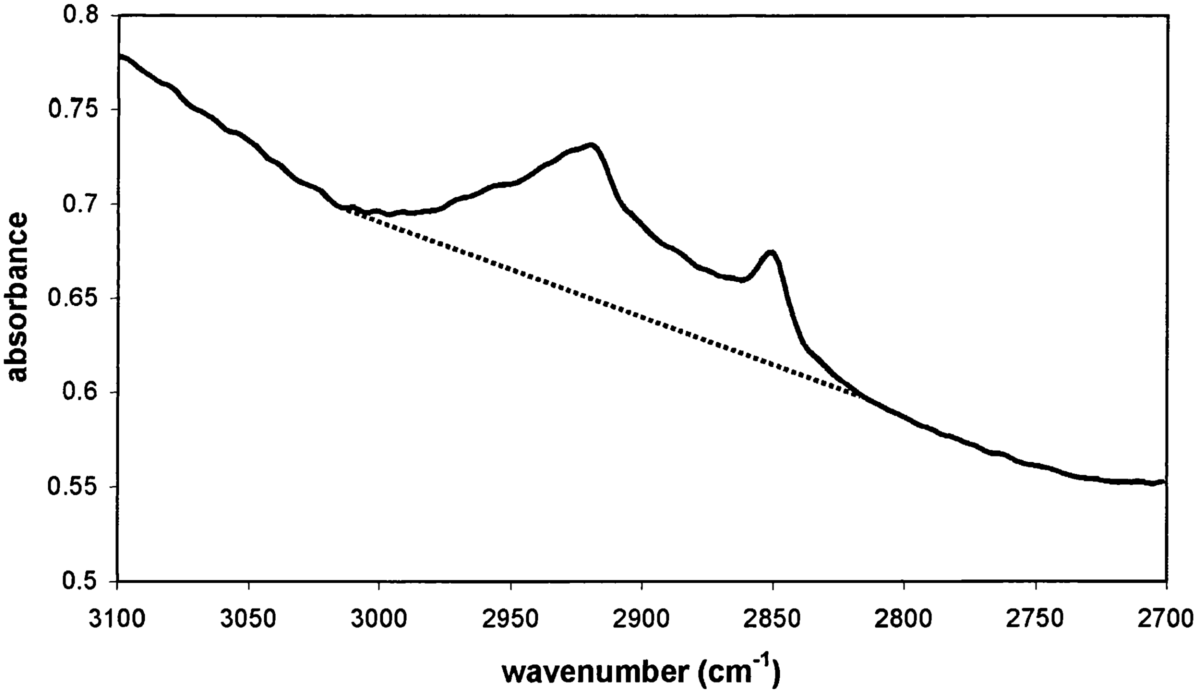

Figure 4.2: DRIFT spectrum in the spectral region of interest. The area between the absorption bands due to C-H stretches in the absorption spectrum (solid line) and the background (dashed line) is a relative measure of the amount of C-H units present in the sample.

4.2.1.1 Further discussion

DRIFT samples soil heterogeneity on a much smaller scale than, for example, bulk extractions carried out on relatively large amounts of material, and this can lead to high variations in the intensity of the C-H absorption bands within sub-samples taken from an individual soil. The high variations between sub-samples occurred despite careful sub-sampling by coning and quartering (Section 2.3), and reflect the heterogeneity of the soils on this mm-scale. Although all soils are of sand texture with minimal clay content (Table 3.2), the Portuguese, Greek and British samples gave high sample-to-sample variations, while the Australian and Dutch samples were more uniform. DRIFT was found to be an analytical technique with less than desirable reproducibility, although the differences in C-H content between the different soil samples examined here were large enough to make comparisons of DRIFT data meaningful.

Sample NL1 has been excluded from the data set in some of the figures (Fig.'s 4.4, 4.6 and 4.16). Regardless of whether the sample had been extracted or not the DRIFT data for NL1 are outliers, suggesting that this atypical behaviour is a property of the soil rather than a consequence of experimental error. However there is nothing unusual about the extraction data or TOC content for NL1 (Tables 3.4 and 4.3 respectively), other than that this soil gives the highest values obtained from this soil set. NL1 has the highest organic content of the soils sampled and it is speculated here that, for this soil, the distribution of organic matter includes a higher fraction of interstitial particulates of predominantly organic character. These organic particles will contribute to both TOC content and extraction amount in a similar way to organic material coated on the mineral grains, but will give an erroneous low response to DRIFT which samples surface material rather than total bulk material.

Although the extracts from both repellent and wettable soils clearly contain compounds that can cause water repellency in soils, and aliphatic C-H units must be contained in the compounds causing repellency, these results indicate that organic compounds responsible for causing water repellency may only represent a fraction of the extract composition. They also support the suggestions made by Horne and McIntosh (2000) and Roy and McGill (2000a) that the presence of water repellency (in a dry soil) is not only a function of certain organic compounds being present in the soil, but also of their structural composition and arrangement.

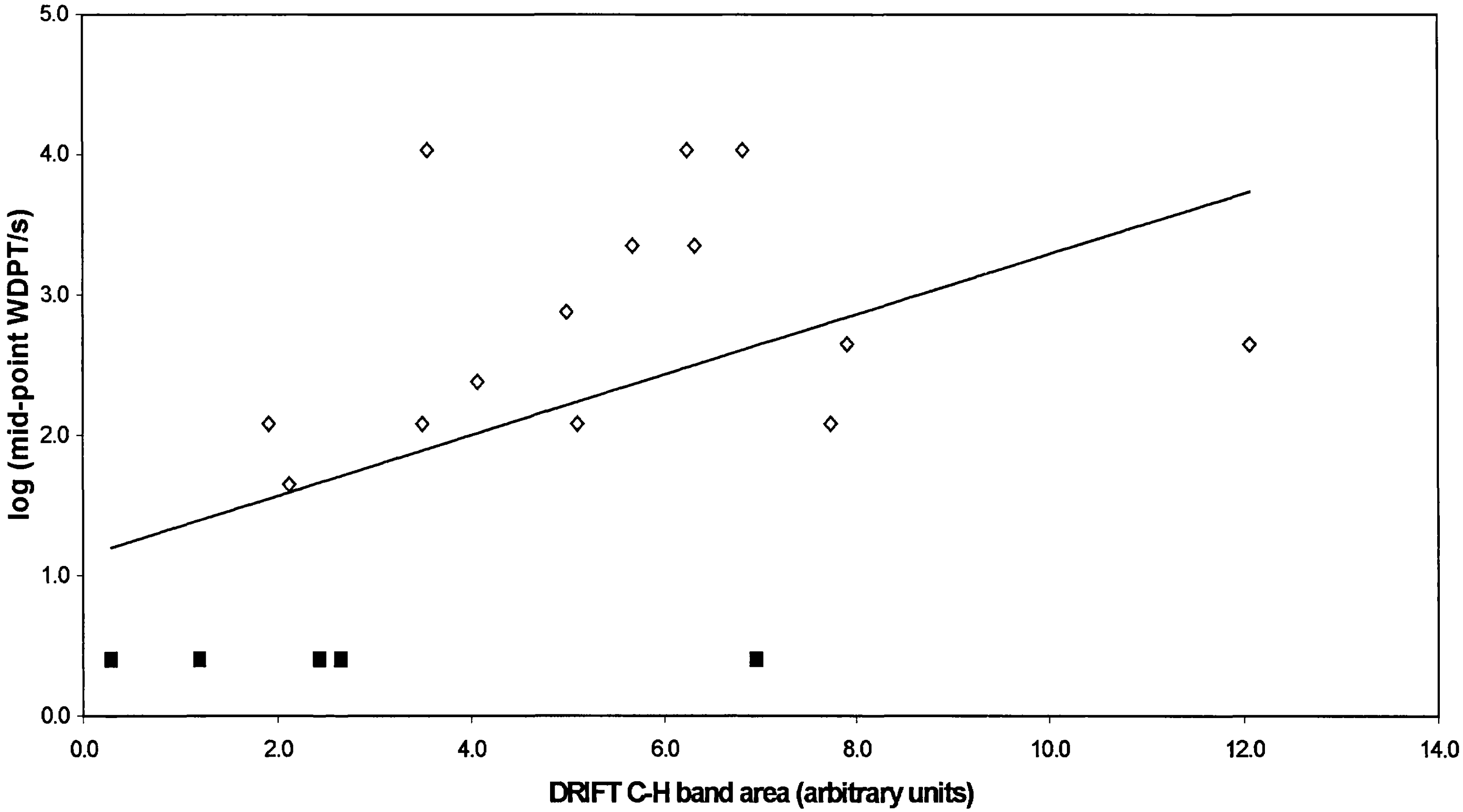

Figure 4.3: log mid-point Water Drop Penetration Times *vs.* DRIFT C-H absorption band area of samples prior to extraction. ◇ = repellent samples; ■ = wettable control samples. $r^2 = 0.23$; slope = 0.2 (±0.1); intercept = 1.1 (± 0.5).

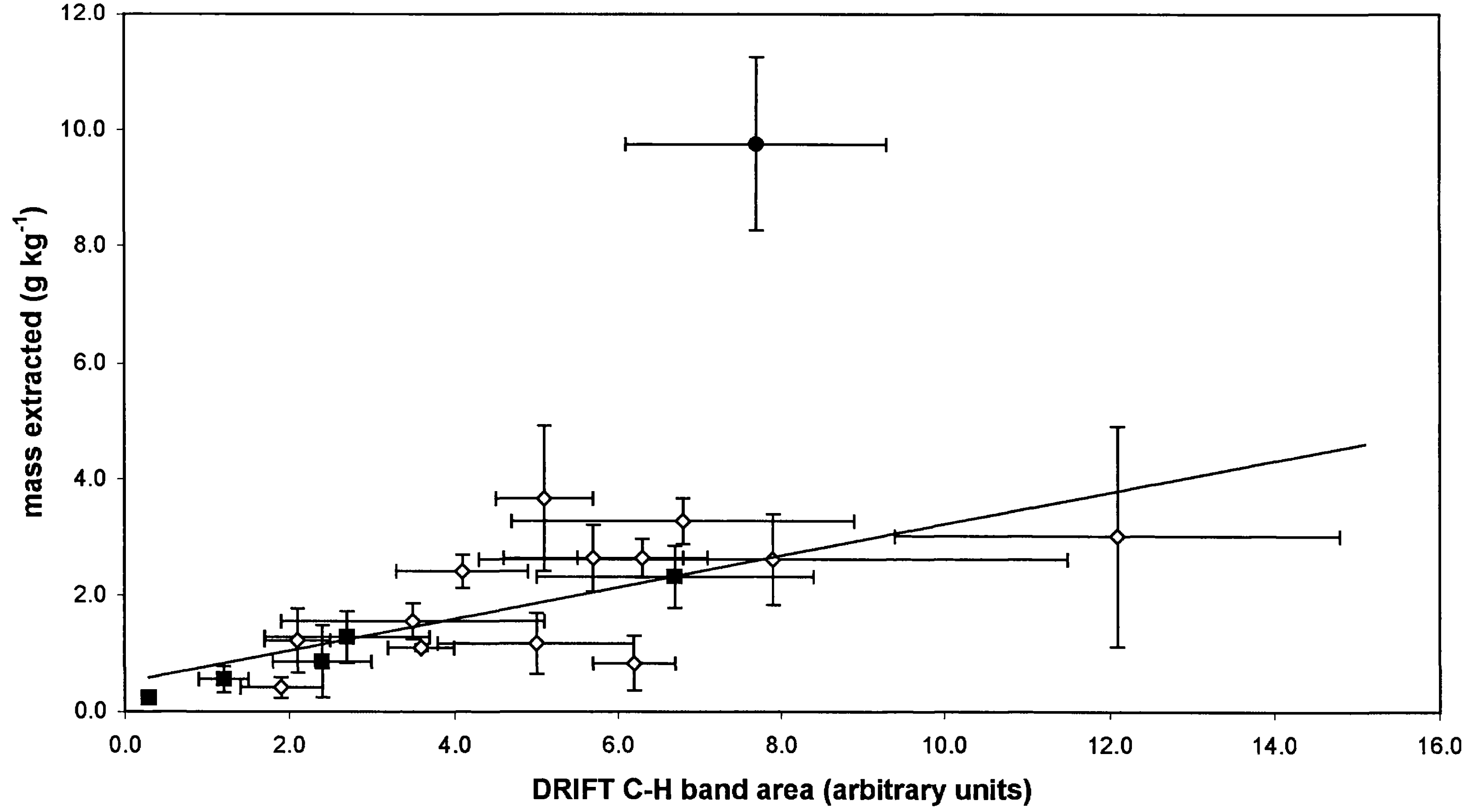

Figure 4.4: Mass extracted *vs.* DRIFT C-H band area. ◇ = repellent samples; ■ = wettable control samples; ● = sample NL1. The straight line shown is for the data set excluding NL1. $r^2 = 0.53$; slope = 0.27 (±0.06); intercept = 0.50 (±0.34). Error estimates based on one standard deviation.

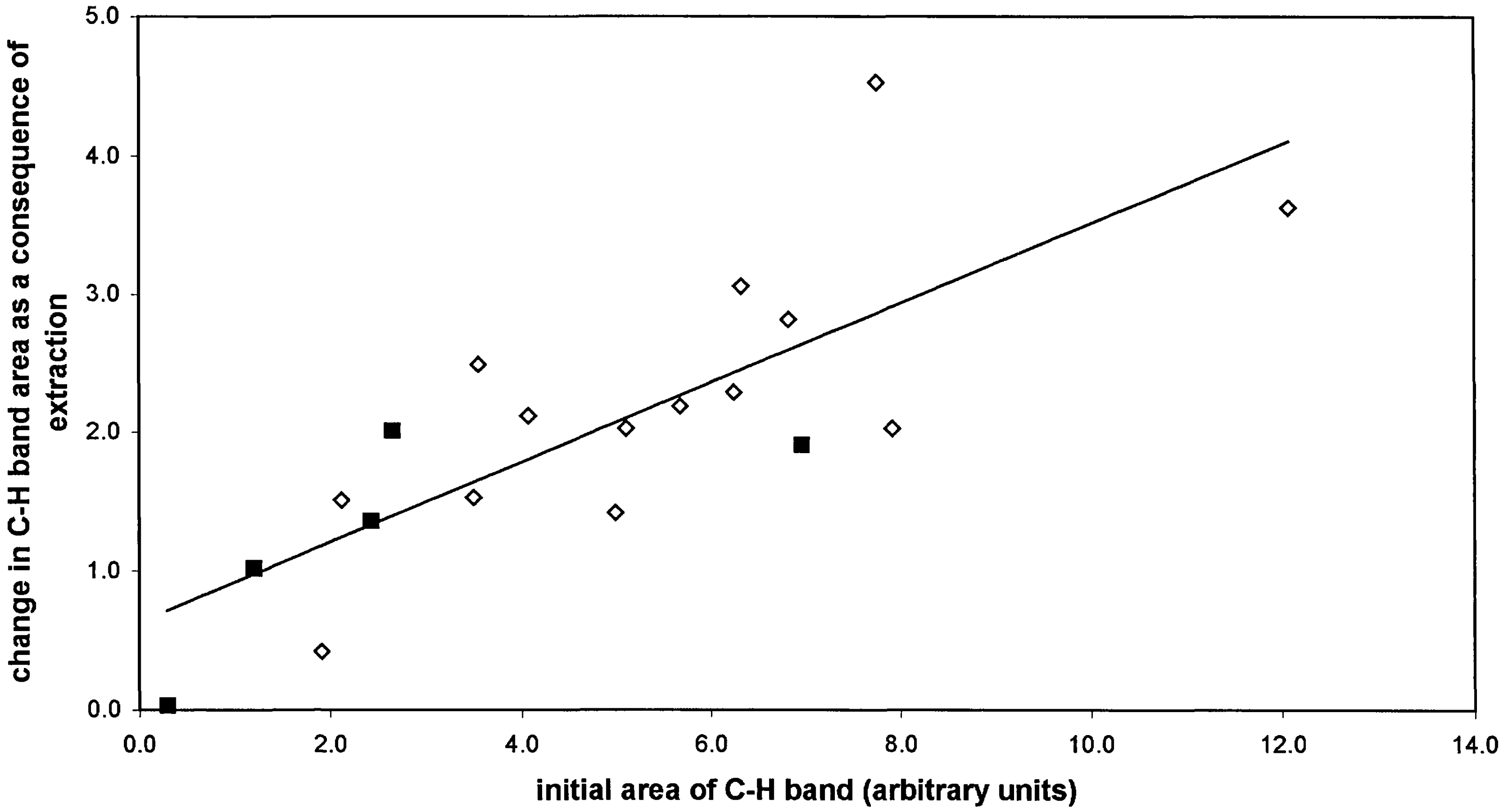

Figure 4.5: The change in DRIFT C-H absorption band area as a consequence of extraction *vs.* the initial area prior to extraction. ◇ = repellent samples; ■ = wettable control samples. $r^2 = 0.61$; slope = 0.29 (±0.06); intercept = 0.63 (±0.31).

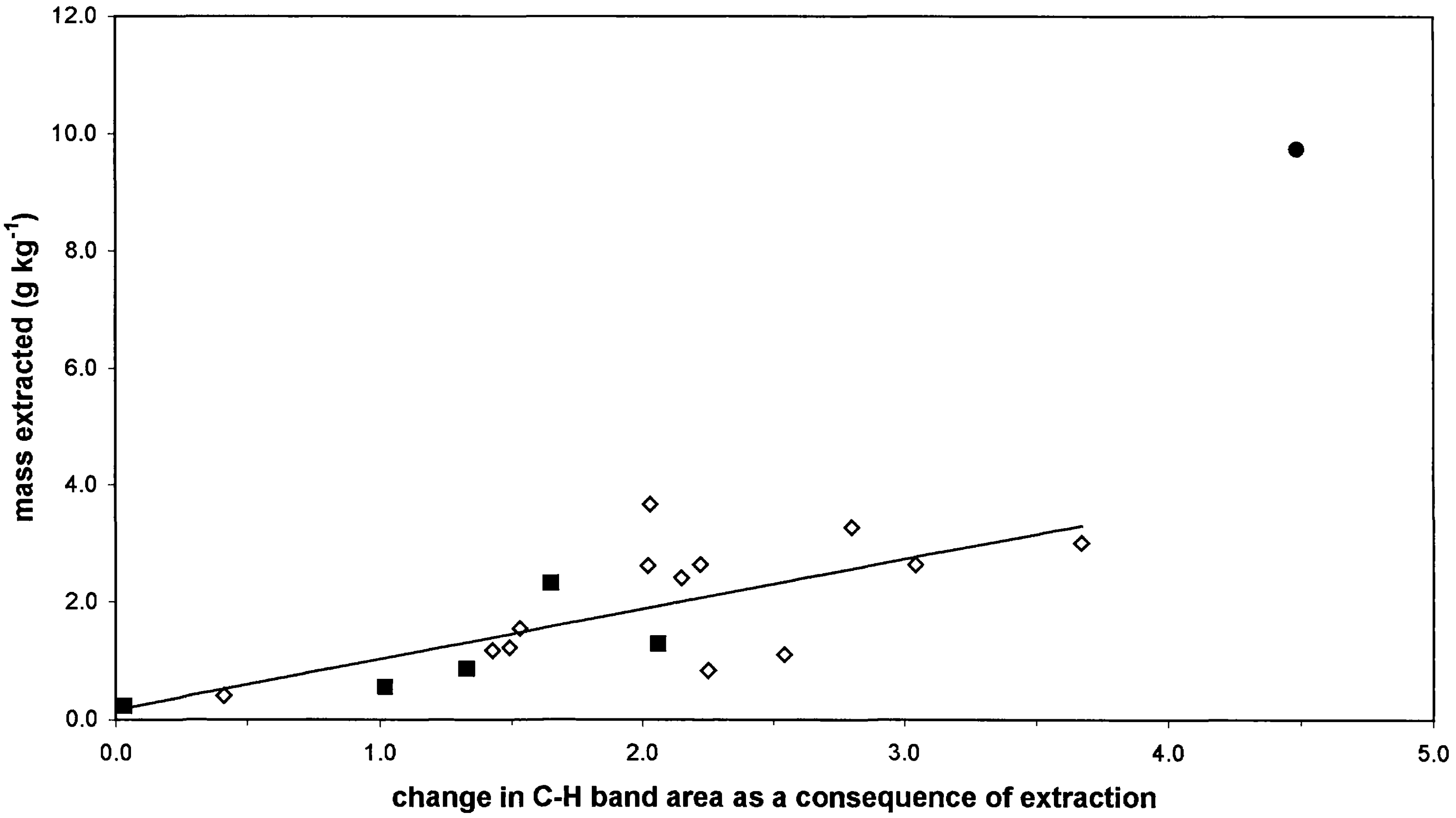

Figure 4.6: The mass extracted *vs.* the change in DRIFT C-H absorption band area as a consequence of extraction. ◇ = repellent samples; ■ = wettable control samples; ● = sample NL1. The straight line shown is for the data set excluding NL1. $r^2 = 0.51$; slope = 0.86 (±0.21); intercept = 0.17 (±0.43).

4.2.1.2 Effect of varying extraction solvent on the removal of aliphatic compounds

As reported in Section 3.2.3, the extraction solvent was varied in order to compare extraction efficiency when using different solvents. Chloroform, tetrahydrofuran, isopropanol, aqueous ammonia and water were used to extract sub-samples of soil UK1c. Amounts of material extracted and post-extraction water repellency levels are given in Table 3.5. DRIFT was used here to assess extraction efficiency in terms of the amount of aliphatic compounds removed according to the change in C-H band area as a consequence of extraction. The results obtained are given in Fig. 4.7. DRIFT analysis of soil UK1c gave a C-H band area of 5.02. Extraction with isopropanol: aqueous ammonia proved to be most efficient in terms of the proportion of aliphatic compounds removed. As a consequence of extraction the DRIFT C-H band area decreased by 38%.

Using both low polarity organic solvents (chloroform, tetrahydrofuran and isopropanol) and polar aqueous solvents (aqueous ammonia, water) resulted in poor extraction efficiency in terms of the proportion of aliphatic compounds removed. Lower polarity organic solvents also resulted in poor extraction efficiency in terms of both mass of material extracted and post-extraction repellency (Section 3.2.3). However, polar solvents were efficient in terms of both mass of material extracted and post-extraction repellency. These observations suggest that most of the material removed by the polar aqueous solvents was not aliphatic compounds and could be inorganic. The fact that extraction with aqueous solvents rendered the soil wettable suggests that only small amounts of aliphatic compounds may be necessary to induce repellency.

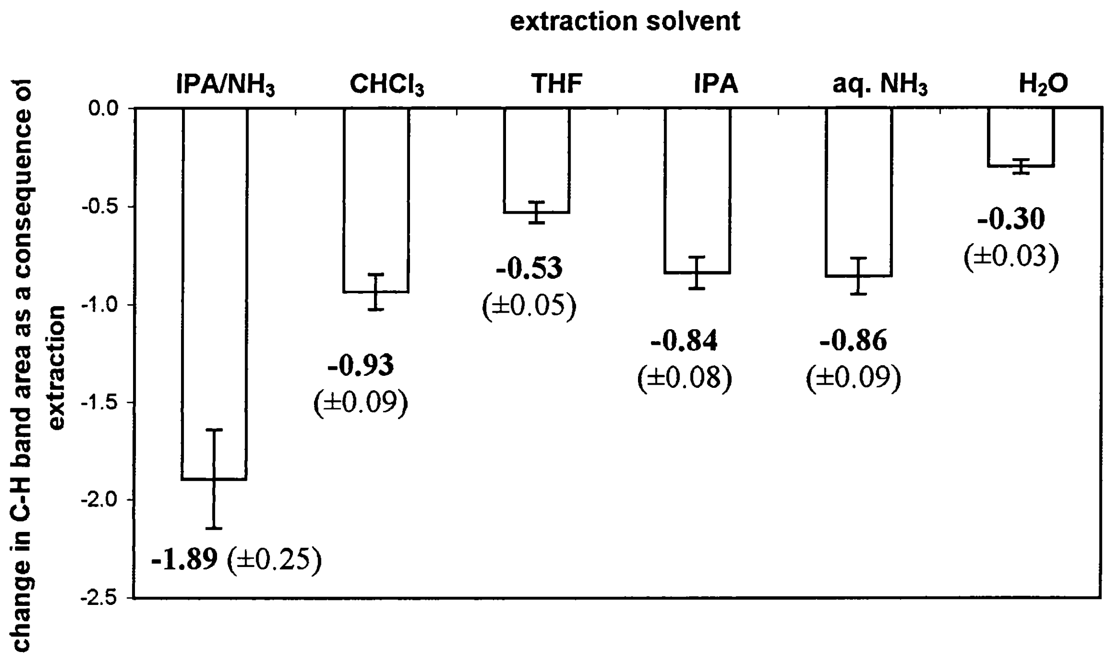

Figure 4.7: Efficiency of Soxhlet extractions with different solvents for sample UK1c in terms of the decrease in DRIFT C-H band area as a result of the removal of aliphatic compounds (C-H band area of soil UK1c pre-extraction = 5.02). Error estimates shown are ± one standard deviation of three independent measurements.

4.2.2 DRIFT on reapplied AWS samples

As a continuation of studies of the ability of soil extracts to induce water repellency (Section 3.2.5), DRIFT spectroscopy was used to assess the aliphatic C-H on acid washed sand samples with soil extracts reapplied, to compare C-H band areas with those obtained from the original soil samples. Measurements were obtained for samples reapplied with: (i) the chloroform-soluble fraction of the isopropanol: aqueous ammonia extract; (ii) the whole isopropanol: aqueous ammonia extract. Mean C-H band area values are given in Table 4.2. Note that the error estimates are considerably smaller for the measurements made on the AWS samples than for the original soil samples. This is possibly due to the relatively homogenous nature of these prepared samples in terms of particle size and shape of the acid washed sand particles and the even distribution of extracted material over the surfaces of the particles as a result of the reapplication procedure (Section 2.4). Sub-sample variation was therefore minimal in comparison to the original soils.

Fig. 4.8 shows that the original soil samples correspond to the lowest DRIFT C-H band areas, whilst analysis of the acid washed sand samples treated with both the chloroform-soluble fraction and the whole extract results in significantly greater values. Those samples reapplied with the whole extract produced slightly greater area values than those reapplied with the chloroform-soluble fraction. The calculated slope value in Fig. 4.9 indicates that the area values obtained from the reapplication of the chloroform-soluble fraction of extracts were 80 (±15) % of those observed as a result of reapplying whole extract. The increase in C-H band area compared to the original soils could be due to the extracted compounds adsorbing/bonding to the surfaces of the acid washed sand particles in a different manner to that found in the original soils. The homogenous nature of AWS particles in terms of size and shape and the difference in the surface area of the particles compared to the original soils could also have influenced how extracted materials coated them. As DRIFT samples surface material rather than the total bulk material the manner in which extracted materials coat the AWS particles could be of significance when measuring the C-H band area here.

Comparisons between water repellency and DRIFT C-H band area for AWS samples reapplied with (i) whole extract from IPA/H_2O and (ii) chloroform-soluble fraction of extract (dried at 20 °C) are shown in Fig. 4.10. The chloroform-soluble fractions induce more severe water repellency upon AWS samples than the whole extract. It is expected that the chloroform-soluble fraction will consist of mainly low polarity organic material whilst the whole extract will also contain more polar material. As described in Section 2.5.1, for each soil both the chloroform-soluble fraction and the whole extract were reapplied at the same mass ratio as the material was extracted initially. Therefore, when treating AWS with the chloroform-soluble fraction of the extracted material the concentration of low polarity organic compounds would be much higher, thus causing more severe water repellency. With r^2 values of 0.09 and 0.06 respectively neither set of treated AWS samples show any correlation between their C-H band areas and water repellency.

Table 4.2: Relative amounts of aliphatic C-H of (i) chloroform-soluble fraction of extracts and (ii) whole isopropanol: aqueous ammonia extracts, reapplied to acid washed sand. Values in brackets are error estimates based on 1 standard deviation of three independent measurements.

Sample code	Relative area under C-H peak	
	$CHCl_3$ fraction on AWS	IPA/NH_3 extract on AWS
PT1	14.8 (±1.7)	10.1 (±0.3)
PT2	13.2 (±1.8)	23.5 (±1.4)
PT3	9.8 (±1.4)	4.8 (±0.9)
PTC	9.2 (±0.9)	14.0 (±1.7)
NL1	38.2 (±5.7)	33.1 (±2.6)
NL2	13.9 (±1.2)	21.1 (±2.0)
NL3	8.2 (±0.3)	7.6 (±1.0)
NLC	9.9 (±1.1)	6.9 (±0.3)
UK1$_b$	13.3 (±2.8)	16.2 (±1.1)
UK2	13.3 (±2.5)	18.8 (±3.8)
UKC	5.7 (±1.1)	5.8 (±0.2)
AU1	15.2 (±0.9)	19.2 (±3.1)
AU2	24.5 (±1.8)	19.3 (±2.6)
AU3	12.2 (±1.5)	19.4 (±2.8)
AUC	5.8 (±1.8)	9.1 (±1.8)
GK1	14.8 (±0.6)	22.5 (±1.5)
GK2	16.2 (±1.5)	17.5 (±3.6)
GK3	5.3 (±0.8)	9.7 (±1.6)
GKC	14.2 (±0.4)	12.6 (±1.3)

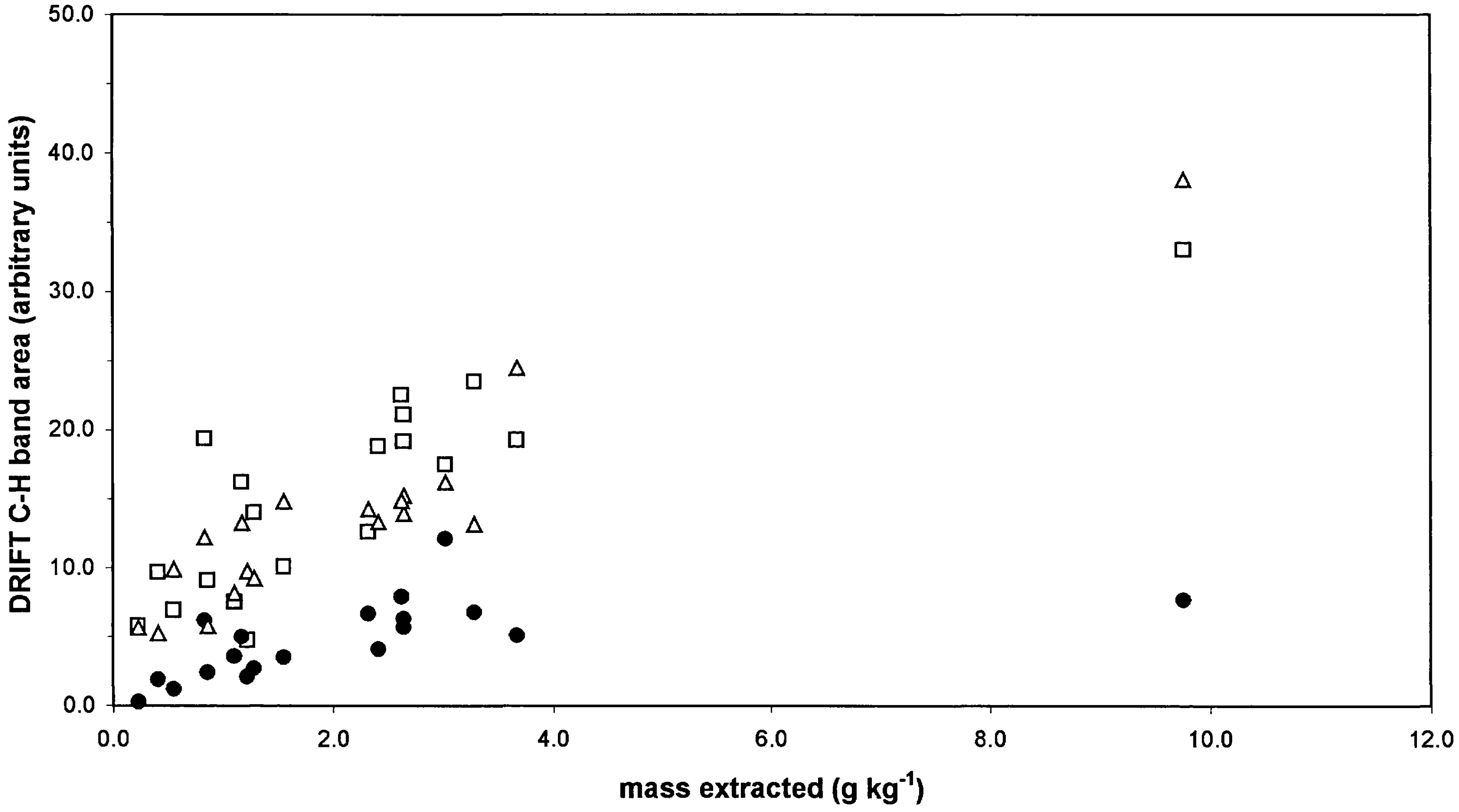

Figure 4.8: Comparison between DRIFT C-H band areas (arbitrary units) for soil pre-extraction (●), and AWS after: (i) reapplication of whole extract from IPA/H_2O (□); (ii) reapplication of chloroform-soluble fraction of the extract (△).

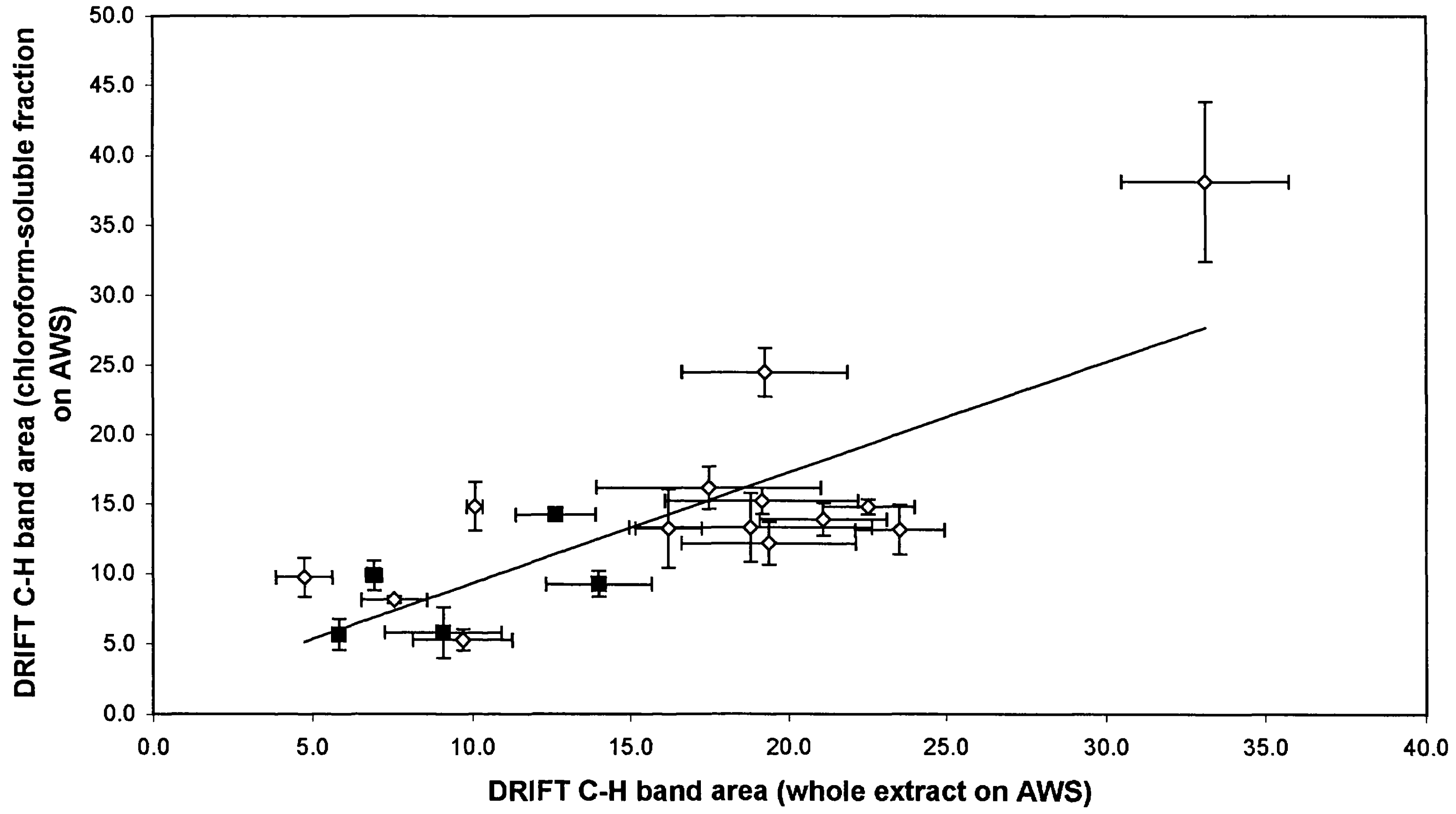

Figure 4.9: Comparison between the DRIFT C-H band areas after reapplication of (i) the whole extract from IPA/H_2O and (ii) the chloroform-soluble fraction. ◇ = extracts from repellent samples; ■ = extracts from wettable control samples. $r^2 = 0.61$; slope = 0.80 (±0.15); intercept = 1.35 (±2.60). Error estimates based on one standard deviation.

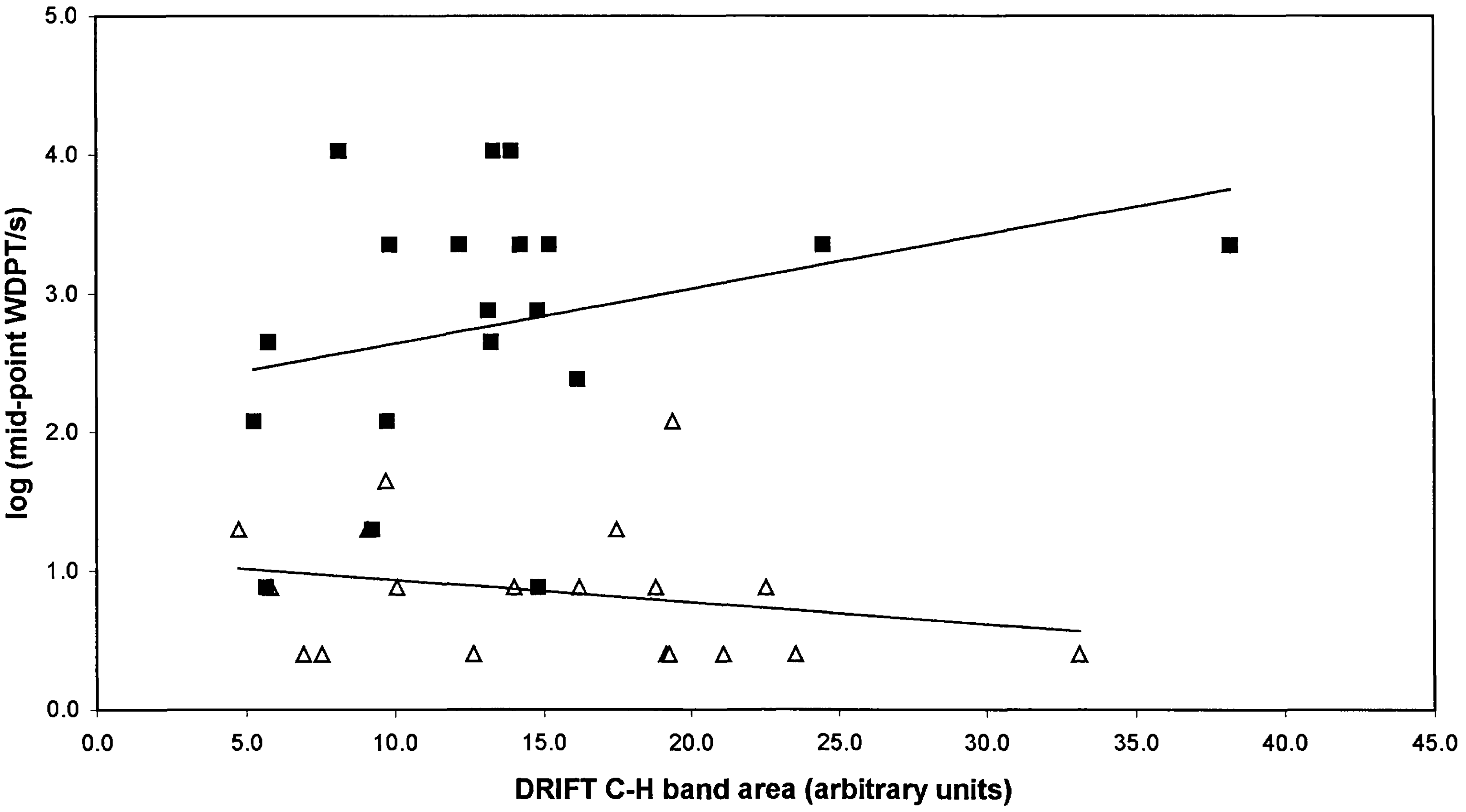

Figure 4.10: Comparison between log mid-point Water Drop Penetration Times and DRIFT C-H band area for AWS samples reapplied with (i) whole extract from IPA/H_2O (△), ($r^2 = 0.06$; slope = -0.02 (±0.02); intercept = 1.09 (±0.27)) and (ii) chloroform-soluble fraction of extract (■), ($r^2 = 0.09$; slope = 0.04 (±0.03); intercept = 2.25 (±0.47)).

4.2.3 Total organic carbon (TOC) content

Total organic carbon measurements were also made on samples pre- and post-extraction (as described in Section 2.6.5) to assess the efficiency of extraction at removing organic matter in general, rather than specifically the aliphatic fraction. Results are given in Table 4.3.

Table 4.3: Total organic carbon values (g kg^{-1} of soil) pre- and post-extraction. Values in brackets are error estimates, typically based on three independent measurements.

Sample code	**Total organic carbon (TOC) content (g kg^{-1})**		**% TOC extracted**
	Pre-extraction	**Post-extraction**	
PT1	6.3 (±0.1)	6.6 (±4.1)	-5 (±3)
PT2	10.3 (±1.5)	9.9 (±2.5)	4 (±1)
PT3	0.6 (±0.4)	None detected	100
PTC	0.1 (±0.2)	None detected	100
NL1	36.2 (±2.9)	25.6 (±1.0)	29 (±3)
NL2	5.9 (±0.3)	3.5 (±0.2)	41 (±5)
NL3	0.8 (±0.2)	None detected	100
NLC	None detected	None detected	N/A
UK1$_b$	11.4 (±2.7)	8.0 (±1.5)	30 (±20)
UK2	7.8 (±1.0)	5.4 (±1.4)	31 (±6)
UKC	3.1 (±0.6)	3.1 (±0.9)	0 (±3)
AU1	11.7 (±1.0)	9.0 (±1.0)	23 (±11)
AU2	14.4 (±0.5)	11.6 (±0.8)	19 (±6)
AU3	6.0 (±1.1)	4.9 (±0.1)	18 (±15)
AUC	2.2 (±0.4)	0.3 (±0.5)	86 (±23)
GK1	10.4 (±0.2)	8.0 (±0.4)	23 (±4)
GK2	21.2 (±0.8)	15.5 (±2.2)	27 (±11)
GK3	1.6 (±0.5)	1.6 (±0.1)	0 (±3)
GKC	6.2 (±0.7)	5.1 (±0.3)	18 (±10)

No correlation is observed between water repellency (WDPT class) and TOC content regardless of whether wettable control samples are included (Fig. 4.11). There are, however, significant correlations between: (i) the change in TOC as a consequence of extraction and the initial TOC (Fig. 4.12); (ii) the mass extracted and initial TOC (Fig. 4.13); (iii) the mass extracted and the change in TOC as a consequence of extraction (Fig. 4.14). The strong linear relationship in Fig. 4.13 indicates that only *ca.* 22 (± 2)% of the organic material has been extracted and this fraction is independent of TOC content. The data in Fig. 4.12 indicate that extraction removes only *ca.* 27 (± 3)% of the TOC initially present whilst the intercepts in Figs. 4.13 and 4.14 suggest that *ca.* 0.8 (± 0.3) g kg^{-1} of the material collected in the extract is not organic carbon and that the amount of this material is similar for all soils. Figs. 4.12-4.14 highlight the facts that the wettable control samples are all relatively low in TOC content (< 6 g kg^{-1}) and the change in TOC content of these soils as a consequence of extraction is also low (< 2 g kg^{-1}).

McKissock *et al.* (2003) obtained $r^2 = 0.36$ for a plot of 'log WDPT (s)' *vs.* 'log organic C (%)', which is a considerably stronger correlation than that observed in Fig. 4.11. Again, the stronger correlation between the two parameters (as was found for aliphatic C and water repellency) may be a result of the relatively narrow geographical range of samples studied.

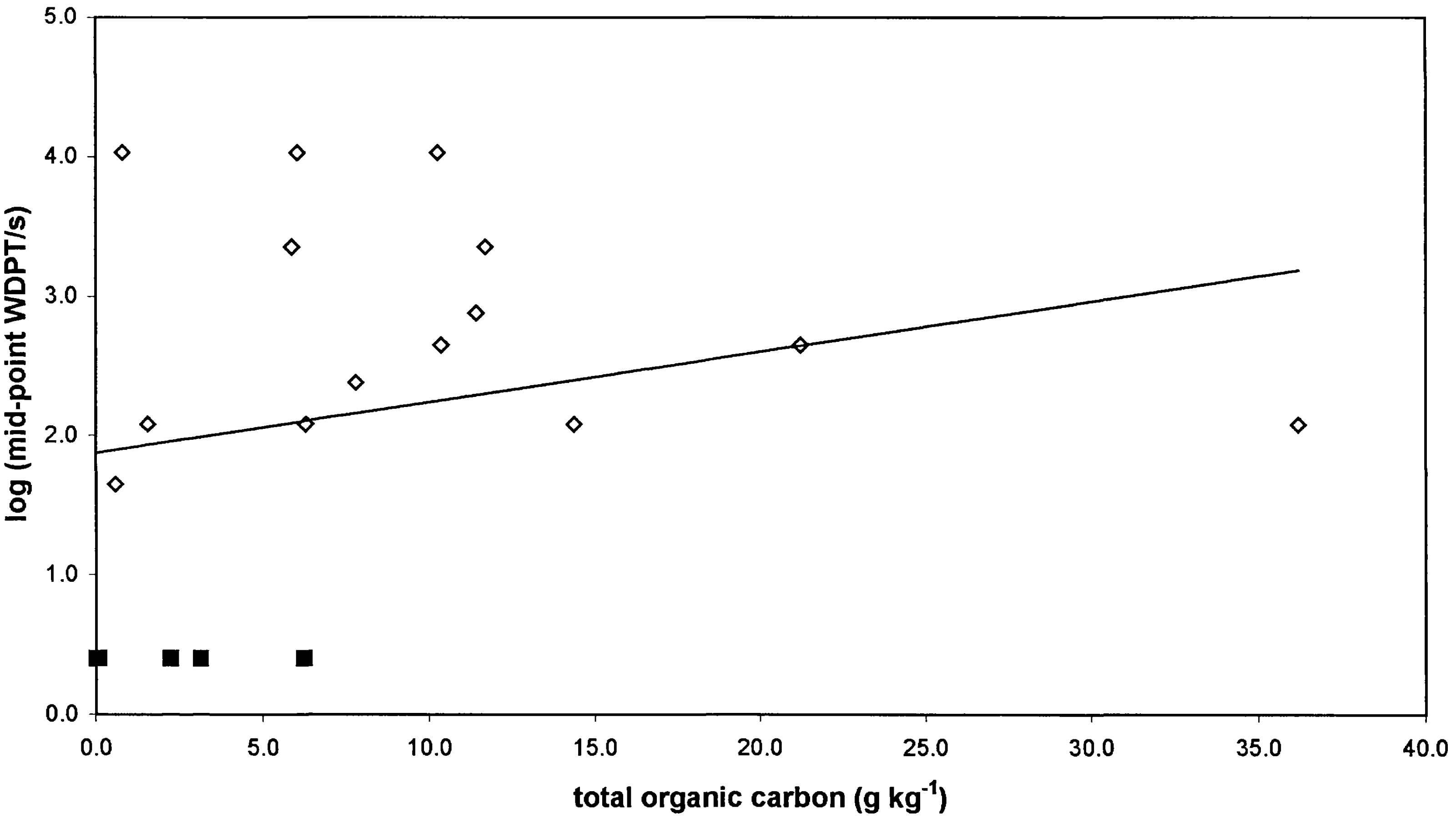

Figure 4.11: Comparison between log-midpoint Water Drop Penetration Times and total organic carbon (TOC) content. ◇= repellent samples; ■= wettable control samples. $r^2 = 0.06$; slope = 0.036 (±0.035); intercept = 1.9 (±0.4).

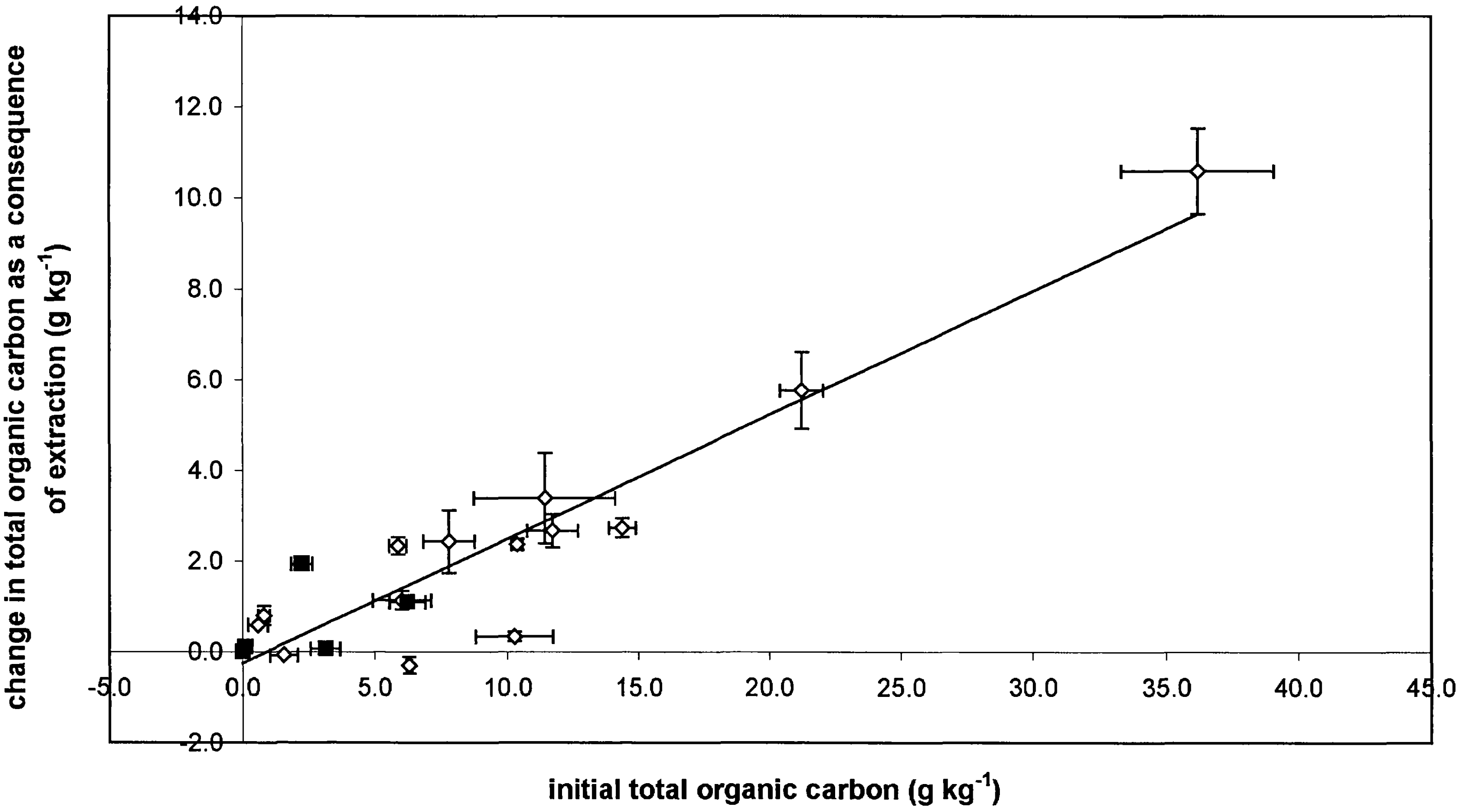

Figure 4.12: Comparison between the change in TOC as consequence of the extraction and initial total organic carbon (TOC) content. ◇= repellent samples; ■= wettable control samples. r^2 = 0.87; slope = 0.27 (±0.03); intercept = -0.25 (±0.31). Error estimates based on one standard deviation.

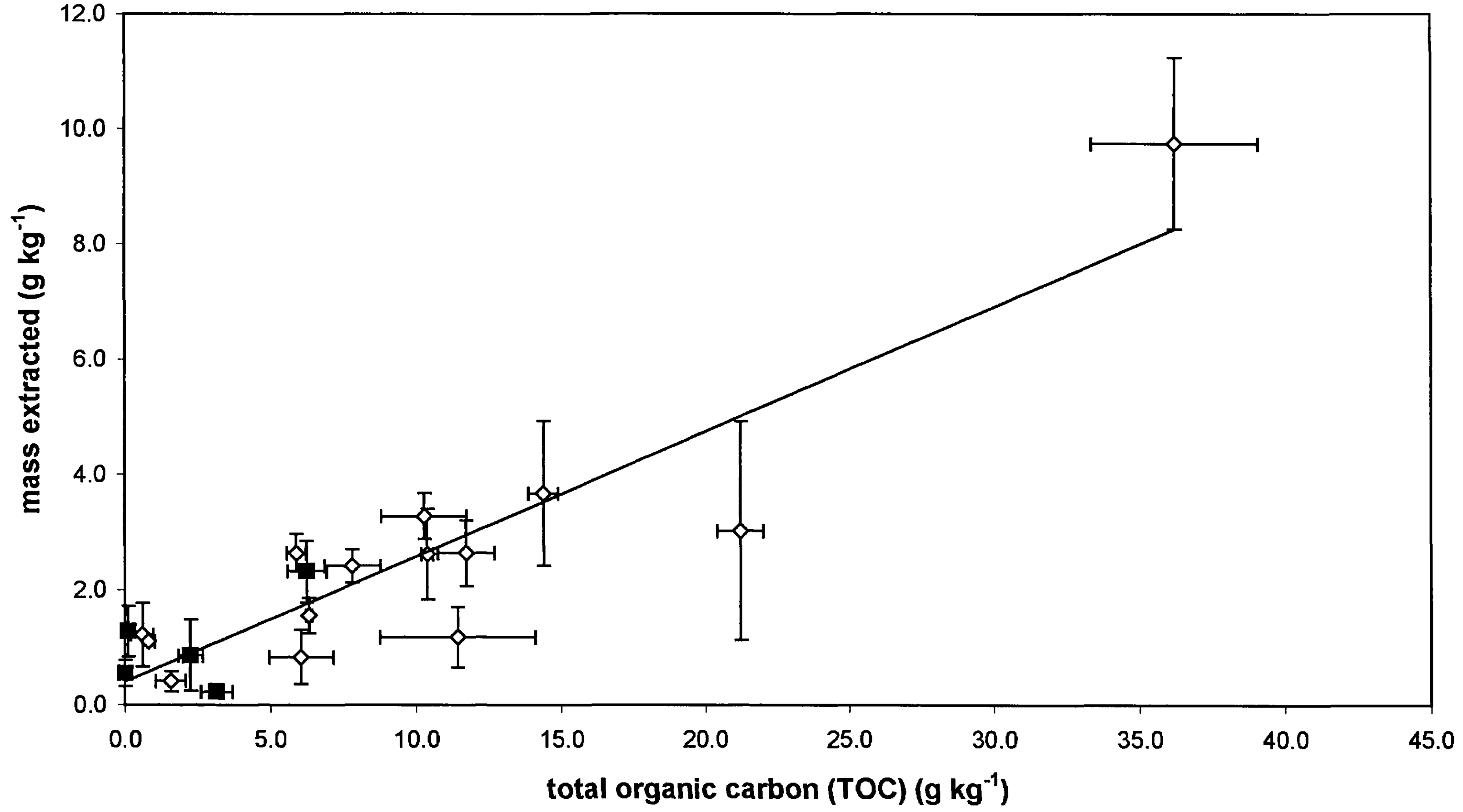

Figure 4.13: Comparison between the mass extracted and the initial total organic carbon (TOC) content. ◇ = repellent samples; ■ = wettable control samples. $r^2 = 0.82$; slope = 0.22 (±0.02); intercept = 0.40 (±0.29). Error estimates based on one standard deviation.

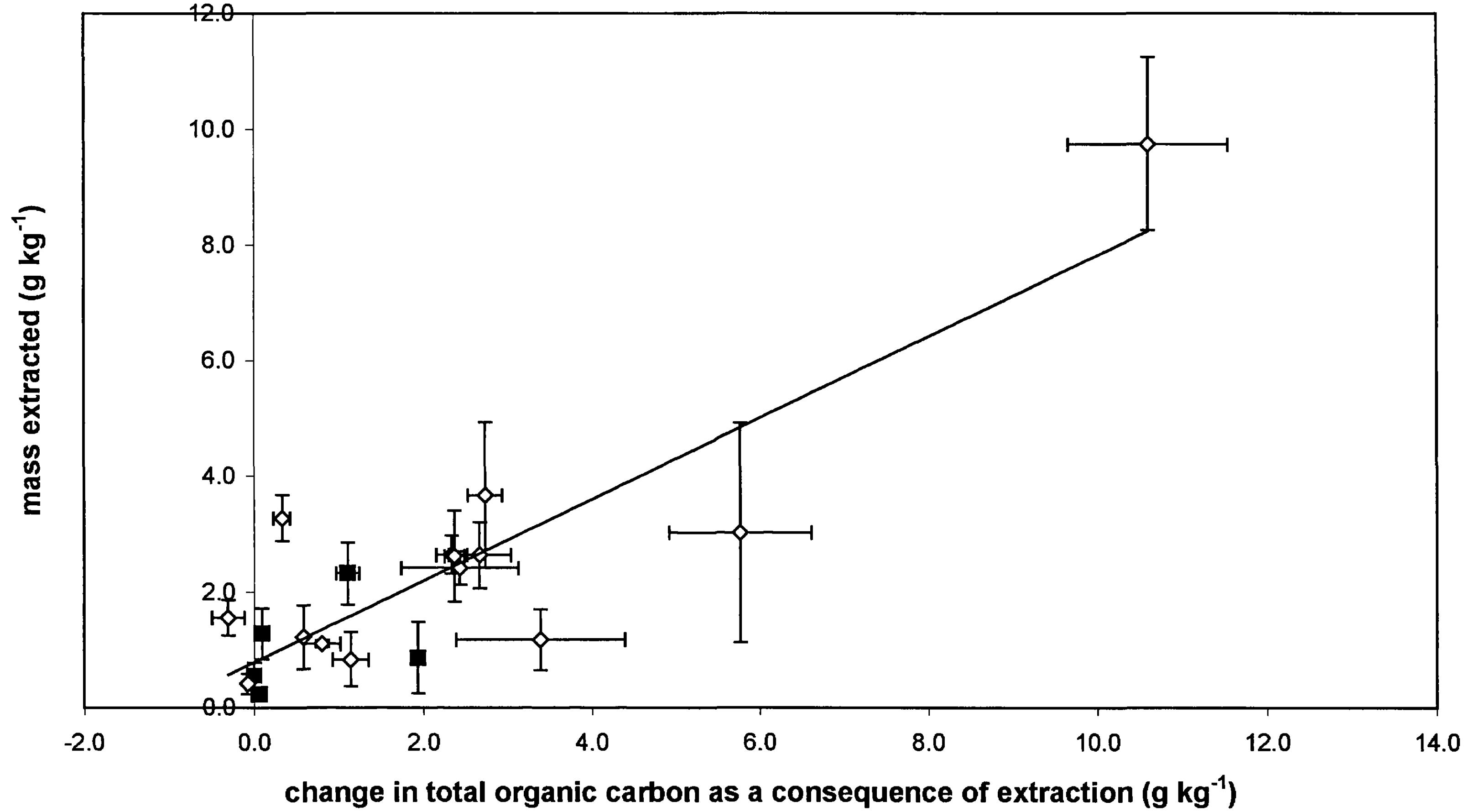

Figure 4.14: Comparison between the mass of material extracted and the change in the TOC content as a consequence of extraction. ◇= repellent samples; ■= wettable control samples. $r^2 = 0.75$; slope = 0.7 (±0.1); intercept = 0.8 (±0.3). Error estimates based on one standard deviation.

4.2.3.1 Effect of varying extraction solvent on TOC content

The extraction solvent was varied in order to compare extraction efficiency when using different solvents (Section 3.2.3). Chloroform, tetrahydrofuran, isopropanol, aqueous ammonia and water were used to extract sub-samples of soil UK1c. Measuring TOC content was used here to assess extraction efficiency in terms of the change in TOC content as a consequence of extraction. The results obtained are given in Fig. 4.15. The TOC content of soil UK1c pre-extraction was 12.9 (±1.4) g kg^{-1}.

Extraction with aqueous ammonia proved to be most efficient in terms of the organic C removed. As a consequence of extraction the TOC content decreased by 46% (5.9 (±1.2) g kg^{-1}). Extraction with isopropanol: aqueous ammonia was less effective with only 15% of the TOC content removed as a consequence of extraction. However, as shown in Fig. 4.7, extraction with isopropanol: aqueous ammonia proved to be the most efficient in terms of the proportion of aliphatic compounds removed (*ca.* 36%). The relative success of aqueous ammonia at extracting organic carbon is not surprising considering the relatively large amount of material extracted (Table 3.5). However, water also removed a relatively large amount of material (rendering the soil wettable), but did not appear to extract any organic carbon. This observation is not in agreement with the DRIFT results (Fig. 4.7) where *ca.* 6% of the initial aliphatic C-H on the soil was extracted. However, as discussed in Section 4.2.3.2, even at zero TOC content there is some residual absorption measured in the DRIFT signal. Once again, the fact that soil samples have been rendered wettable regardless of the quantity of organic carbon removed, suggests that very small amounts of aliphatic compounds may be responsible for inducing repellency.

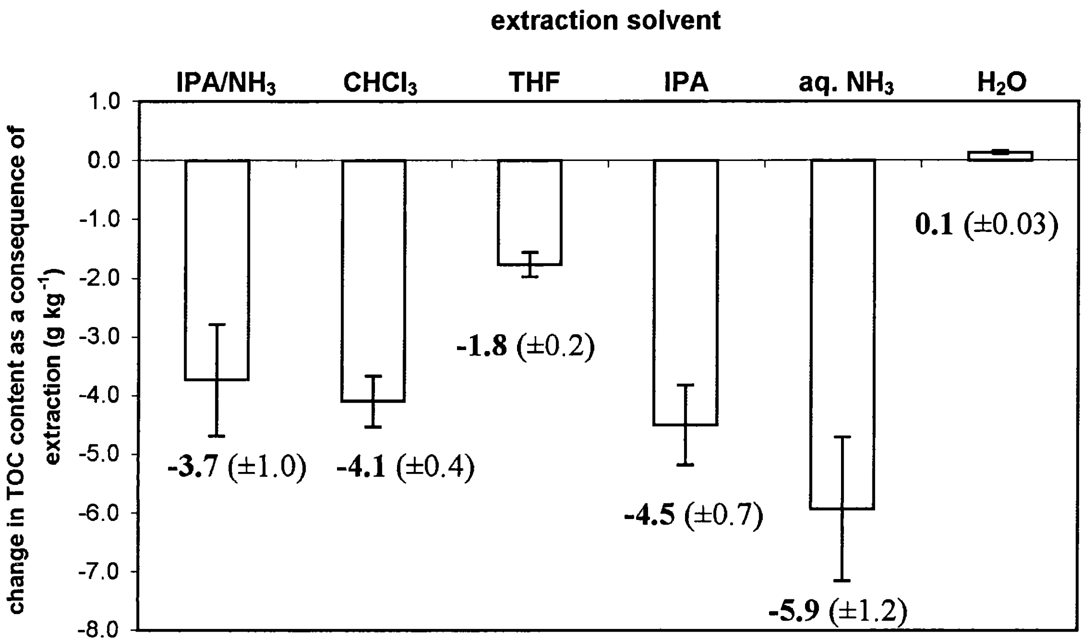

Figure 4.15: Efficiency of Soxhlet extractions with different solvents on sample UK1c in terms of the change in TOC content as a result of extraction (TOC content of soil UK1c pre-extraction = 12.9 (±1.4) g kg^{-1}). Error estimates shown are ± one standard deviation of three independent measurements.

4.2.3.2 Comparison of aliphatic C-H and TOC content

There are strong linear relationships between: (i) DRIFT signal and TOC for samples both pre- and post-extraction (Fig. 4.16); (ii) the mass extracted and change in DRIFT signal (Fig. 4.6), provided data for sample NL1 are removed.

The positive intercept in Fig. 4.16 indicates that even at zero TOC content there is some residual absorption measured in the DRIFT signal, suggesting some systematic error in the procedure used, such as a weak overlapping band of non-organic origin, which may not have been possible to remove from the band area calculation. Treating the data pre- and post-extraction as two separate sets gives a smaller intercept for the latter case. However, the quality of the data is such as to preclude a definitive statement concerning the possible extraction of inorganic compounds that have DRIFT absorption bands in the 2800-3000 cm^{-1} region.

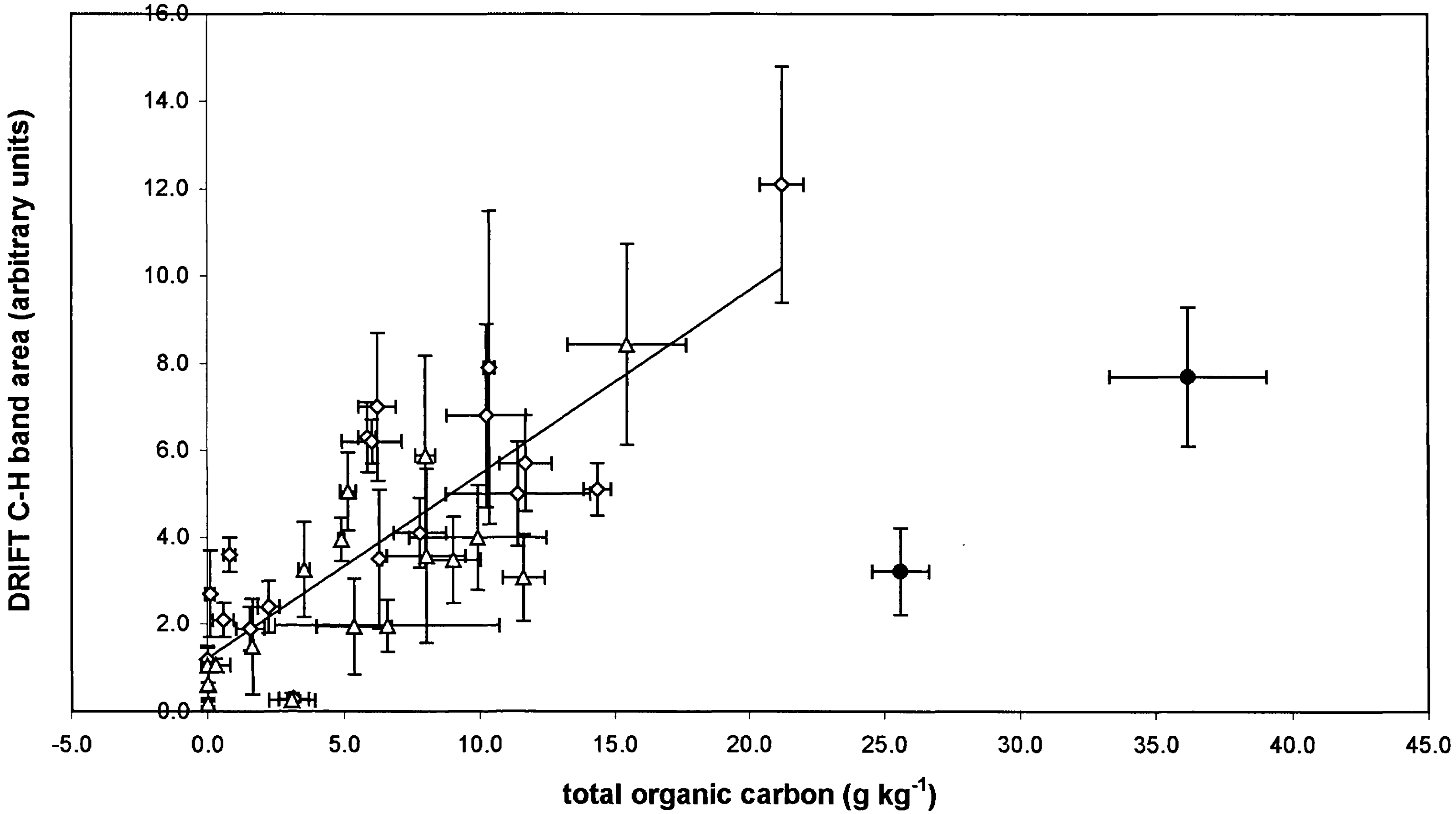

Figure 4.16: Comparison between the DRIFT C-H absorption band area and total organic carbon (TOC) content for all samples, pre- and post-extraction. ◇ = pre-extraction; △ = post-extraction; ● = sample NL1. The straight line shown is for the data set excluding NL1. $r^2 = 0.66$; slope = 0.42 (±0.05); intercept = 1.2 (±0.4). Error estimates based on one standard deviation.

4.3 Chapter summary

In the first part of this chapter DRIFT spectroscopy was assessed as a means of analysing aliphatic carbon in water repellent soils, to identify any relationship between the amount of aliphatic C-H units present in the wide range of soils selected and their water repellency, as measured by DRIFT analysis and water drop penetration time (WDPT) results. Solvent extracted soils were also included to assess the efficiency of the extraction procedure at removing aliphatic compounds. The second part focussed on the total organic carbon content (TOC) of the soils and the relationship between TOC content and water repellency, as well as measuring solvent-extracted soils to assess the efficiency of the extraction procedure at removing organic C. The main findings were:

1. Water repellency correlated better with DRIFT C-H band area (or aliphatic content) than TOC content, although neither parameter correlated well with water repellency.
2. Strong correlations were observed between the mass of material extracted from the soils and: (i) the initial aliphatic C-H content (providing sample NL1 was excluded as discussed in Section 4.2.1.1); (ii) the initial TOC content.
3. In no case did the isopropanol: aqueous ammonia extraction procedure remove all organic C or aliphatic compounds from the soils. Measurements indicated that extraction removed *ca.* 29 (±6)% of the initial aliphatic C-H and *ca.* 27 (±3)% of the initial TOC content.
4. Strong linear correlations were observed between DRIFT signal and TOC content for samples both pre- and post-extraction.
5. For all soils *ca.* 0.8 g kg^{-1} of the extracted material was not organic carbon.

6. DRIFT was a useful technique as it allowed a rapid and non-destructive measurement of the aliphatic C-H content of the raw soil samples without the need to extract soils to obtain material for analysis. The reproducibility of DRIFT measurements was less than desirable, although the high differences in C-H content between the different soil samples were enough to make the data meaningful.

7. DRIFT analysis of AWS samples treated with both the chloroform-soluble fraction and the whole extract resulted in significantly greater C-H band areas compared to those obtained from the original soil samples.

8. For soil UK1c, isopropanol: aqueous ammonia was the most efficient solvent at removing aliphatic compounds whilst aqueous ammonia alone was most efficient at removing organic C.

Chapter 5

Kinetics, efficiency and selectivity of Soxhlet extractions

5.1 Introduction

In Chapter 3 it was shown that Soxhlet extraction of sandy soils with an isopropanol: aqueous ammonia mixture (7:3, v:v) for 24 h removed water repellency from twelve of fourteen initially repellent soil samples, while two samples retained some level of repellency. The composition of Soxhlet extracts from five of the initially repellent samples has been determined by Mainwaring *et al.* (2004) and resembled those of the extracts from comparable wettable soils in most respects. The main types of compounds in all extracts were identified as fatty acids, amides, alkanes, aldehydes or ketones and complex ring-containing structures. It was speculated that the relative abundances of these compound types and/or their molecular arrangement or conformation on the surfaces of the soil particles were important in the expression of water repellency (Mainwaring *et al.* 2004).

In this chapter, an investigation aimed at exploring the nature of the solvent extraction procedure in more detail was carried out by assessing the change in: (i) the soil properties (water repellency level and organic carbon content) and (ii) the composition of the soil extract at intervals throughout a 24 h extraction period. The temporal selectivity of the extraction procedure was therefore investigated. In addition, it was thought that if there was an order in which compound types were removed during the extraction procedure it may imply a certain molecular arrangement or conformation on the soil's surface which can cause water repellency.

The sandy soil sample used throughout this study was sample UK1c (sample details in Table 2.2). This particular sample was selected as it was both strongly water repellent and stock was easy to replenish as it was sampled only a few miles from the

University. Initially, an evaluation of the kinetics and efficiency of Soxhlet extraction using an isopropanol: aqueous ammonia mixture was carried out by varying the extraction time (1-24 h). Each extraction was carried out on a separate sub-sample of soil UK1c. For each extract obtained the mass of material extracted was determined and the composition of the chloroform-soluble fraction (as used by Ma'shum *et al.* 1988 for treating AWS) analysed by gas chromatography – mass spectrometry (GC-MS). For the extracted soil samples, WDPT tests were carried out after drying in order to assess how the level of water repellency had changed, and amounts of aliphatic C-H and organic carbon were measured by DRIFT and TOC respectively. In addition to this, both chloroform and tetrahydrofuran (low polarity organic solvents) were used as the extraction medium for 24 h and their effect in terms of compound types extracted was compared to that of the isopropanol: aqueous ammonia mixture to assess the selectivity of extraction using lower polarity solvents. Gas chromatography with flame-ionisation detection (GC-FID) was also used in an exploratory attempt to provide semi-quantitative data on the amounts of individual alkanes present in a soil extract.

5.2 Results and discussion

5.2.1 Mass of material extracted

The mass of material extracted using isopropanol: aqueous ammonia increased with extraction duration. Mass extracted ranged from *ca.* 500 mg kg^{-1} for the 1 h extraction to *ca.* 1500 mg kg^{-1} for the 24 h extraction (Fig. 5.1). The rate at which material was extracted decreased with time. Over the first hour extraction rate was 480 mg kg^{-1} h^{-1}, whereas for the final 16 hours the rate was constant at 20 mg kg^{-1} h^{-1}. Approximately 1/3 of the total material extracted over 24 h was removed within the first hour. This proportion increased to approximately 2/3 and 4/5 within the first 4 h and 8 h respectively. As the mass extracted did not increase considerably after 8 h this may have coincided with the loss of ammonia to the atmosphere (and therefore decrease in the concentration of ammonia in the extraction solvent mixture) as discussed in Section 3.2.3. It has been shown that extracting soil UK1c with aqueous ammonia alone resulted in more than a six-fold increase in extraction efficiency in a 24 h period (Table 3.5). It could therefore be speculated that if the concentration of ammonia in the extraction solvent mixture was kept constant throughout the 24 h extraction period, a decrease in the rate at which material was extracted may not have been observed so soon into the extraction period.

Chloroform or tetrahydrofuran as the extraction solvent removed significantly less material over 24 h (120-250 mg kg^{-1}) than the isopropanol: aqueous ammonia mixture, suggesting that a more polar medium is able to dissolve a larger proportion of the organic matter present in the sample.

5.2.2 Water repellency assessments

Before extraction, soil UK1c exhibited extreme water repellency (WDPT class: 18000 s). Generally, the repellency of the extracted samples decreased as extraction duration increased, with samples extracted for 16 and 24 h being rendered wettable (WDPT class < 5 s) (Fig. 5.2). It could be speculated that a threshold was exceeded (between 8 and 16 h of extraction) whereby once a certain proportion of the surface material had been extracted a large enough proportion of the particle surface area was exposed to render the soil wettable. Also, the fact that extraction for 8 – 16 h removes just over 1 g of material per kg of soil and renders it wettable is further evidence for the notion that only small amounts of material (or particular compound types) are required to induce water repellency.

A similar study on a severely water repellent Australian soil (MED: 3.5 mol dm^{-3}, comparable to WDPT: 900-3600s) was carried out by Ma'shum *et al.* (1988). Soxhlet extractions using a range solvents (tetrachloroethylene, chloroform, ether, benzene: ethanol (2:1, v:v), methanol, isopropanol: water (7:3, v:v) and isopropanol: aqueous ammonia (7:3, v:v)) were carried out for 8, 16, 24, 32, 40 and 48 h. Isopropanol: aqueous ammonia was found to be the most effective solvent in terms of its capability to render the water repellent soil wettable. Soxhlet extraction with isopropanol: aqueous ammonia rendered the soil wettable within 8 h , having extracted *ca.* 1.9 g kg^{-1} of soil.

5.2.3 Analysis of organic material by DRIFT and TOC

Fig. 5.3 shows the change in the area of the DRIFT C-H band (and therefore amount of aliphatic compounds in the soil, as discussed in Chapter 4) as extraction time was increased. The rate at which aliphatics were removed decreased with time. The C-H band area decreased by *ca.* 38%, from *ca.* 5.0 before extraction to *ca.* 3.1 after a 24-hour extraction. Approximately half of the aliphatic material extracted over 24 hours was removed within the first hour of extraction, corresponding to a decrease of *ca.* 0.9 area units. A similar decrease was observed for the remaining 23 hours of extraction.

In the same way as post-extraction water repellency and the amount of aliphatic compounds present in the soil, TOC content also decreased with extraction time (Fig. 5.4). The rate at which organic carbon was removed also decreased with time.

The TOC content before extraction was *ca.* 12.9 g kg^{-1}. On average, the rate at which organic carbon was removed was greatest during the first hour of extraction with a decrease of *ca.* 3.2 g kg^{-1}. Relatively little extraction of organic carbon was observed for the final 23 hours of extraction. 9.71 (±2.10) g kg^{-1} organic carbon remained on the soil after 1 h compared to 9.16 (±2.13) g kg^{-1} after 24 h.

In the same way as for the mass of material extracted, after 1 - 4 h of extraction the amount of organic material (both organic carbon and aliphatic C-H) extracted was small. Again, this could be attributed to the decrease in concentration of ammonia in the extraction solvent mixture. As discussed in Section 3.2.3, it is expected that both the polarity and alkalinity of the ammonia assists in the extraction of compounds such as carboxylic acids. The extraction of acids would probably also assist the removal of low-polarity compounds such as alkanes, as the two compound types would be weakly 'bound' together by their long aliphatic chains. As the affinity of low-polarity compounds (e.g. alkanes) for the aqueous extraction medium is probably very low, it is speculated that the decline in extraction of acids could also, therefore, lead to a decline in the extraction of alkanes.

5.2.4 Separation and identification of compounds

GC-MS was used to separate and identify compounds in each soil extract as described in Section 2.6.8. To compare the compositions of the materials extracted under different conditions, 27 main peaks were selected in the GC-MS trace obtained following 24 h extraction with isopropanol: aqueous ammonia. GC-MS chromatograms of the chloroform fractions of extracts after 1, 4, 8, 16 and 24 h extractions are shown in Figs. 5.5-5.9 (note: each extraction was carried out on a separate sub-sample of soil UK1c). Retention times, chemical formulae and names of the compounds represented by the 27 main peaks are given in Table 5.1. The compounds were identified on the basis of their EI mass spectra using the NIST mass spectral search program and NIST/EPA/NIH mass spectral library v.2.0. Peak heights were measured for each extract and used to indicate relative abundance. Three main types of compound occurred in all extracts: fatty acids, alkanes and amides. Other compound types such as phthalates and cholesterol/stigmasterol-type compounds were also present although the structures of some of these could not be determined on the basis of their EI mass spectra alone. They have therefore been classed together as 'others' for the purpose of this study.

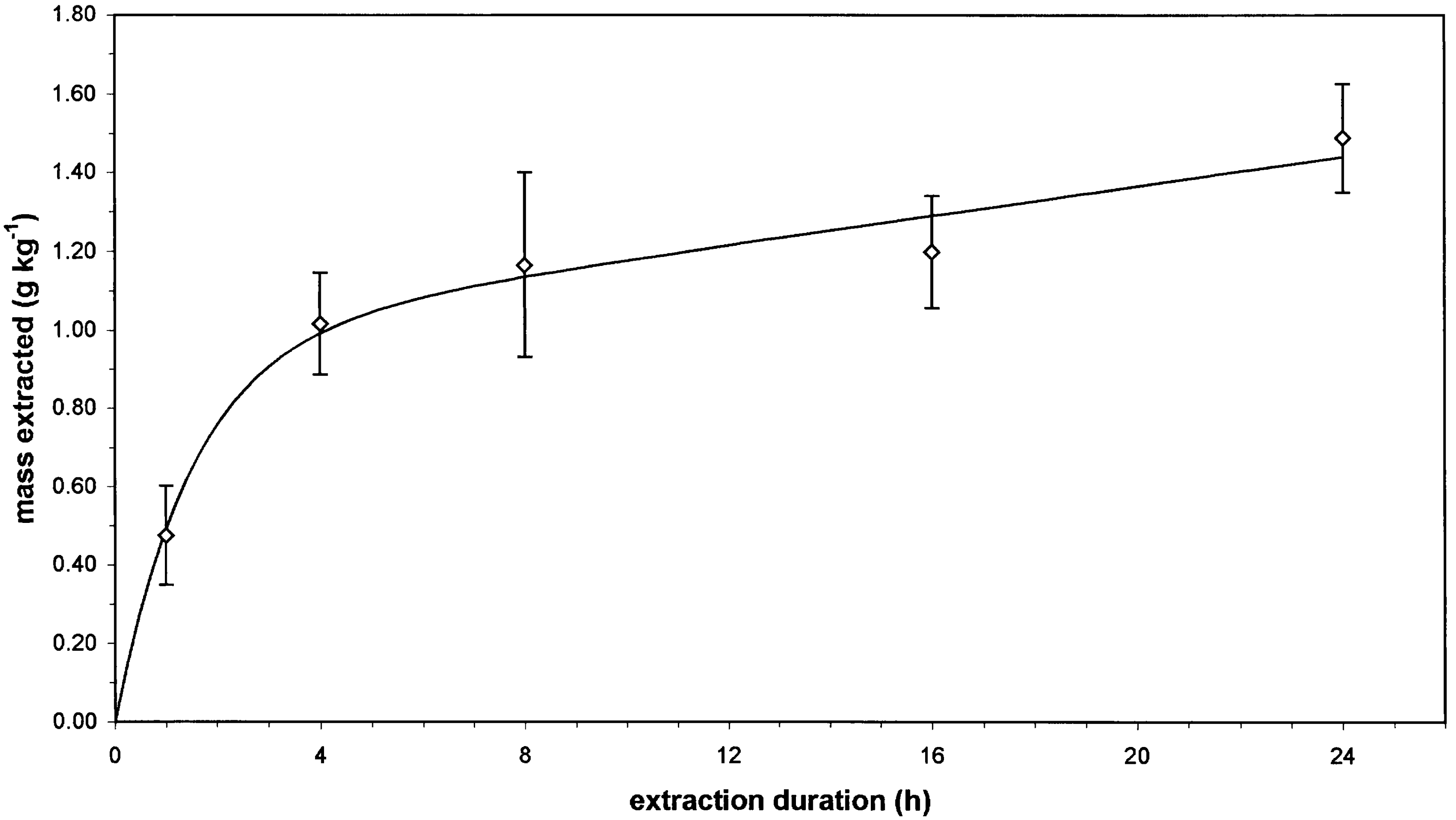

Figure 5.1: Mass of material extracted *vs.* extraction duration. Error estimates based on one standard deviation of three independent extractions.

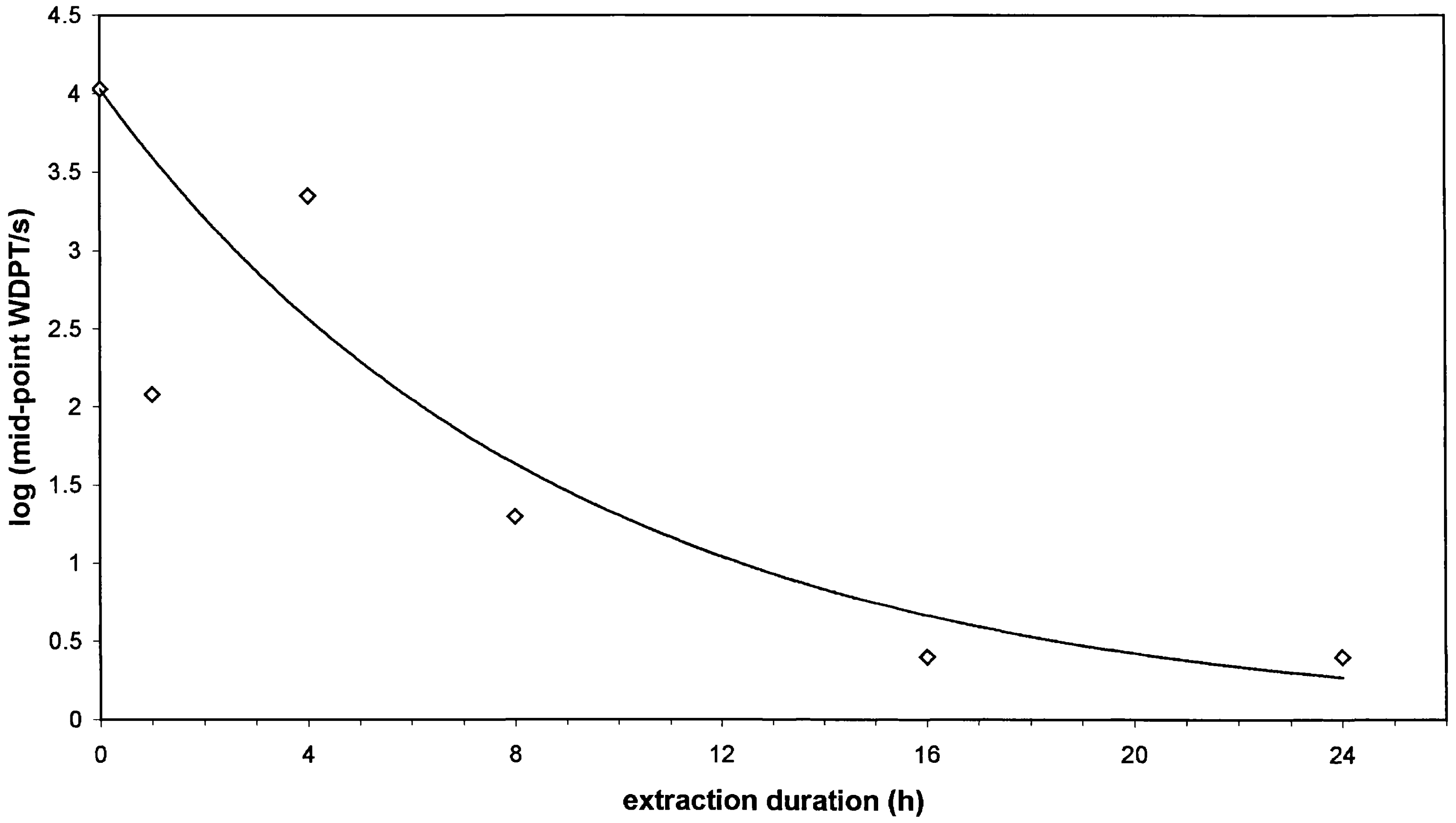

Figure 5.2: Post-extraction water repellency level (log mid-point WDPT / s) of soil sample *vs.* extraction duration. (Errors in log mid-point WDPT cannot be estimated easily as WDPT values are recorded according to distinct repellency classes rather than exact time values).

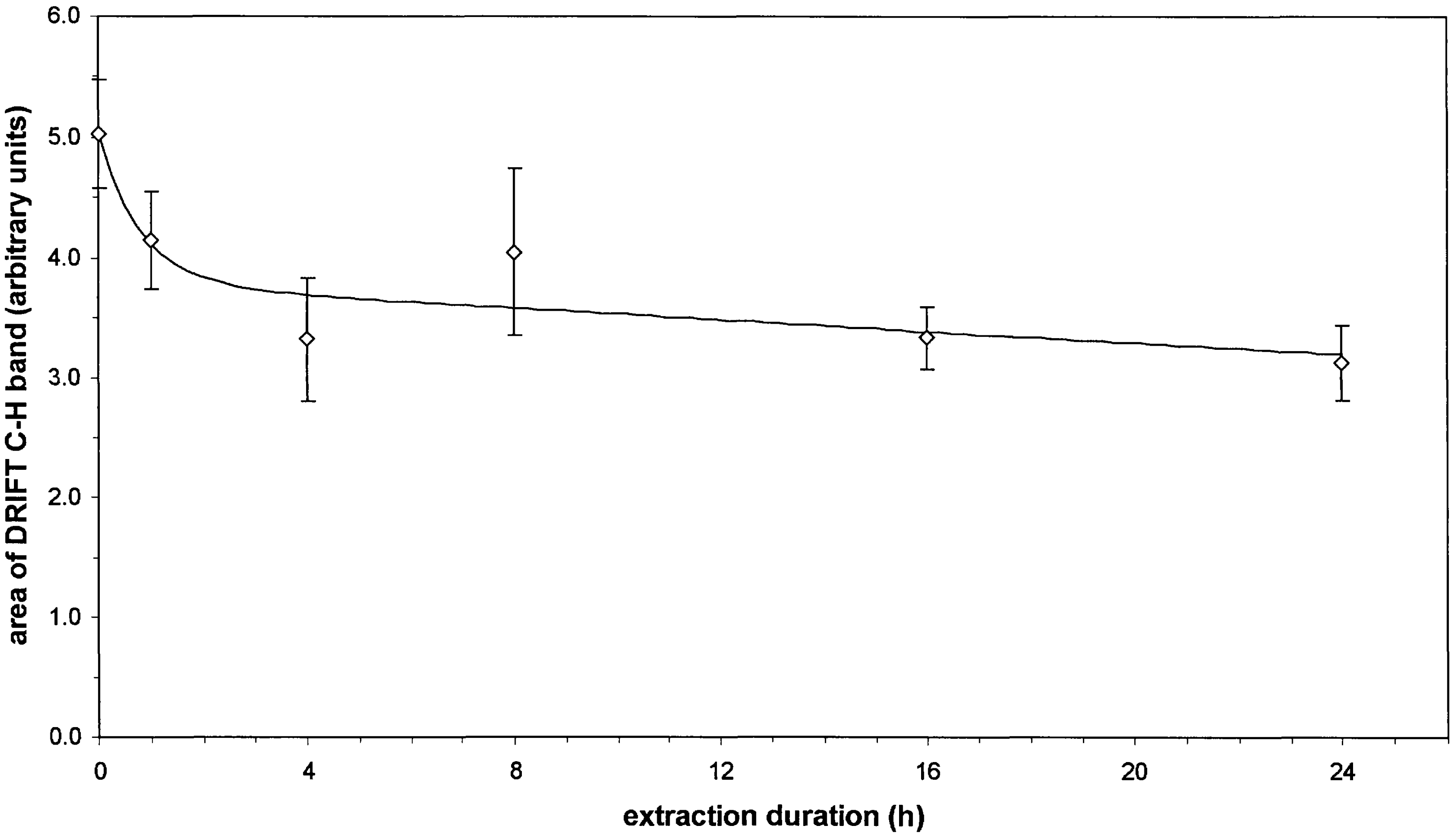

Figure 5.3: Area of C-H band as determined by DRIFT *vs.* extraction duration. Error estimates based on one standard deviation of three independent measurements.

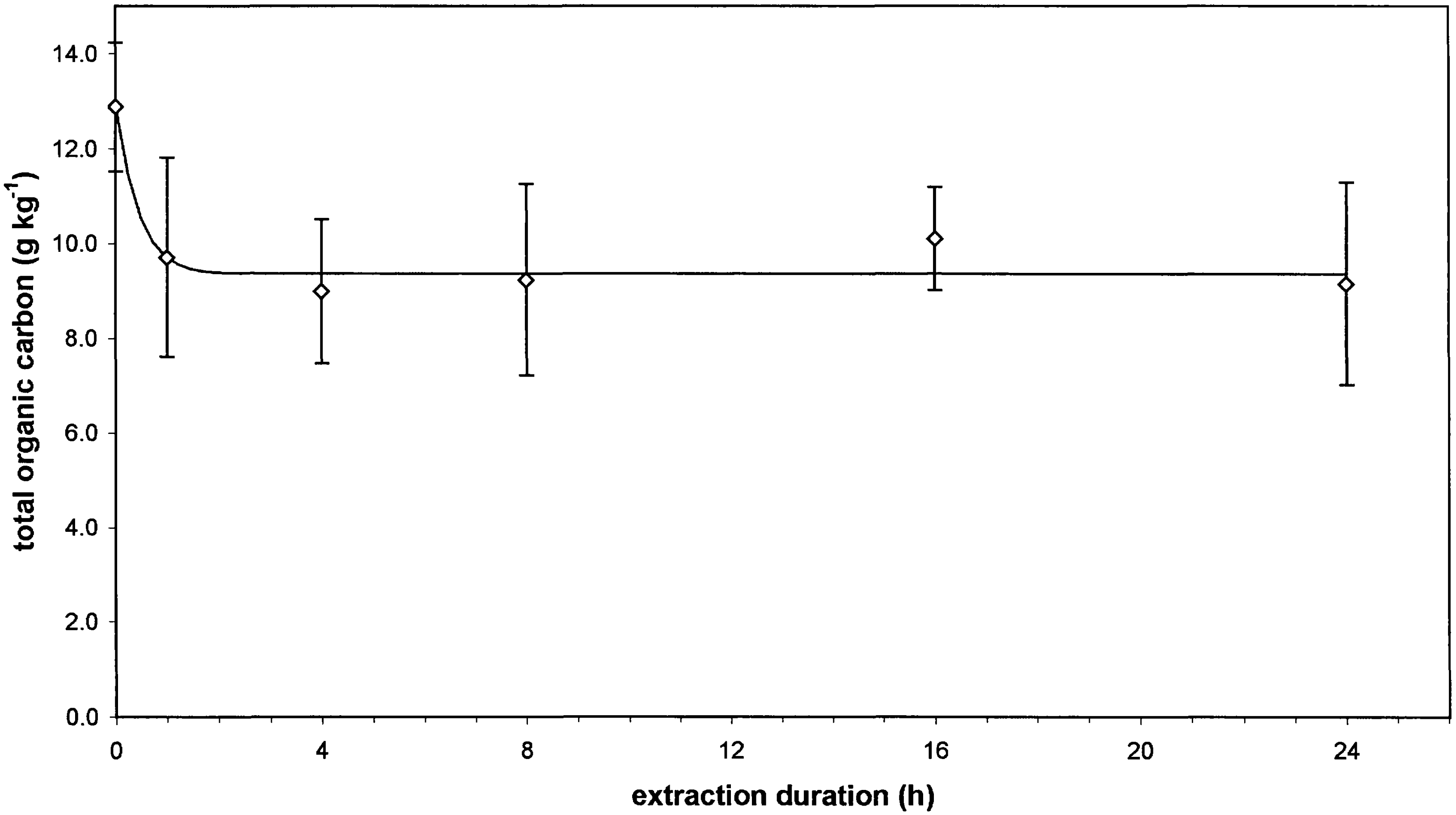

Figure 5.4: Total organic carbon (TOC) content *vs.* extraction duration. Error estimates based on one standard deviation of three independent measurements.

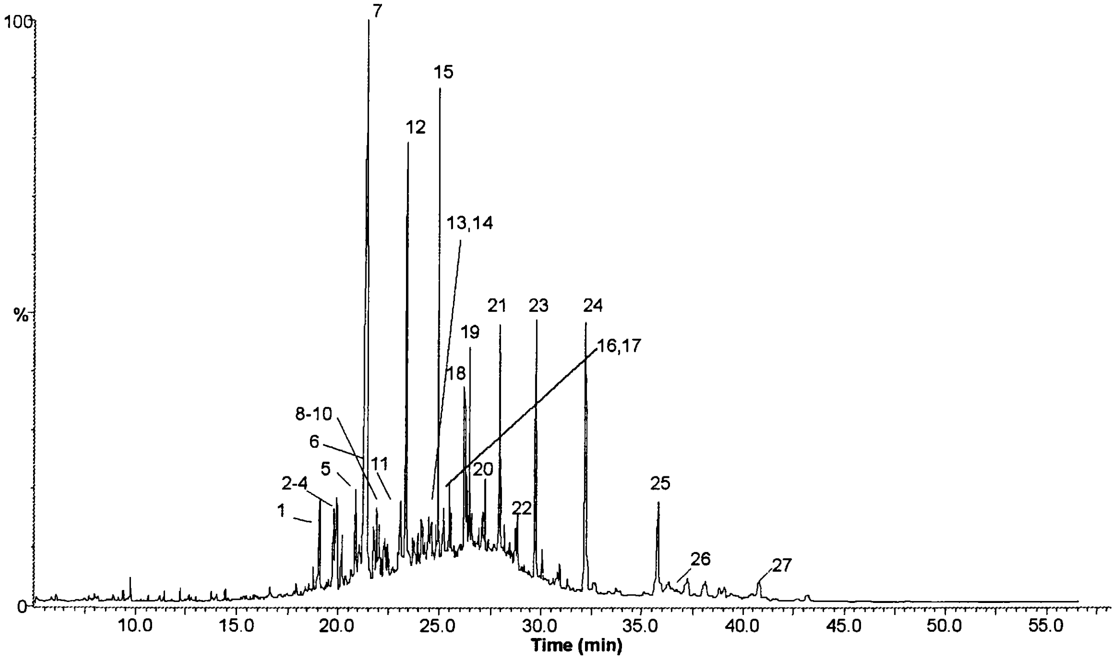

Figure 5.5: GC-MS chromatogram of isopropanol: aqueous ammonia extract (chloroform-soluble fraction) after 1 h extraction.

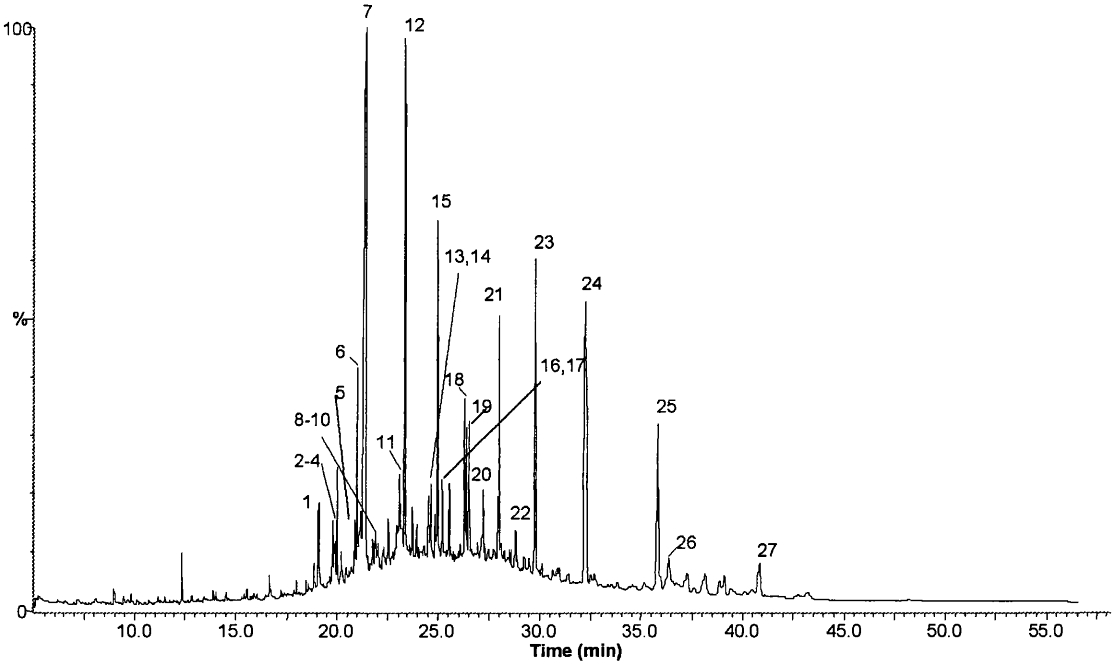

Figure 5.6: GC-MS chromatogram of isopropanol: aqueous ammonia extract (chloroform-soluble fraction) after 4 h extraction.

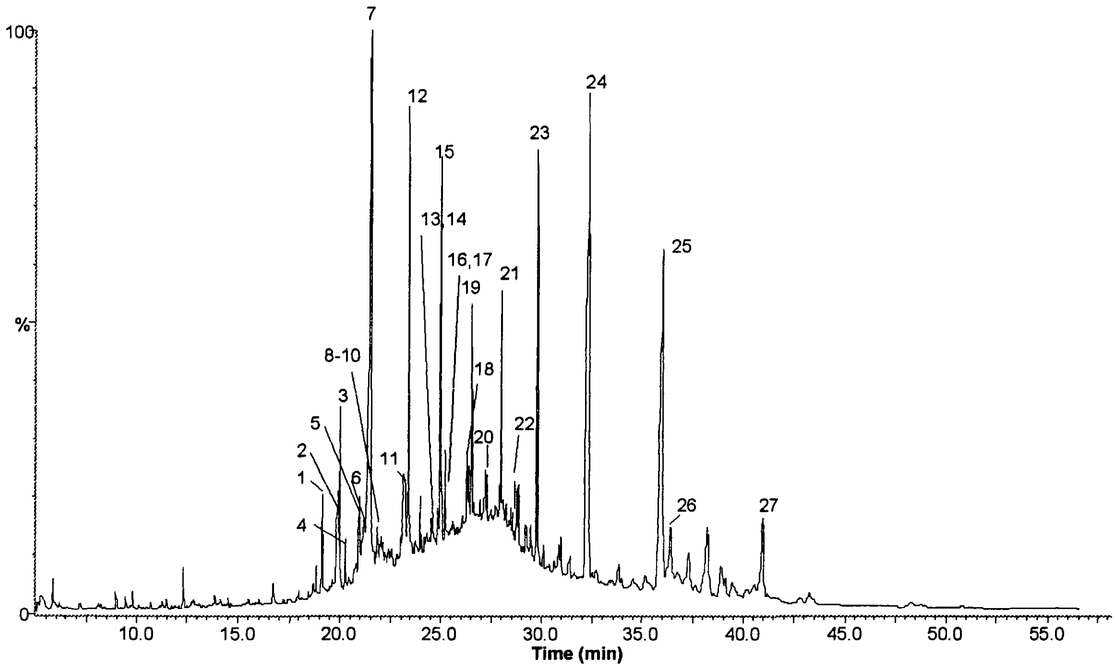

Figure 5.7: GC-MS chromatogram of isopropanol: aqueous ammonia extract (chloroform-soluble fraction) after 8 h extraction.

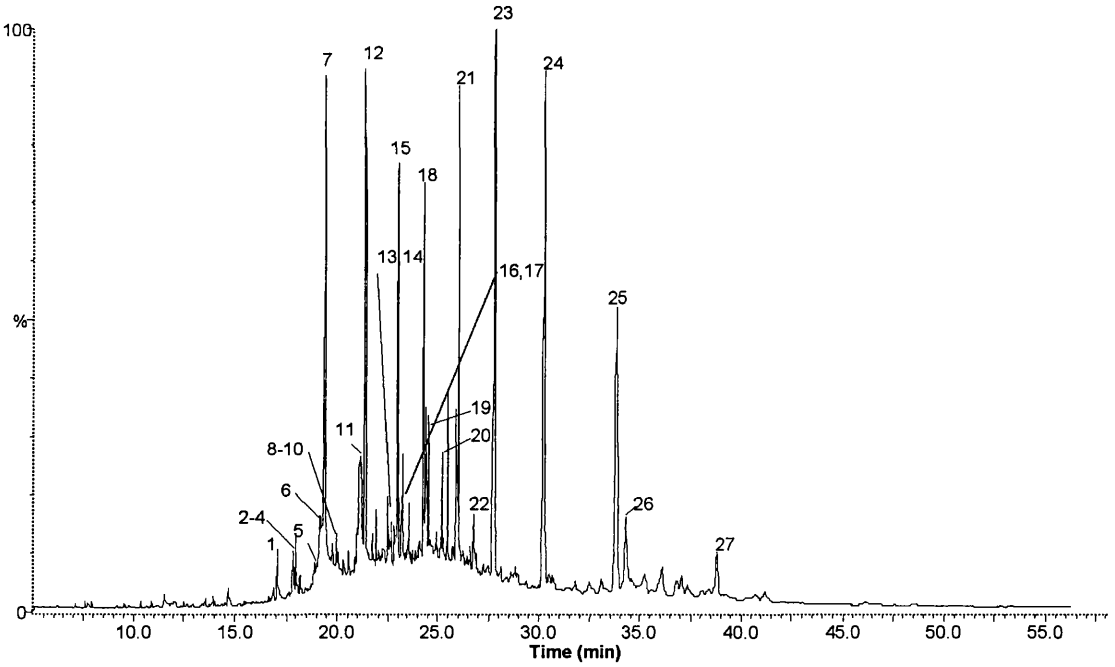

Figure 5.8: GC-MS chromatogram of isopropanol: aqueous ammonia extract (chloroform-soluble fraction) after 16 h extraction.

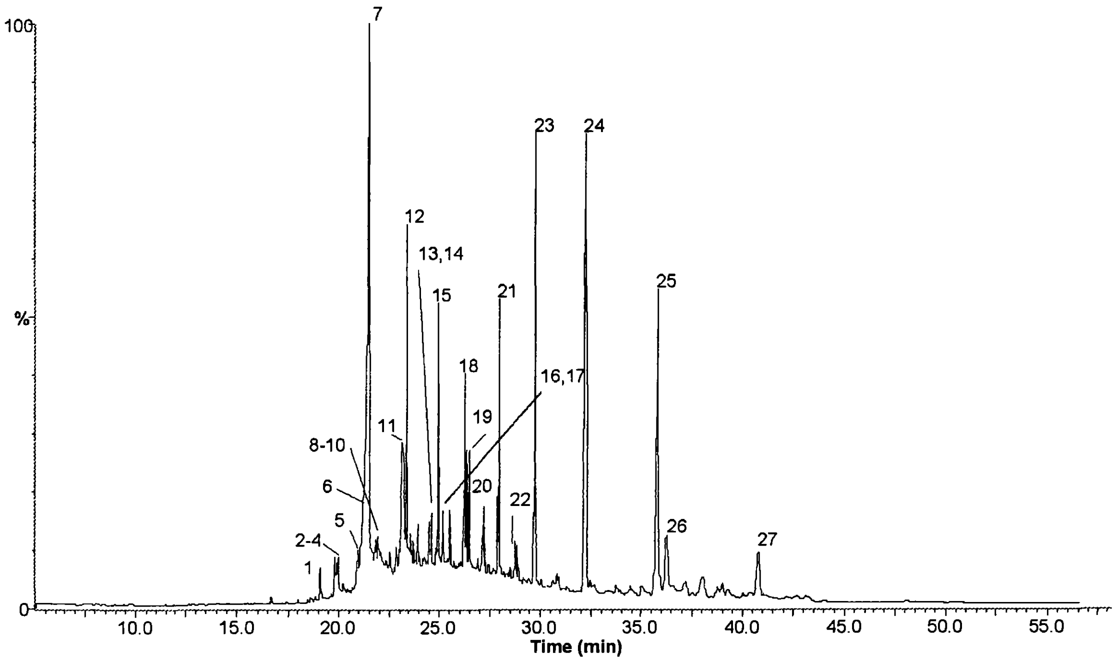

Figure 5.9: GC-MS chromatogram of isopropanol: aqueous ammonia extract (chloroform-soluble fraction) after 24 h extraction.

Table 5.1: Assignments* of selected peaks present in GC-MS chromatograms of all extracts (see Figs. 5.5-5.9).

Peak No.	Retention time (min)	Identification	Formula
1	19.1	tetradecanoic acid	$C_{14}H_{28}O_2$
2	19.8	pentadecanoic acid	$C_{15}H_{30}O_2$
3	19.9	C_{16} acid[†]	$C_{16}H_{32}O_2$
4	20.2	C_{16} acid[†]	$C_{16}H_{32}O_2$
5a**	21.0	phthalate (1,2-benzene dicarboxylate)[§]	not known
5b**	21.0	C_{16} acid[†]	$C_{16}H_{32}O_2$
6a**	21.2	C_{16} acid[†]	$C_{16}H_{32}O_2$
6b**	21.2	C_{17} acid[†]	$C_{17}H_{34}O_2$
7a**	21.5	C_{16} acid[†]	$C_{16}H_{32}O_2$
7b**	21.5	C_{17} acid[†]	$C_{17}H_{34}O_2$
8a**	21.9	C_{16} acid[†]	$C_{16}H_{32}O_2$
8b**	21.9	C_{18} unsaturated amide[†]	$C_{18}H_{35}NO$
9a**	22.0	amide[§]	not known
9b**	22.0	C_{17} acid[†]	$C_{17}H_{34}O_2$
10	22.1	heptadecanoic acid	$C_{17}H_{34}O_2$
11	23.2	oleic acid (cis-9-octadecenoic acid)	$C_{18}H_{34}O_2$
12a**	23.4	C_{18} saturated acid[†]	$C_{18}H_{36}O_2$
12b**	23.4	C_{16} amide[†]	$C_{16}H_{33}NO$
13	24.5	unidentified	not known
14	24.6	C_{23} alkane[†]	$C_{23}H_{48}$
15	25.0	4,8,12,16 - tetramethylheptadecan-4-olide	$C_{21}H_{40}O_2$
16	25.2	octadecanamide	$C_{18}H_{37}NO$
17	25.5	unidentified	not known
18	26.2	pentacosane	$C_{25}H_{52}$
19	26.5	phthalate[§]	not known
20	27.2	C_{22} acid[†]	$C_{22}H_{44}O_2$
21	28.0	heptacosane	$C_{27}H_{56}$
22	28.8	cholesterol/stigmasterol-type compound[§]	not known
23	29.8	nonacosane	$C_{29}H_{60}$
24a**	32.2	cholesterol/stigmasterol-type compound[§]	not known
24b**	32.2	hentriacontane	$C_{31}H_{64}$
25	35.8	tritriacontane	$C_{33}H_{68}$
26	36.3	cholesterol/stigmasterol-type compound[§]	not known
27	40.8	pentatriacontane	$C_{35}H_{72}$

* Compounds identified based on retention times, mass spectral interpretation, use of the NIST mass spectral search program and NIST/EPA/NIH mass spectral library v.2.0.

** Only one peak was observed as two compounds co-eluted.

[†] Although the molecular formula and the principal functional groups present have been established, the structures of these compounds could not be determined on the basis of their EI mass spectra alone.

[§] The molecular ion for this peak was not detected.

5.2.5 Summary of the compounds represented by the selected peaks in all extracts

GC-MS analysis indicated the presence of long chain fatty acids with 14-22 carbon atoms (C_{14}, C_{15}, C_{16}, C_{17}, C_{18} and C_{22}). An unsaturated C_{18} acid (oleic acid) was also detected. Even chain acids predominated. A similar distribution of mostly even-numbered long chain acids was noted by Ma'shum *et al.* (1988) and Morley *et al.* (in press) in organic fractions responsible for water repellency in some Australian and Dutch soils (samples NL1, NL2, NL3 (details in Table 2.2)) respectively. However, higher chain length distributions than that found here were observed in both studies. Ma'shum *et al.* (1988) noted C_{16}-C_{32} acids whilst Morley *et al.* (in press) noted C_{16}-C_{24} acids. Franco *et al.* (1994) and Horne and McIntosh (2000) have also shown the presence of long chain acids in water repellent soils from Australia and New Zealand respectively. The presence of long chain acids is not surprising as they may originate from a range of sources including plant cuticles (Hayes 1998). They are also environmentally persistent, being particularly difficult to degrade, especially in sandy soils as investigated here (Hayes and Graham 2000). Fatty acids are thought to contribute to the hydrophobic behaviour which humic substances display in some circumstances (Clapp *et al.* 1993).

Alkanes of C_{23}, C_{25}, C_{27}, C_{29}, C_{31}, C_{33} and C_{35} chain length were detected. Their chain length distribution was higher than that of the acids and all those detected had an odd number of carbon atoms. As most hydrocarbons found in plants are straight chain, saturated compounds with an odd number of carbon atoms (Eglinton *et al.* 1962), the alkanes detected here were probably of plant origin rather than products of microbial or fungal metabolism. The presence of alkanes in sandy water repellent soils was also noted by Franco *et al.* (1994), Horne and McIntosh (2000) and Morley *et al.* (in press).

Amides were also detected. A saturated C_{18} amide (octadecanamide) was detected as well as an unsaturated C_{18} amide. Another peak, whose mass spectrum resembled that of an amide, was also detected, but the molecular ion was not observed. Its retention time of 22.1 minutes was close to that of octadecanamide (21.9 minutes), so it may have been an isomer of this compound. Morley *et al.* (in press) also noted the presence of amides. In that study, there appeared to be an amide of the same chain length as many of the acids observed and it was suggested that the amides were not originally present in the soils but were formed as a result of heating the acids for long periods in the presence of ammonia. However, more recent work has shown this not to be the case (Mainwaring, personal communication).

Other compounds detected include: 1,2-benzene dicarboxylates or phthalates (peaks 5a and 19), which may be contaminants from the plastic bags used for storing the soil; cholesterol/stigmasterol-type compounds (peaks 22 and 24); 4,8,12,16-tetramethylheptadecan-4-olide (peak 15).

Kolattukudy (1976) summarised that alkanes have been identified in natural waxes from a wide range of sources which include bacteria, fungi, algae, plants, insects and higher animals, including mammals. In addition, it was stated that acids have been identified in 'every living organism'. Tulloch (1976) also summarised that both alkanes and acids are found in most plants. It therefore appears that both polar and non-polar species such as alkanes and acids (*i.e.* the types of organic compounds thought to cause water repellency) are common in soils. It is speculated that the source of these compounds, however, is likely to vary depending on the nature of the soil's environment and it is probable that more than one source will contribute to the pool of organic compounds required for water repellency to occur.

5.2.6 Change in extract composition as extraction duration increases

The compound types in each extract were similar regardless of the duration of extraction. However, as shown in Figs. 5.1-5.4, the mass extracted increased whilst the water repellency and organic matter content decreased with time. It was therefore thought that the relative abundances of the compounds identified could be an important factor in determining the severity of water repellency. It was also hypothesised that if organic material on the surfaces of soil particles was arranged in layers, certain compound types may be more strongly bound and/or closer to particle surfaces than others, thus potentially increasing the selectivity towards particular compound types being extracted more rapidly than others. Fig. 5.10 shows the relative abundances of the compounds represented by the 27 selected peaks in each extract based on peak height.

As discussed in Section 5.2.4, compounds present in the isopropanol: aqueous ammonia extracts were grouped into four generic types: fatty acids, alkanes, amides and 'others'. The cumulative temporal change in composition of the extract during 24 h of extraction is summarised in Fig. 5.11, in terms of the amount of each compound type present (note: for the purposes of generating Fig. 5.11, in the event of two compounds co-eluting (Table 5.1) the height of the observed peak was shared equally between the two compound types). After 1 h, acids accounted for *ca.* 37% of the extract, alkanes for *ca.* 25%, 'other' compounds for *ca.* 29% and amides for *ca.* 10%. As extraction time increased to 8 h, the proportions of the four compound types remained relatively constant, with acids being the major compound type present. Thereafter the proportion of alkanes increased considerably to *ca.* 40% of the total whilst the proportion of acids decreased to 25-30%. The proportions of amides and other compound types also decreased, although to a lesser extent. This suggests that after *ca.* 8 h of extraction, most extractable acids, amides and 'other' compound types had been removed, whilst the alkanes continued to be extracted. It is speculated that if the extraction time were to be increased further, alkanes would continue to be removed. This would not be surprising as the presence of residual hydrocarbons in samples of similar soils, having been extracted using the same method, has been demonstrated by DRIFT analysis (Chapter 4). However, if most acids, amides and 'other' compounds cease to be extracted after *ca.* 8 h, this suggests that the remaining alkanes, alone, are incapable of inducing water repellency as the soil is rendered wettable after 16 h of extraction. This, therefore, implies that a combination of more than one compound type is required to confer water repellency. This was also suggested in studies by Mainwaring (personal communication), which found that AWS treated with polar compounds such as acids became water repellent but when treated with non-polar compounds such as alkanes no effect was observed. However, applying C_{18} alkane with C_{18} acid (1:1) to AWS led to much enhanced repellency compared to the effect of acid or alkane alone. In addition, treating a wettable control soil (rather than AWS) with alkane induced severe water repellency, suggesting that polar compounds already on the soil particles are required to induce water repellency.

There is clearly a dependence of the ease of extraction on compound polarity. This was also observed by Roy *et al.* (1999) in a Canadian study on water repellent oil-contaminated soils. The distribution of a compound between a solid phase and a liquid phase is a reflection of the *relative* strengths of its interactions with each phase. Given the high polarity of the isopropanol: aqueous ammonia mixture being used, compounds such as fatty acids, which are themselves highly polar, will interact much more strongly than non-polar compounds with the liquid phase. Thus, whilst alkanes are unlikely to be strongly bound within the soil sample, their lack of polarity means that their affinity for the aqueous medium is extremely low and may therefore not be so easily extracted.

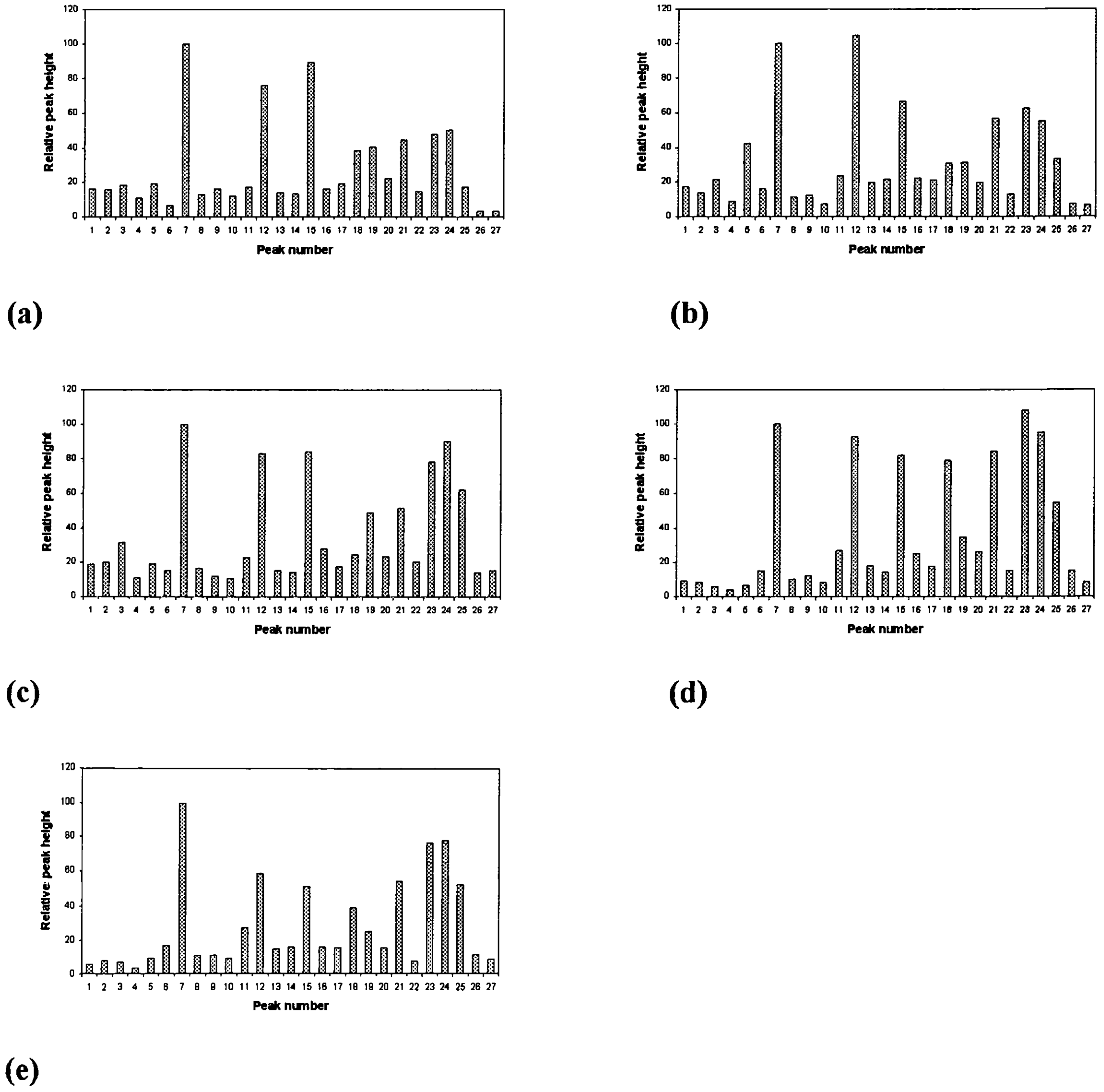

Figure 5.10: Compound distribution in isopropanol: aqueous ammonia extract (chloroform-soluble fraction) after **(a)** 1 h, **(b)** 4 h, **(c)** 8 h, **(d)** 16 h and **(e)** 24 h extraction. Peaks normalized using peak 7.

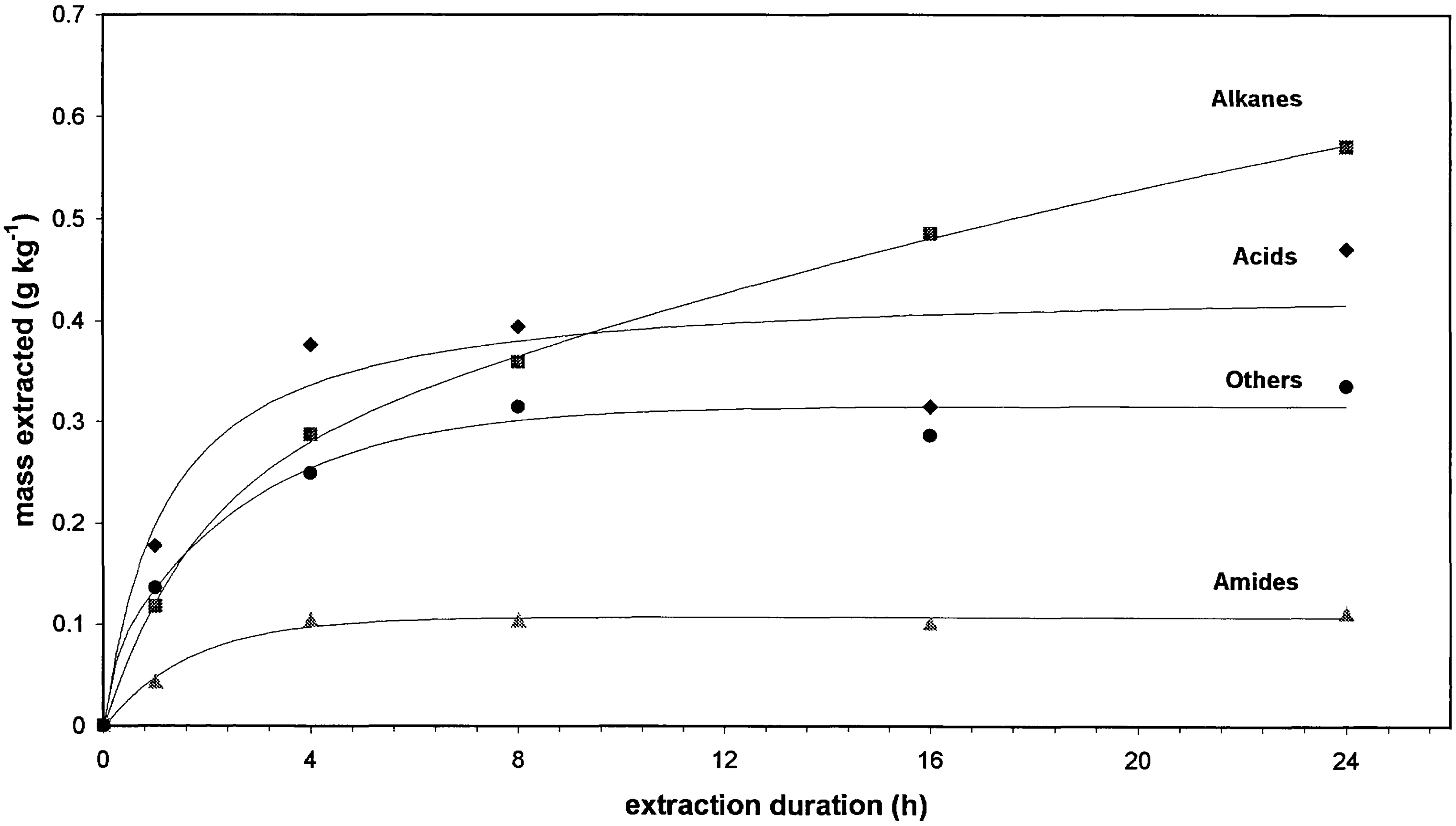

Figure 5.11: Mass of each compound type extracted as a function of extraction time, calculated on the basis of the percentage composition as measured by GC-MS and the total amount of extract obtained.

5.2.7 Varying extraction solvent

In addition to the isopropanol: aqueous ammonia mixture, chloroform and tetrahydrofuran were also each used as the extraction solvent to identify any selectivity of low polarity organic solvents towards extracting particular compound types.

Figs. 5.12 and 5.13 show the GC-MS chromatograms of the chloroform and tetrahydrofuran extracts respectively whilst Figs. 5.14 and 5.15 show the relative abundances (according to peak height) of the compounds represented by the 27 selected peaks in the chloroform and tetrahydrofuran extracts respectively (note: these are the same 27 peaks that were selected from the GC-MS chromatogram of the 24 h isopropanol: aqueous ammonia extract). Comparison of these with Fig. 5.10(e) shows that isopropanol: aqueous ammonia extracts a broader range of compounds from the soil sample than chloroform or tetrahydrofuran. In particular, the chloroform and tetrahydrofuran extracts contain a greater proportion of alkanes (especially C_{27} alkanes and above), reaching 49% and 63% of the total respectively, compared to 38% in the case of isopropanol: aqueous ammonia (alkanes are represented by the peaks shaded in black in Figs. 5.14 and 5.15). Note that this result does not imply that chloroform or tetrahydrofuran removes alkanes more effectively than isopropanol: aqueous ammonia. It must also be remembered that isopropanol: aqueous ammonia extracts approximately six times more material in total than chloroform and twelve times more than tetrahydrofuran.

As shown in Chapter 3 (Table 3.5) chloroform or tetrahydrofuran as the extraction solvent removed significantly less material over 24 h (117 and 250 mg kg^{-1}

respectively) than the isopropanol: aqueous ammonia mixture, suggesting that a more polar medium is able to dissolve a larger proportion of the organic matter present in the sample. Extraction with either chloroform or tetrahydrofuran also increased the level of repellency (WDPT >18000 s), whilst isopropanol: aqueous ammonia rendered the soil wettable (WDPT <5 s).

Three key differences between the two types of extraction solvent may be identified: (i) isopropanol: aqueous ammonia extracts more material; (ii) the chloroform and tetrahydrofuran extracts contain a greater proportion of alkanes; (iii) the lower polarity solvents may have an effect on the orientation/distribution of the residual organic matter, as suggested by McGhie and Posner (1980). Any one or combination of these characteristics may be responsible for the observed differences in post-extraction sample repellency.

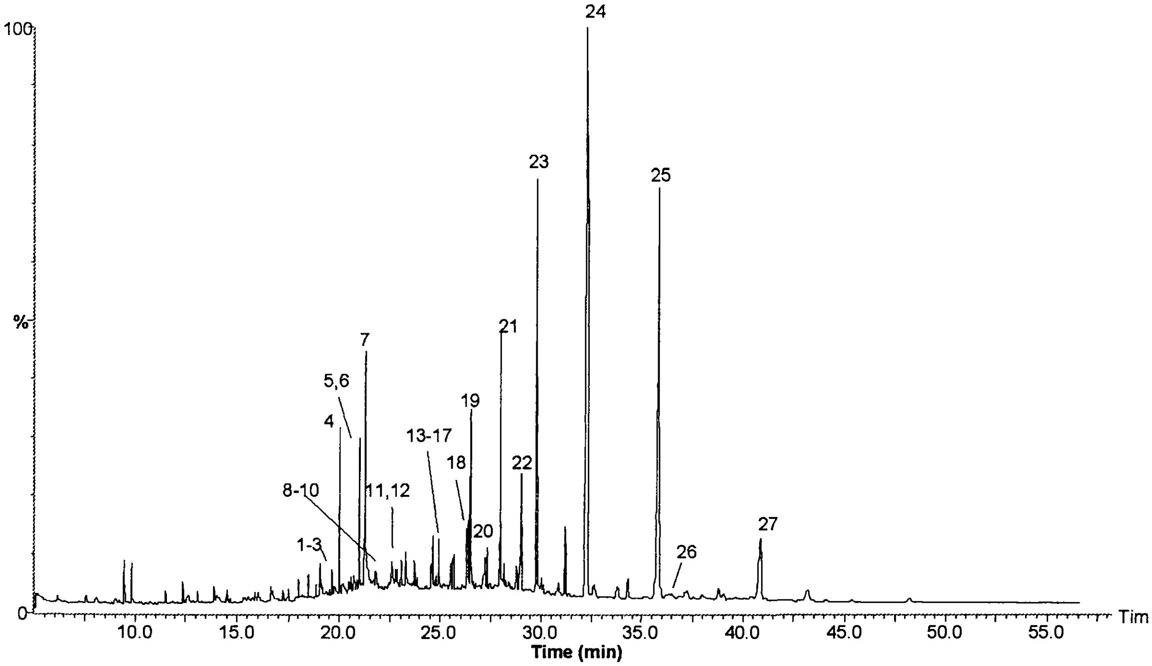

Figure 5.12: GC-MS chromatogram of chloroform extract after 24 h extraction.

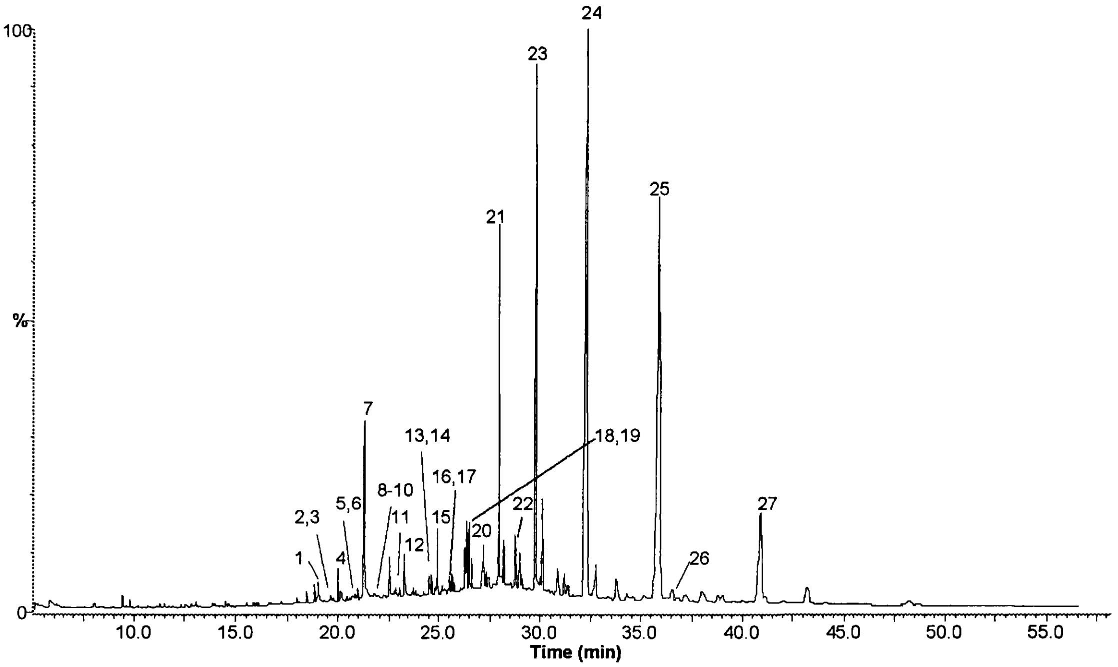

Figure 5.13: GC-MS chromatogram of tetrahydrofuran extract after 24 h extraction.

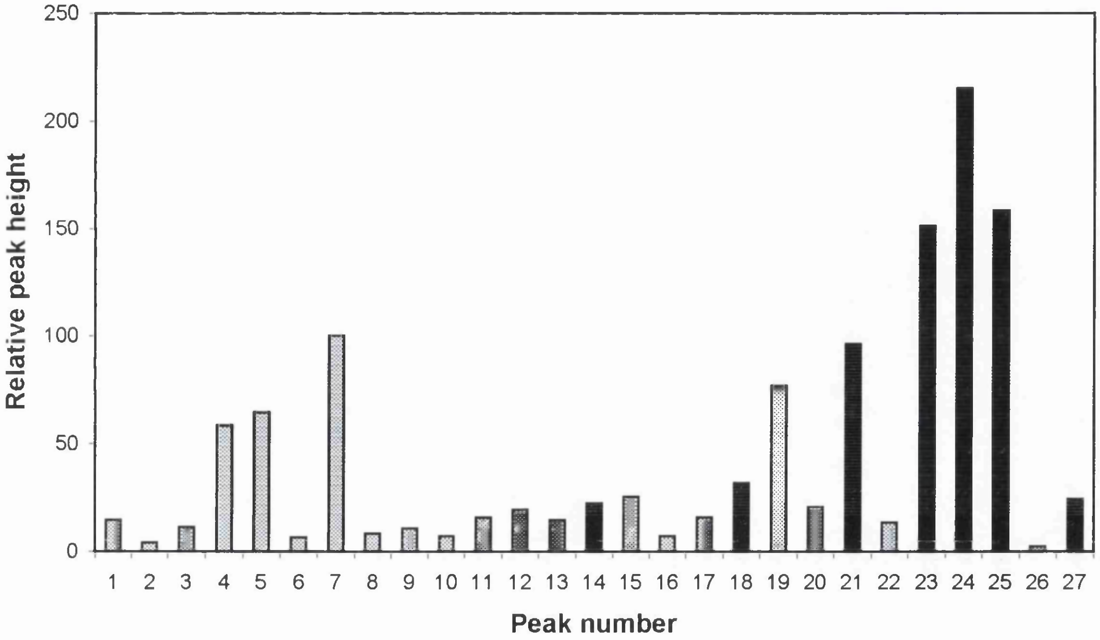

Figure 5.14: Compound distribution in chloroform extract after a 24 h extraction. Peaks normalized using peak 7. Alkanes are represented by the peaks shaded in black.

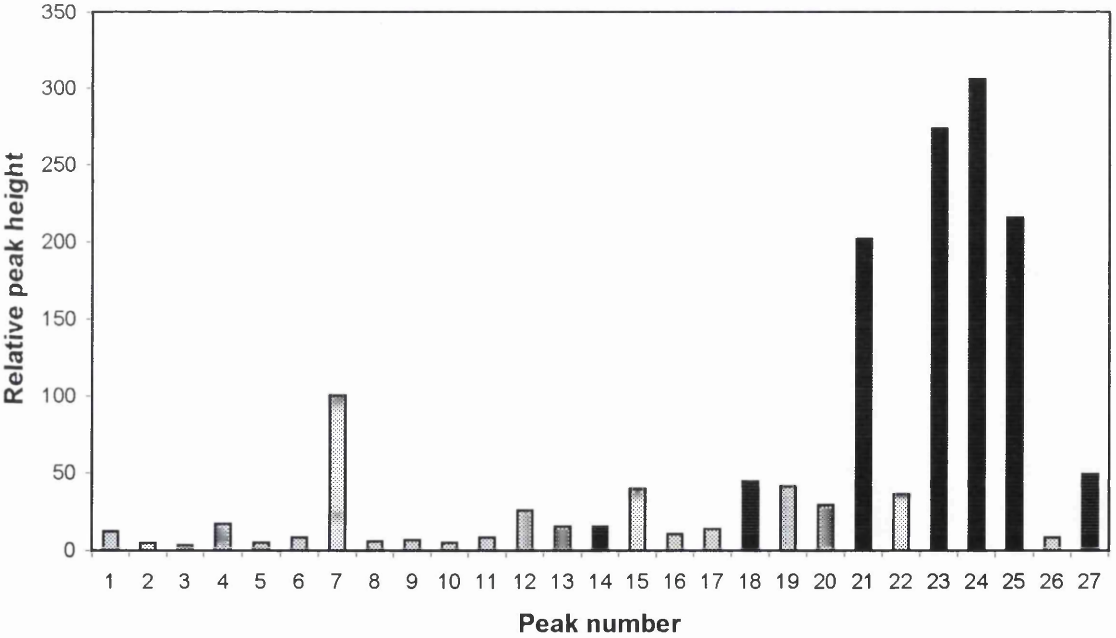

Figure 5.15: Compound distribution in tetrahydrofuran extract after a 24 h extraction. Peaks normalized using peak 7. Alkanes are represented by the peaks shaded in black.

5.2.8 Analysis by gas chromatography-flame ionisation detection (GC-FID)

GC-FID was used (as described in Section 2.6.7) to quantify the amounts of particular compounds present in an extract of soil UK1c (after 24 h extraction). Using the ratio of alkane response factor to that of the internal standard (triacontane) it was possible to calculate the mass of each alkane (C_{27}, C_{29}, C_{31}, C_{33}) injected onto the GC column. This assumes that when the soil extract was partitioned between chloroform and water, all alkanes partitioned into the chloroform fraction. From these values the mass of each alkane extracted per kg of soil was estimated. Odd-chain alkanes in the range C_{27}-C_{33} were the predominant alkanes identified in soil UK1c and were present in *ca.* 140-300 μg kg^{-1} concentrations (Table 5.2). These values are likely to be somewhat lower than the actual amounts in the soil as the presence of residual hydrocarbons after extraction has been demonstrated by DRIFT and TOC analysis (Figs. 5.3 and 5.4 respectively). However, the values serve as a useful approximation of the amounts of individual organic compounds present in a water repellent soil. Spadek *et al.* (1994) detected both alkanes and fatty acids in similar concentrations in Australian water repellent soils.

Table 5.2: Mass of each alkane extracted per kg of soil

Alkane	Mass extracted (μg kg^{-1})
Heptacosane ($C_{27}H_{56}$)	175 (±5)
Nonacosane ($C_{29}H_{60}$)	240 (±12)
Hentriacontane ($C_{31}H_{64}$)	307 (±19)
Tritriacontane ($C_{33}H_{68}$)	142 (±48)

5.3 Chapter summary

As extraction duration was increased: the mass of material extracted from soil UK1c increased (although the rate at which it was extracted decreased); the severity of water repellency decreased; and the organic content (both aliphatic and TOC content) decreased. It must be noted that there was no significant decrease in organic carbon content after *ca.* 1 h of extraction, and even after a 24 h extraction residual hydrocarbons were present on the soil.

Three main compound types were detected in the chloroform-soluble fraction of the isopropanol: aqueous ammonia extract: fatty acids, alkanes and amides. Other compound types were also detected but it was not possible to identify their precise chemical structure based on their EI mass spectra alone. Even chain acids (C_{14}-C_{22}) and odd chain alkanes (C_{23}-C_{35}) predominated. The odd chain alkanes suggest the compounds were of plant origin (Eglinton *et al.* 1962). The removal of alkanes from the soil was less rapid than that of other compound types. They were extracted throughout the 24 h extraction period whilst the extraction of acids, amides and 'other' compounds ceased to be significant after *ca.* 8 h of extraction. The low polarity alkanes are likely to have a low affinity for the aqueous extraction medium and thus not be extracted as rapidly.

Isopropanol: aqueous ammonia extracted a broader range of compounds from the soil than the lower polarity solvents such as chloroform and tetrahydrofuran. The low polarity solvent extracts contained a greater proportion of alkanes (an average of 56% of the total, compared to 38% in the case of isopropanol: aqueous ammonia) although this does not imply that chloroform and tetrahydrofuran extract alkanes more effectively than isopropanol: aqueous ammonia.

Amounts of odd chain alkanes (C_{27}-C_{33}) in the UK1c soil extract (after 24 h extraction) were measured in the concentration range 140-300 $\mu g\ kg^{-1}$ of soil. These values are likely to be somewhat lower than the actual amounts in the soil as the presence of residual hydrocarbons after extraction has been shown by DRIFT and TOC analysis. However, the removal of compounds in that concentration range did induce wettability, suggesting that only a small amount of organic material is required to cause soil water repellency.

The aim of the experiments reported in this chapter was to investigate the temporal selectivity of the extraction procedure and to gain information regarding the molecular arrangement on the soil's surface by assessing any particular order in which compound types were removed during the extraction procedure. From the results obtained there is no suggestion that a specific molecular arrangement exists on the water repellent soil's particle surfaces. However, results suggest that after *ca.* 8 h of extraction most polar compounds such as acids and amides have been extracted. Alkanes are extracted less rapidly and it is speculated that they would continue to be extracted if the extraction was extended further than 24 h (the presence of residual hydrocarbons in samples of similar soils after extraction has been shown by DRIFT analysis). These observations suggest that the alkanes, alone, are incapable of inducing water repellency as the soil is rendered wettable after 16 h of extraction. This, therefore, implies that a combination of more than one compound type is required to confer water repellency.

Chapter 6

Conclusions and implications

6.1 Introduction

This chapter summarises the main findings, synthesis of ideas and conclusions of the thesis and their wider implications. In this study, 14 water repellent soils (of varying repellency level) sampled from sites in five different countries (Australia, Greece, Portugal, The Netherlands, U.K.) were characterized by a range of physical and analytical chemical methods. In addition to these samples, a wettable soil was sampled from each site to act as a control. This is a much broader sample range (geographically) than has been examined in previous studies and the inclusion of wettable soils as control samples had not been used previously. Due to the broader sample range, the following key findings are therefore thought to be of relatively wide applicability.

6.2 Main findings and conclusions

6.2.1 Relationship of aliphatic C and TOC with soil water repellency

TOC analysis and DRIFT spectroscopy were used to examine the total organic carbon content and aliphatic content (C-H units) respectively in the soils. Water repellency correlated slightly better with DRIFT C-H band area (aliphatic content) than TOC content, although neither correlated well with water repellency. It can, therefore, be concluded that neither the TOC content nor aliphatic C-H containing material on the soil, alone, determine the water repellency of a soil. The conclusion that aliphatic content (as measured by DRIFT) is a poor predictor of water repellency is an important one as previous studies by Capriel *et al.* (1995) and McKissock *et al.* (2003) suggested otherwise. However, their conclusions were based on narrower ranges (geographically) of samples compared to this study and are not, therefore, of wide applicability.

6.2.2 Extraction of compounds for further analysis

Isopropanol: aqueous ammonia (0.88 SG) (7:3, v:v) solvent mixture was used to Soxhlet extract all soil samples. This was an effective method for extracting compounds causing water repellency from the soils as it rendered 12 of the 14 initially water repellent soils wettable (measured using WDPT) whilst removing relatively large amounts of material from the soils, and had no unwanted effects on the wettability of non-repellent control samples. Previous studies also found isopropanol: aqueous ammonia to be an effective extraction solvent mixture (Ma'shum *et al.* 1988, Franco *et al.* 1994, 2000a, Horne and McIntosh 1994, 2000 and others summarised in Table 1.1). The efficiency of the extraction procedure was also assessed by other methods. Water repellency testing (WDPT) was carried out on (initially wettable) AWS with extracted material reapplied in both isopropanol/water (whole extract) and chloroform (chloroform-soluble fraction), following the procedures of Ma'shum *et al.* (1988). Extracted material induced water repellency on AWS in all cases (including wettable control samples). Whilst it is not possible unequivocally to demonstrate that the extracts contain all of the compounds responsible for causing water repellency in the samples investigated, the fact that extracts were capable of inducing considerable repellency in AWS suggests that the extracts contain at least some of the material responsible for repellency in the soils investigated. In addition to this, these substances retained their ability to bond to silicate particle surfaces and impart water repellency after being subjected to the extraction procedure. Thus, the procedure carried out in this study is considered to be suitable for extraction of water repellent compounds from soils for subsequent further separation and characterization. It is evident that extracts from wettable control soils also contain hydrophobic substances capable of inducing water repellency. This suggests that either: these compounds are present in too low a quantity in these soils to induce water repellency; other compounds present confer soil wettability even in the presence of these hydrophobic materials; or the particular molecular adsorption at the soil surface of these nominally hydrophobic materials is such as to mask their hydrophobic nature.

Extracted soils were also included in the TOC and DRIFT analyses to assess the efficiency of the extraction procedure at removing organic carbon and aliphatic compounds respectively. Strong correlations were observed between the mass of material extracted from the soils and both initial aliphatic C-H and initial TOC content. However, the mass of organic material extracted from soils was poorly related to the water repellency of a sample, indicating that hydrophobic compounds responsible for water repellency may only represent a fraction of the extract composition and that the presence of water repellency (in a dry soil) is not only a function of certain organic compounds being present in the soil, but their structural composition and arrangement. In no case did the isopropanol: aqueous ammonia extraction procedure remove all organic C or aliphatic compounds from the soils. Approximately 29 (±6) % of the initial aliphatic C-H and 27 (±3) % of the initial TOC content was removed. It is speculated that the remaining carbon could be present as interstitial particulate matter, such as partially decomposed plant material (*e.g.* lignocellulose).

If we accept that the experiments in Chapter 5 using a single water repellent soil (UK1c) have widespread applicability (although obviously more experiments will be necessary to verify this) the following conclusions can be drawn. A range of extraction solvents was used to assess and compare the efficiency of each at removing water repellency. Isopropanol: aqueous ammonia was the most efficient in terms of removing aliphatic compounds but not particularly efficient in terms of the organic carbon removed. Aqueous ammonia alone rendered the soil wettable and proved to be the most efficient at removing organic carbon, but inefficient in terms of the proportion of aliphatic compounds removed, suggesting that most of the material it removed was not aliphatic (it could possibly be inorganic). The relative success of aqueous ammonia at extracting organic carbon is not that surprising, however, as a relatively large amount of material (the most of any of the solvents used) was extracted. Water also removed a relatively large amount of material (rendering the soil wettable) but appeared to extract very little, if any, organic carbon. The fact that soil samples have been rendered wettable regardless of the quantity of organic carbon removed suggests that provided there is some aliphatic material present, the amount is less important than its constitution and/or molecular arrangement.

Using lower polarity solvents (chloroform, tetrahydrofuran and isopropanol) resulted in poor extraction efficiency in terms of mass of material extracted and the proportion of aliphatic compounds removed. For the removal of organic carbon, both chloroform and isopropanol were of similar efficiency to isopropanol: aqueous ammonia but not as efficient as aqueous ammonia alone, whilst tetrahydrofuran was relatively inefficient. Sample repellency actually increased as a result of using low-polarity solvents (a phenomenon also observed in previous studies such as Ma'shum *et al.* 1988, McGhie and Posner 1980, Roy *et al.* 1999), despite some non-polar hydrocarbons having been removed. This supports the notion that organic compounds which are soluble in low polarity solvents (such as alkanes) are not, in themselves, the main cause of water repellency in soils.

In the final section of this research, varying extraction times from 1 to 24 h were used to assess the kinetics and efficiency of extraction using isopropanol: aqueous ammonia. Increasing extraction time caused an increase in the mass of material extracted (although the rate at which material was extracted decreased with time) and a decrease in soil water repellency. A decrease in repellency with extraction time was also observed in a study in which an Australian water repellent soil was extracted with isopropanol: aqueous ammonia (Ma'shum *et al.* 1988). Organic content (both aliphatic and TOC content) decreased, although it must be noted that there was no significant decrease in either TOC or aliphatic content after *ca.* 1 - 4 h of extraction. Even after a 24 h extraction, residual hydrocarbons were present on the soil. The same compound types were detected by GC-MS in all extracts, but their proportions varied with extraction time. In particular, the removal of alkanes from the soil sample was less rapid than that of more polar compounds. Three main compound types were detected in the chloroform-soluble fraction of the isopropanol: aqueous ammonia extracts: fatty acids, alkanes and amides. Even chain acids (C_{14}-C_{22}) and odd chain alkanes (C_{23}-C_{35}) predominated. Similar distributions of mostly even-numbered long chain acids were detected in organic fractions responsible for water repellency in some Australian and Dutch soils by Ma'shum *et al.* (1988) and Morley *et al.* (in press) respectively. However, higher chain length distributions than that found here were observed in both studies. Ma'shum *et al.* (1988) noted C_{16}-C_{32} acids whilst Morley *et al.* (in press) noted C_{16}-C_{24} acids. The presence of long chain acids in water repellent soils from Australia and New Zealand was shown by Franco *et al.*

(1994) and Horne and McIntosh (2000) respectively. The presence of long chain acids is not surprising as they may originate from a range of sources including plant cuticles (Hayes 1998). The presence of alkanes in sandy water repellent soils was also noted in previous studies (Franco *et al.* 1994, Horne and McIntosh 2000 and Morley *et al.* in press). The predominance of odd chain alkanes detected in this study suggest the compounds were probably of plant origin rather than microbial or fungal metabolism (Eglinton *et al.* 1962). Alkanes were extracted throughout the 24 h extraction period whilst the extraction of acids, amides and 'other' compounds ceased to be significant after *ca.* 8 h of extraction. This has been attributed to a dependence of the ease of extraction on compound polarity. Highly polar compounds such as fatty acids will interact more strongly with the polar extraction solvent mixture than non-polar compounds such as alkanes and will therefore be extracted more rapidly. Extractions were also carried out using lower polarity solvents (chloroform and tetrahydrofuran). Isopropanol: aqueous ammonia extracted a broader range of compounds from the soil than the lower polarity solvents. In particular, the chloroform and tetrahydrofuran extracts contained a greater proportion of alkanes, which can again be attributed to the greater affinity of the compounds for the extraction medium.

Amounts of odd chain alkanes (C_{27}-C_{33}) in the UK1c soil extract were found to be in the concentration range 140-300 $\mu g\ kg^{-1}$ of soil. Spadek *et al.* (1994) detected both alkanes and fatty acids in similar concentrations in Australian water repellent soils. The amounts of organic compounds present in the soil are therefore small, implying that only small amounts are required for water repellency to occur. In turn, this could imply that only relatively small amounts of wetting agent (surfactant) or other chemical treatment would need to be applied to water repellent soil in order to ameliorate the problem, which would be economically and environmentally favourable.

6.2.3 Origin of soil water repellency

The observations made in this research are compelling evidence that the simple presence or absence of specific organic compounds is not enough alone to determine water repellency. Hydration effects and the intermolecular arrangement of material are suggested as important factors. The fact that wettable soils contain organic compounds which can induce water repellency is evidence enough that water repellency is not determined by specific organic compounds but rather by the proportions of different compound types, such as polar and non-polar compounds, in a soil and their conformation at the surface. Figure 6.1 illustrates the current hypothesis of how organic compounds induce water repellency in soil.

6.3 Limitations of the thesis, research gaps and suggested future research directions

The results of the study of the Soxhlet extraction (isopropanol: aqueous ammonia) procedure, suggest that it might be beneficial to replenish the extraction solvent mixture with ammonia at regular intervals after the first hour of extraction. This would allow more material to be extracted and analysed. However, the extraction procedure used here did remove water repellency in most soils so whether this additional step is required is questionable. The success of this extraction procedure demonstrates the effectiveness of the alkalinity and polarity of the extraction medium in the removal of compounds associated with soil water repellency.

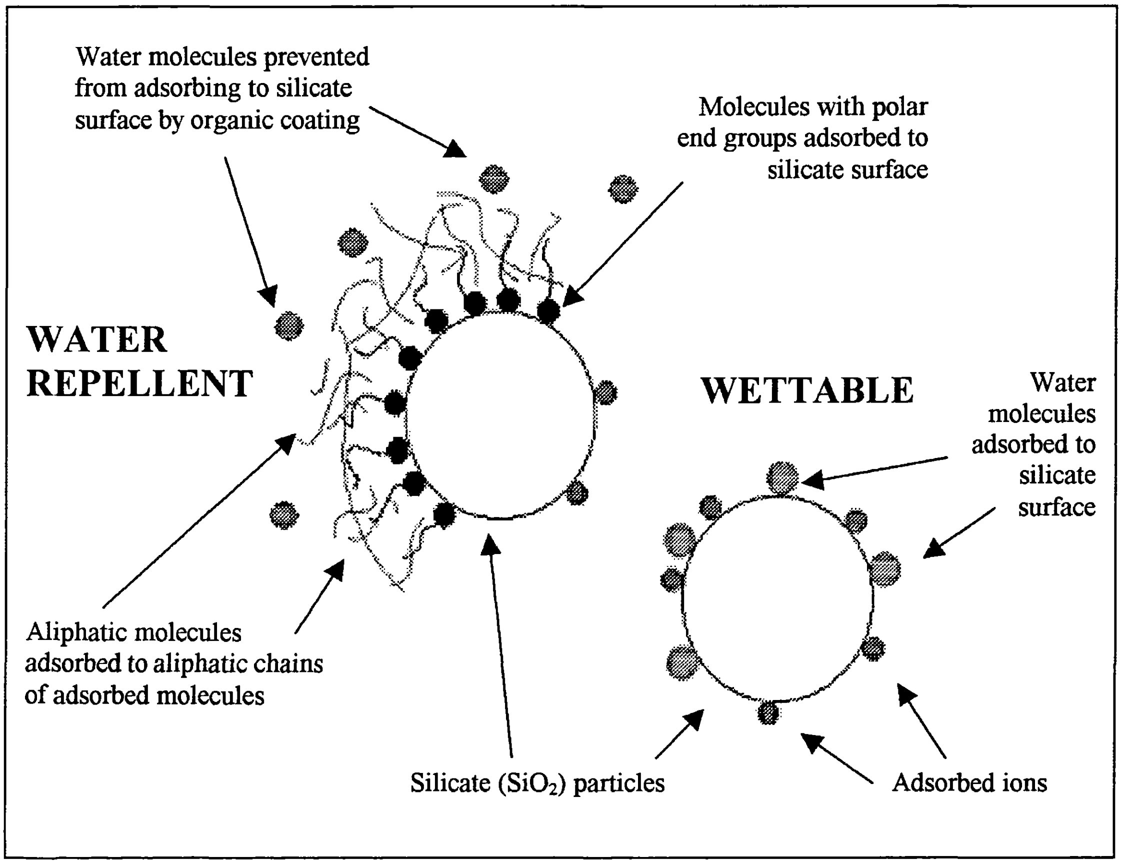

Figure 6.1: Hypothesis of how organic compounds induce water repellency in soil.

Additional methods of analysing soil extracts should be employed to overcome the limitations caused by extract solubility. In this study only the chloroform-soluble fraction of soil extracts was analysed as: (i) it was thought that it would contain hydrophobic organic compounds responsible for causing water repellency and (ii) chloroform is a volatile organic solvent suitable for GC analysis. A useful addition would be to carry out LC-MS analysis on the water-soluble fraction of soil extracts to complement the analysis of the chloroform-soluble fraction. In addition to this, LC techniques could be used to assess the composition of aqueous extracts obtained in this study. Alternatively, techniques where the solubility of extracts is not important, such as pyrolysis GC-MS (as used by Nierop and Buurman 1998) could also be employed to analyse whole soil extracts rather than fractions of extracts. Such a technique could also be used to compare the compounds extracted (analysis of the soil extract) with the compounds on the soil initially (analysis of soil sample).

Although amelioration strategies, such as applying wetting agents (surfactants) to water repellent soils have been relatively successful at reducing water repellency (Wallis and Horne 1992, Blackwell 1993 and 2000, Kostka 2000), the success is often short lived. Wetting agents, therefore, need to be reapplied to affected soils regularly in order to maintain wettability, which is inconvenient for land managers in addition to being a financial (and possibly environmental, depending upon the agent used) concern. The problem remains that the specific combinations and/or arrangements of compounds responsible seem to return to the state (or a similar one) in which they existed prior to treatment. It would therefore be beneficial to address the origin of the problem more directly; in addition to simply analysing the compounds present in water repellent soils it would be useful to investigate the origins of such compounds (furthering the research of others discussed in Section 1.4.3) by assessing the 'behaviour' of plants, fungi and microorganisms from a wide range of locations where water repellent soils have been identified. Controlled experiments in the field could be carried out whereby the concentrations of compounds (thought to be associated with water repellency) released into the soil by plants and/or fungi and/or microorganisms are monitored and correlated with severity of soil water repellency. A study such as this is clearly challenging to carry out, but could have a potentially large impact on amelioration strategies used. A 'prevention is better than cure' strategy would be desirable, whereby materials responsible for causing water repellency would be prevented from entering the soil rather than attempting to alter their arrangement or remove them once they are in the soil. To do this would mean attempting to control the concentration of fungi and/or microorganisms in the soil and/or removing certain plant or crop types from the land.

The spatial location and accessibility of hydrophobic compounds in water repellent soils also needs greater study. Investigating this could explain why the DRIFT-WDPT relationship was not better. DRIFT is a measure of the amount of aliphatic C-H present in a sample but the way in which the aliphatic compounds are distributed on the surface of the mineral particles would have no effect on the DRIFT measurement. However, their distribution is likely to have a major effect on the water repellency of the soil. A given amount of aliphatic material could be distributed in layers, entirely covering the mineral particle surfaces which would be very likely to cause water repellency. However, the same amount of material could be distributed in a less uniform manner as globules, thus exposing parts of the hydrophilic mineral surfaces and allowing water to infiltrate the soil.

Additionally, an extension to work by Mainwaring (personal communication), in which compounds or combinations of compounds known to induce water repellency are (quantitatively) added to wettable soils in the field could be carried out to determine the effects of those compounds or combinations of compounds on the severity of water repellency induced. The experiments could also be used to assess the effect of the environmental conditions (fluctuating moisture and temperature, degradation by microorganisms *etc.*) on these compounds. Similar experiments monitoring the fate (*e.g.* natural degradation) of surfactants after application would also be useful in evaluating the processes occurring in water repellent soils.

In addition to analysing the organic compounds found in water repellent soils, a study focussing on the inorganic material in water repellent soils could also be useful. For example, identifying water repellent soils containing mineral particles other than silica could be useful in assessing how important the inorganic component of the soil is at inducing water repellency, *e.g.* the way in which organic compounds 'bond' to different mineral surfaces could potentially cause differences in the severity of water repellency exhibited.

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Appendix A

Publications and Conference Contributions

Peer reviewed international journals

Doerr S. H., Llewellyn C. T., Douglas P., Morley C. P., Mainwaring K., Haskins C., Johnsey L., Ritsema C. J., Stagnitti F., Ferreira A. J. D. and Ziogas A. K. Extraction of compounds associated with water repellency in sandy soils of different origin. ***Australian Journal of Soil Research***, (in press).

Llewellyn C. T., Douglas P., Doerr S. H., Morley C. P. and Mainwaring K. A. (2004). Soxhlet extraction of organic compounds associated with soil water repellency. ***Environmental Chemistry Letters*** 2 (1), 41-44.

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Book chapters

Doerr S. H., Douglas P., Morley C. P., Llewellyn C. T., Mainwaring K. A., Haskins C., Johnsey L., Ritsema C. J., Stagnitti F., Ferreira A. J. D., Ziogas A. K. Organic compounds associated with water repellency in sandy soils. In: Huang, P.M. (Ed.), ***Abiotic and Biotic Interactions: The Impact on the Ecosystems & Human Welfare***, Part V - Rhizosphere Processes, Chapter 20, Science Publishers, Enfield, USA (in press).

Conference contributions

Doerr S. H., Douglas P., Morley C. P., Llewellyn C. T., Mainwaring K. A. and Schabauer J. The role of soil organic matter in causing water repellency in soils: evidence and hypotheses. ***Eurosoil 2004***, 4–12 September, 2004, Freiburg, Germany.

Doerr S. H., Douglas P., Mainwaring K. A., Morley C. P., Llewellyn C. T. and Schabauer J. (in press). Hypotheses and experimental evidence for the role of specific organic compounds in causing soil hydrophobicity. ***XVIth British Organic Geochemistry Society Conference***, 14-15 July 2004, Nottingham, UK.

Mainwaring K. A., Doerr S. H., Douglas P., Llewellyn C. T. and Morley C. P. Isolation and chemical characterisation of organic compounds from sandy soils and their effects on soil water repellency. ***European Geosciences 1st General Assembly***, 25-30 April 2004, Nice, France.

Llewellyn C. T., Doerr S. H., Douglas P., Mainwaring K. A. and Morley C. P. Kinetics and efficiency of Soxhlet extraction for compounds associated with water repellency in a sandy soil. ***6th International Symposium on Environmental Geochemistry***, 7-11 September 2003, Edinburgh, UK.

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