THE GENERATION OF WATER REPELLENCE IN SANDS, AND ITS AMELIORATION BY CLAY ADDITION.

Philip R. Ward

Thesis submitted for the degree of
Doctor of Philosophy

in

The University of Adelaide
Faculty of Agricultural and Natural Resource Sciences
Department of Soil Science

April 1993

Awarded 1993

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Abstract

A review of the literature concerning water repellence and hydrophobic organic compounds in soils is presented. The need for research into the generation of water repellence, and its amelioration by clay amendment, was highlighted.

The generation of water repellence was shown to be dependent on moderate temperatures (70°C) and microbial activity at low water contents. Repellence could not be induced in sterile soil. Microbial activity probably resulted in degradation of the more hydrophilic organic matter, which freed the hydrophobic compounds to coat the sand surfaces. Direct production of the causal compounds by microorganisms was unlikely because hydrophilic (water soluble) organic matter alone could not generate repellence with the aid of natural microbes.

Clays are known to reduce repellence, and the interaction of model hydrophobic compounds with clay minerals was studied. For both montmorillonite and kaolinite, adsorption of cetyl alcohol and palmitic acid reached a plateau at about 3 μmol m^{-2}, based on external surface area. This corresponds with calculations for a bilayer adsorbed parallel to the clay surface. There was little difference between Ca^{2+}- and Na^{+}-saturated clays. About half the cetyl alcohol and 20% of the palmitic acid was readily desorbed in hexane.

Water repellence induced by cetyl alcohol on acid-washed sand was reduced by all clays after wetting and drying. The clays with the highest external surface area were most effective, reducing the M.E.D. value to 0.0. This suggests that clays adsorbed the cetyl alcohol, and their large surface area compared with the sand diluted the hydrophobic compounds, leaving the sand surfaces wettable. Exchangeable cation had little effect.

However, in natural sand, after wetting and drying, kaolinite was far more effective than montmorillonite, regardless of surface area. Kaolinite did not adsorb more natural organics, but was effective because the particles remained spread over the sand grains and masked the hydrophobic surface, whereas montmorillonite tended to be deposited in micro-aggregates between sand grains. Wetting and drying also virtually eliminated clay leaching through the sand, and so clay application appears promising for amelioration of water repellence in the field.

A simple test, using readily available materials, was developed to ascertain the effectiveness of a given field clay in reducing water repellence.

This work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

I give consent to this copy of my thesis, when deposited in the University Library, being available for photocopying and loan.

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Acknowledgements

Firstly, my sincere thanks go to my supervisor, Professor Malcolm Oades. His helpful encouragement and advice have been invaluable over the period of my study. I also wish to thank the Department of Soil Science and the University of Adelaide for allowing me to study for my Ph.D. Special thanks to Drs. Chris Franco, Philip Clarke, Cameron Grant, Jeff Baldock, Max Tate, Graeme Currie, David Lewis, Rob Murray and Tony Dexter for their advice and thought-provoking discussion along the way.

Samples of natural water repellent sand and useful clays were supplied by the South Australian Department of Primary Industry (ex Agriculture). The help of Melissa Cann, Phil Michelsen, and Dale Lewis is gratefully acknowledged.

For technical assistance, I wish to thank Angela Waters (Surface area measurements and generally helpful hints for all sorts of equipment), Stuart McClure (S.E.M.), Philip Clarke (N.M.R.), Les Janik (I.R.) and David Lewis (X.R.D.). Bernie Foley and Anna Sullivan helped with lots of little things around the laboratory.

The work reported in this thesis was fully funded by the Land and Water Resources Research and Development Corporation, incorporating the National Soil Conservation Programme.

Finally, but certainly not leastly, thanks to my wife, Judy-anne, for her constant support and understanding. We did it together!

CHAPTER 1. LITERATURE REVIEW

1.1 Introduction

Water repellent soils are soils which do not readily absorb water when dry, despite having favourable pore size distributions. A drop of water placed on a horizontal surface of a water repellent soil will 'ball up', and in extreme cases may evaporate before it can soak in. This occurs because the soil particles have developed an apparent soil/water contact angle greater than 90°. In the field, the phenomenon is characterised by uneven soil wetting. Dry soil patches can often be found even after substantial rainfall. Water repellent soils are usually sandy in texture, although the condition occasionally develops in finer textured soils.

Other terms used to describe water repellence in soils include hydrophobic, non-wetting, and oily soils.

Probably the first scientific description of a water repellent soil was made by Schreiner and Shorey (1910). Since then, water repellence has been investigated in many different countries and climatic zones, e.g. Russia (Vityn', 1961; cited by Rybina, 1973), India (Adhikari and Chakrabarti, 1976), Japan (Nakaya *et al.*, 1977), Italy (Giovannini and Lucchesi, 1984), Scotland (Mallik and Rahman, 1985), New Zealand (Tillman *et al.*, 1989), Canada (Barrett and Slaymaker, 1989), Spain (Sevink *et al.*, 1989), South Africa (Scott and Van Wyk, 1990) and The Netherlands (Van Dam *et al.*, 1990). However, the most extensive areas of water repellent soils have been reported in Australia and the U.S.A., and these countries have contributed most to the research into this phenomenon.

In the USA, water repellence has been reported in California, Washington, Oregon, Idaho, Montana, Colorado, Utah, Nevada, and Arizona in the west (Schreiner and Shorey, 1910; DeBano, 1969a), and Florida in the east (Jamison, 1946). Water repellence in western USA is often associated with burnt areas (Savage *et al.*, 1972).

Water repellent soils are widespread across the southern Australian cereal belt, and were first described by Prescott and Piper (1932). Specific areas include the southern and western coasts of Western Australia (McGhie and Tipping, 1983), Eyre Peninsula (Wetherby, 1984), and the south-east of South Australia extending into Western Victoria (Bond, 1969a). The total area affected in Australia has been estimated at over two million hectares, and the loss in production due to water repellence is in excess of 10 million dollars annually.

1.2 Measurement

1.2.1 Contact angle

A droplet of water carefully placed on a water repellent sand tends to 'ball up', forming a contact angle with the sand surface of greater than 90° (figure 1.1). The more repellent the surface is, the greater the contact angle. The actual contact angle is therefore a good measure of the severity of water repellence, and can be measured directly from photographs (Bond, 1968; Letey, 1969; Wessell, 1988). Alternatively, the contact angle can be calculated from the maximum height of a large flat droplet on a smooth soil surface (Fink and Myers, 1969; Fink, 1970).

However, as pointed out by Bond and Hammond (1970) and Philip (1971), the apparent contact angle measured on a porous surface is usually different to the actual contact angle due to the effects of the pores. For this reason, several methods of calculating the contact angle from infiltration and capillary rise measurements have been devised. Letey *et al.* (1962a) measured the height of capillary rise in a sand column after an abritrary period of 24 hours, and calculated the contact angle using the equation below.

$$h = \frac{2\gamma \cos\theta}{\rho g r}$$

where h = height of capillary rise
γ = surface tension of liquid
θ = contact angle
ρ = density of liquid
g = acceleration due to gravity
r = average pore radius

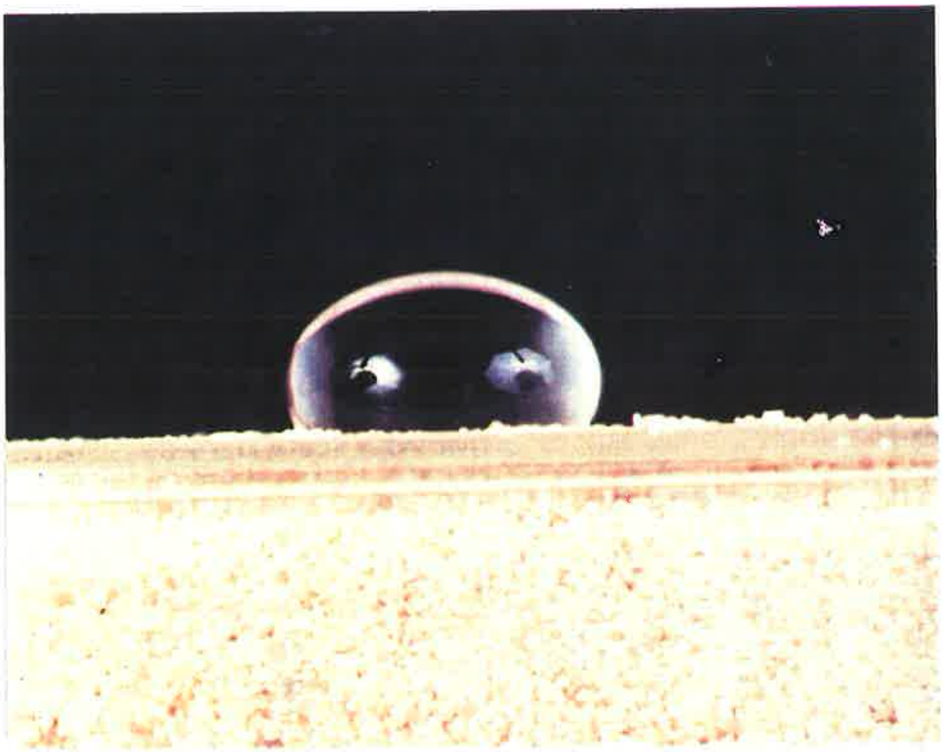


Figure 1.1. *A water droplet on a water repellent sand.*

This equation is usually used to determine r, the average pore radius, for a soil type by assuming the contact angle is 0°, and therefore $\cos\theta = 1$. In this situation, where the contact angle is obviously not 0°, the average pore radius was measured on the same sample using ethanol, which does have a 0° contact angle. Emerson and Bond (1963) used a similar method, but estimated r by measuring capillary rise in the same sand column after ignition. However, Bahrani *et al.* (1973) concluded that the ignition process may alter the pore size distribution, and Tschapek *et al.* (1973) found that ignition did not always reduce the contact angle to zero, and so this technique is not often used. Both these studies suggested the use of *n*-heptane to calculate r. Emerson and Bond (1963) and Hammond and Yuan (1969) described a dynamic capillary rise technique, where the initial rate of capillary rise (or horizontal flow) was used to estimate the actual final capillary rise. This method had the advantage of speed, which is particularly important because the contact angle in a water repellent sand is not constant, but changes with time.

DeBano (1969b) suggested that the change in contact angle was due to adsorption of water vapour molecules on the hydrophobic surface ahead of the wetting front. However, Barrett and Slaymaker (1989) concluded that it was due to soil organic matter gradually dissolving in the water, reducing the surface tension and therefore reducing the contact angle.

1.2.2 Rate of infiltration

The obvious effects of water repellence on infiltration led to the first attempts to quantify its severity. Jamison (1942) developed the 'relative rate of wetting', which was defined as the average rate of infiltration (ml min^{-1}) over the first 5 minutes. He later refined this (Jamison, 1945) to the 'relative time of wetting', which is the time taken for 100 g soil to absorb 20 ml water. Wander (1949) developed an even easier method, known as the 'Water Drop Penetration Time' (WDPT), which is simply the time taken for a drop of water to be absorbed by the soil. This measure has been used extensively in water repellence research (e.g. Letey, 1969; McGhie, 1979; King, 1981;

Wessel, 1988). McGhie (1979) classified soils according to their WDPT values, such that wettable soils had WDPT of zero seconds, slightly water repellent soils had WDPT values greater than 0 seconds but less that one minute, and severely repellent soils had WDPT values greater than one minute. Although Scholl (1975) and King (1981) showed that WDPT was closely correlated with contact angle, the actual mathematical relationships were different, probably because of the different techniques used to measure the contact angle. Watson and Letey (1970) concluded that the WDPT was a useful measure of the persistence of water repellence, rather than a measure of the initial repellence of a soil.

Fink and Myers (1969) and Fink (1970) used resistance to infiltration to measure water repellence. They defined the 'breakthrough pressure' as the threshold pressure (i.e. depth of water) required to force water into water repellent soil pores, and concluded that this was useful for extremely repellent soils. However, because it is relatively difficult to measure, and the contact angle (and hence breakthrough pressure) tends to change with time, this measure is not commonly used.

The ratio of intrinsic sorptivity of ethanol to that of water has been proposed as a Repellency Index (Tillman *et al.*, 1989). This index (RI) appears to be particularly useful for measurement of repellency where the contact angle is less than 90°. Wallis *et al.* (1991) used the R.I. to show that even when WDPT was zero seconds, repellence could slow the infiltration rate to less than the rainfall rate, and therefore create erosion problems. However, because R.I. measurement is a two step process, relying on infiltration of ethanol and water, it is unlikely to be used extensively in situations where the contact angle is greater than 90°, and simpler measures are available.

In a water repellent sand, infiltration tends to occur in 'fingers', rather than uniformly through the soil. The distribution of water in a cross section of a large soil column can be measured by Computer Aided Tomography, and provides an index of water repellence (Sawada *et al.*, 1989), which has proved useful for studying the effects of wetting agents on water repellence. However, the equipment required is expensive, and measurements can be time consuming.

1.2.3 Critical surface tension

The phenomenon of water repellence is due primarily to the high surface tension of liquid water. Letey *et al.* (1962a) suggested that the surface tension of a liquid which just wetted the soil with zero contact angle would provide a simple index of the severity of water repellence. Progressively stronger solutions of ethanol in water provide a good range of surface tensions (Janczuk *et al.*, 1989), and Watson and Letey (1970) proposed that the surface tension of the droplet of ethanol solution which was absorbed by the soil in five seconds would be a useful index of repellency.

King (1981) further refined this technique, and developed the Molarity of Ethanol Droplet (M.E.D.) test. In this test, aqueous ethanol solutions prepared at 0.2 M intervals are applied to the soil surface, and the Molarity of Ethanol Droplet which is absorbed in ten seconds is called the M.E.D. value of the soil. M.E.D. values of field soils range from 0.0 (wettable) to about 4.0 (severely water repellent), although artificial soils can be prepared with M.E.D. values up to 7.0 (Ma'shum, 1988). Soils with an M.E.D. value of 0.0 may still have contact angles high enough to significantly alter infiltration rates (Wallis *et al.*, 1991), and therefore the M.E.D. technique is only appropriate for high contact angles. Because surface tension of a liquid varies with temperature, this method is not ideal for use in the field. The advantages of this technique are that it is very quick, and can be performed on a very small sample. King (1981) showed that the M.E.D. value is highly correlated with contact angle and WDPT, and is very useful for contact angles greater than 90°. The M.E.D. test has become a standard measure of repellence in Australia under laboratory conditions.

1.3 Effects of water repellence on soils and plants

1.3.1 Infiltration and soil water content

Reduced infiltration is one of the most obvious effects of water repellence. Barratt and Slaymaker (1989) measured long term infiltration rates of less than 2 mm day^{-1} into a water repellent soil, most of which occurred as vapour. More commonly, however, infiltration is initially very slow, but increases with time up to a maximum (DeBano, 1969b, 1971). This is because water repellence affects the wetting process, but once the soil particles are wet, water can flow through the pores virtually unaffected (Rybina, 1973). This leads to the formation of preferential flow paths through the soil, as wet channels conduct water away before it has time to penetrate into dry soil patches (van't Woudt, 1954; Bond, 1964, 1965; Tillman *et al.*, 1989; Van Dam *et al.*, 1990).

Preferential flow paths through the soil result in uneven wetting of the soil. Jamison (1946) found water content varied from field capacity to air dry over distances of 5cm in a water repellent sand. Similarly, van't Woudt (1954), Bond (1964), and others, have described large water content variation over short distances in water repellent soils.

1.3.2 Plant growth

Plants require water to live and grow. Therefore, the effect of water repellence on water flow through soils has a profound effect on plant growth. In particular, germination and establishment is affected. In the 'wet' soil patches, plants can germinate and survive even in relatively dry conditions, because the soil effectively 'harvests' rainfall and concentrates it in these patches. However, in 'dry' soil areas, germination can be delayed, and even if germination occurs, plants often die from moisture stress. The resulting patchy plant growth is characteristic of water repellent soils in the field (Hedrick and Mowry, 1952; Bond, 1964, 1965, 1968).

Dinel *et al.* (1992) investigated the effects of long chain aliphatic compounds isolated from beeswax and added to a sand (up to 2%) on germination and growth of corn, radish and spinach. Germination of the small-seeded radish and spinach was reduced by the addition of long chain aliphatics, but corn germination was not affected. Growth of all species was substantially reduced by the hydrophobic effects of the long chain aliphatics on water relations in the sand, but the compounds had no direct phytotoxic effect. Osborn *et al.* (1964) reported difficulty in establishing ryegrass on a water repellent soil in California. Similarly, in a field trial on Eyre Peninsula in South

Australia, Bond (1972) recovered viable ungerminated barley seed three months after sowing, and this was also due to the effects of water repellence. In southern Australia, the effective delay in germination reduces the eventual yield of the crop by shortening the available growing season (French and Schultz, 1977). Water repellence also causes staggered germination of weed seeds, and this creates problems for weed and pest control. In a non-agricultural situation, water repellence has caused patches of dead or wilted turf in sandy golf greens (Wilkinson and Miller, 1978; Tucker *et al.*, 1990). Low soil water content also influences nutrient availability and microbial activity, which can affect plant growth (Braids and Miller, 1975).

Water repellence has also been linked with problems in established perennial crops. Jamison (1942) described a condition called 'tree decline' in a mature orange orchard in Florida, which eventually caused the death of the tree. He concluded that tree decline was closely correlated with water repellence in the soils, although there was no definite 'cause and effect' relationship. However, effects of this nature on established plants appear to be rare.

The compounds that cause water repellence may also have a direct toxic effect on plants. Braids and Miller (1975) suggested that these compounds may lower the surface tension of water, and Fraps (1915) found that dihydroxystearic acid (similar to the compounds that have been linked with repellence) reduced plant growth in solution culture. However, no studies have detected a toxic effect on plants grown in soil.

1.3.3 Runoff and erosion

Because infiltration is severely restricted by water repellence, runoff can occur during intense rainfall. This results in erosion, which has been particularly harsh on forested hill slopes in California (e.g. Osborn *et al.*, 1964; DeBano and Rice, 1973), and also in Spain (Sevink *et al.*, 1989). In these situations, water repellence often occurs as a layer approximately 5-10cm below the soil surface. Biswell (1974) concluded that the soil above the water repellent layer becomes saturated, and the resulting low resistance to shear stress allows the soil to virtually flow down the slope.

In a study using paired catchments, one of which was water repellent after a bushfire (see section 1.4.3), Scott and van Wyk (1990) found that burning and water repellence increased total stream flow over 1 year, and increased soil loss by about 400%. In Australia, McGhie (1980) and Burch *et al.* (1989) have reported increased runoff caused by water repellence, and McGhie (1980) also measured higher rates of soil loss.

Wind erosion has also been a problem on water repellent sands, especially in southern Australia. Dry, bare patches of sandy soil (characteristic of water repellence) are susceptible to erosion by moderate winds, which are common early in the growing season when the soil is least protected. When wind erosion commences, sand blasting of young plants around the edges of the bare patches quickly extends the boundaries of the patches, exposing more of the soil to the risk of wind erosion. Wetherby *et al.* (1983) concluded that water repellence was the major cause of erosion on Eyre Peninsula in southern Australia in 1975-77.

1.3.4 Beneficial effects

Although water repellence is recognised as a major problem in many areas, it can have some beneficial effects. Some researchers have even tried to generate artificial repellence to make use of its advantages. One of these advantages is in the area of water harvesting. In areas with a dry climates, water harvesting can increase the amount of water available for irrigation or town water supply. Water repellence can increase the amount of water collected from a given area (Fink and Myers, 1969; Fink, 1970). However, for this to be effective, the soil must be stabilised to prevent erosion, as increased runoff can lead to rill and gully erosion (section 1.3.3).

Many workers have reported decreased evaporation from a soil surface due to water repellence (e.g. Bowers and Hanks, 1961; Olsen *et al.*, 1964; Barrett and Slaymaker, 1989; Sharma, 1990). As the topsoil dries, its water repellence prevents capillary flow from the subsoil to the topsoil. Therefore, the only way for water to move from the subsoil to the topsoil is in the vapour phase, and this is a very slow process. In some areas, the reduction of evaporation allows greater water use, particularly for deep-rooted perennial plants. However, Bond (1968) measured greater evaporation from a water repellent soil, because a lot of water was retained at the surface of the soil, and very little penetrated into the subsoil.

Hydrophobic compounds also increase aggregate stability of soils, by reducing the rate of wetting (Hedrick and Mowry, 1952; Giovannini *et al.*, 1983; Sharma, 1990). Stable hydrophobic aggregates may even increase seedling emergence by preventing the formation of a hard crust (Rawitz and Hazan 1978). However, water repellence usually occurs naturally in a sandy soil, and in these soils aggregate stability is of little importance.

1.4 Causes of water repellence

There is no doubt that water repellence is caused by naturally occurring hydrophobic organic molecules. However, the origin and nature of the molecules, and the environmental conditions leading to water repellence, are not well understood.

1.4.1 Origin of hydrophobic compounds

In one of the first investigations into water repellence, Greig-Smith (1910, 1911) isolated the cause as ether-soluble plant remains, which he called 'agricere'. Many other authors have also implicated plants as the major source of hydrophobic compounds causing water repellence. In Florida, Jamison (1946) found that water repellence occurred in the leaf drip zone of citrus trees, but not between rows of trees. Giovannini and Lucchesi (1984) concluded that repellence was due to plant remains not yet humified. Similarly, Holzhey (1969) and Biswell (1974) found that plant litter was responsible for water repellence. McGhie (1979) suggested that perennial plants may actively induce repellence around themselves to reduce competition from annual plants, and to direct rainfall to their own roots. In this way, repellence may give a competitive advantage to some plants.

Water repellence can also be induced in wettable soils by the addition of ground plant fragments. McGhie and Posner (1980, 1981) found that residues from several different plant species, including *Eucalyptus astringens* (brown mallett) and *Trifolium subterraneum* (subterranean clover), but not *Triticum aestivum* (wheat) or *Avena sativa* (oats) induced water repellence in a sandy soil. Similarly, Roberts and Carbon (1972) induced repellence in sands with ground fragments of *E. marginata* (Jarrah), *Medicago sativa* (lucerne), and *T. subterraneum*.. However, as pointed out by Wallis and Horne (1992), these studies did not include any root material, and may not be a true representation of the development of water repellence.

It is also possible that plant fragments do not directly cause repellence, but rather stimulate the microbial community. Fungi, in particular, have been implicated in the development of water repellence. Bond (1964) concluded that different microbial populations associated with different vegetation types may cause variation in repellence. Bond and Harris (1964), Bond (1965, 1969b) and DeBano and Rice (1973) found that water repellence was usually associated with conspicuous growth of fungi, often basidiomycetes. However, several attempts to isolate a fungus and generate water repellence in a wettable sand have failed (e.g. Wilkinson and Miller, 1978). Savage *et al.* (1969a) grew a wide range of fungi in wettable sands, and found that only one (*S. atra*) induced measurable repellence. After heating (approximately 250°C) the sandy fungal cultures, however, most species did generate repellence (Savage *et al.*, 1969b). Therefore, they concluded that fungi could be involved in repellence caused by fires (see section 1.4.3).

Overall, there is as yet no conclusive proof that the compounds that cause water repellence are dominantly of either plant or microbial origin. Several studies have shown that soil lipids or aliphatics are mostly of plant origin (e.g.Stevenson, 1966; Tschapek *et al.*, 1973; Braids and Miller, 1975; Tegelaar *et al.*, 1989; Dinel *et al.*, 1990). By the same token, Schnitzer and Neyroud (1975) and Capriel *et al.* (1990) concluded that soil fatty acids and aliphatics were predominantly of microbial origin. Ultimately, organic additions to soil are almost exclusively from plants, and this in turn influences the microbial population. Therefore, the vegetative community probably determines to a large degree the development of water repellence.

1.4.2 Characterisation of hydrophobic compounds

In 1926, Albert and Köhn stated that 'humus molecules...range themselves in regular formation on the surface of the sand grains in such a way that "lyophobe" groups of molecules are directed outwards'. Later, Bozer *et al.* (1969) and Savage *et al.* (1969b) concluded that compounds which cause water repellence in soils must contain a polar site, for attachment to the soil particle, and a relatively large non-polar section which produces the repellence. Fatty acids and waxes satisfy these criteria, and because they are common in plants, they were prime suspects. Indeed, Greig-Smith (1910, 1911) found that waxy, fatty ether-soluble compounds caused repellence. However, Jamison (1945, 1946) could not reduce water repellence by extracting the soil with a range of fat solvents. Similarly, Van't Woudt (1959) found that water repellence was not affected by 20 hours of Soxhlet extraction with ether. These authors concluded that the compounds responsible for water repellence could not be waxes or lipids. A link between Ca and Mg fertiliser application and repellence led Wander (1949) to propose the formation of insoluble Ca- and Mg-soaps, and this was supported as a possibility by Wilkinson and Miller (1978). However, Bond (1969b) and Tucker *et al.* (1990) have ruled out this possibility, and Prusinkiewicz and Kosakowski (1986) found that Ca and Mg fertilisers were associated with increased soil wettability. Because most of the studies discussed above could not extract and characterise the compounds responsible, their conclusions were essentially negative. They tried to exclude classes of compounds, but could not conclusively say what did cause repellence.

Several attempts have been made to isolate water repellence-causing compounds in the traditional but poorly defined humic and fulvic acid fractions. Savage *et al.* (1969a) found that microbial humic acids did not generate repellence, but Roberts and Carbon (1972) concluded that a stable humic acid complex did cause repellence. Ivanek and Schmidt (1991) used IR to determine that humic acid 'molecules' caused hydrophobicity on quartz by occupying the silanol surface groups, which in the absence of organic matter act as sites of attraction for water molecules. Fulvic acid has also been implicated (Miller and Wilkinson, 1977). However, the chemical nature of these organic classes has made characterisation of the compounds difficult.

Giovannini *et al.* (1983) successfully reduced repellence by extracting with benzene, and showed that the extract produced repellence in wettable sand. Using this extract and differential thermal analysis, Giovannini and Lucchese (1984) concluded that a phenol/polysaccharide ester was the principal cause of water repellence. However, complete extraction of hydrophobic materials by a selective solvent was not achieved until Ma'shum *et al.* (1988) tried a mixture of *iso*-propanol and ammonia solution. This extract was then examined by chromatographic and spectroscopic methods including Infra-Red and Nuclear Magnetic Resonance. They concluded that repellence was caused by free and esterified straight chain fatty acids, with carbon chain lengths ranging from 16-32 atoms. These are the types of compounds excluded by earlier studies on the basis of their non-extractability in traditional fat solvents. These compounds must be held tightly by the soil particles, and only the amphiphilic *iso*-propanol/ammonia solvent could break the bonds between the functional group and the sand grains. Interestingly, Stevenson (1966) also found that in a 'normal' soil, the lipid fraction was composed of waxy esters of long straight carbon chains, dominated by even numbers of carbon atoms.

1.4.3 Conditions for development of water repellence

Fire has often been recognised as a factor in the generation of water repellence, particularly in the USA. Fire has been shown to decrease the total lipid content of the soil, but still increases repellence, possibly by redistribution and selective oxidation of hydrophilic molecules (Chen and Schnitzer, 1978; Almendros *et al.*, 1990). DeBano *et al.* (1970) and Savage (1974) suggested that heat volatilised the hydrophobic molecules, which then moved into the soil and condensed to form a water repellent layer in the soil. Scholl (1975) and Scott and Van Wyk (1990) showed that the hotter the fire, the deeper and more intense was the subsequent layer of repellence. DeBano and Rice (1973) and Giovannini and Lucchese (1983) found that very intense fires may reduce repellence, by oxidising the organic matter responsible.

Although water repellence has occasionally been reported in loams or clays (Lunt *et al.*, 1963; McGhie and Posner, 1980; Giovannini and Lucchese, 1983; Barrett and Slaymaker, 1989), it is most common in sandy soils. The main reason for this is the low specific surface area associated with large sand grains. Ma'shum *et al.* (1989) showed that the amount of hydrophobic organic matter required to induce repellence was positively correlated with the specific surface area of the soil. Therefore, because a sandy soil has a much lower specific surface area than a loam or clay soil, a much smaller amount of hydrophobic organic matter is sufficient to coat the sand grains and allow repellence to become a problem.

Microbial activity in sandy soils is also often lower than in soils of heavier texture. Kaiser *et al.* (1992), in a survey over 27 soils, found that microbial biomass was related to organic matter and clay content, and inversely related to sand content. In soils with higher biological activity (i.e. loams and clays), hydrophobic organics are more likely to be degraded before they accumulate to levels that cause water repellence. Valat *et al.* (1991) found that microbial degradation of peat and compost caused them to become more wettable as decomposition proceeded.

Because water repellence is induced by organic matter, there may be a relationship between organic matter content and severity of water repellence. This was observed by Scholl (1971), and DeBano *et al.* (1976). However, Bond and Harris (1964) could not find a correlation, and Van Dam *et al.* (1990) described a wettable sand with 2.0% OM and 5% clay, and a repellent sand with 1.5% OM and 3% clay. Obviously, it is not necessarily the total organic content that is important, but rather the balance of hydrophobic to hydrophilic organic compounds, and the specific surface area of the soil.

Water repellence is not confined to a specific climatic region. It has been reported in subalpine/alpine areas (Barrett and Slaymaker, 1989), through Mediterranean zones (Bond, 1969a), to arid areas (DeBano, 1969a). However, it appears to be more common in the Mediterranean zones, with cool, wet winters and hot, dry summers.

Clearly, the development of water repellence is affected by many factors. In general, sandy soils with some organic matter are prone to water repellence, particularly if they are exposed to a moderate fire. However, the actual process of the generation of water repellence, and why repellence does not occur in all sandy soils, is not well understood.

1.5 Amelioration of water repellence

Despite the beneficial effects mentioned earlier, water repellence is usually seen as a problem in agricultural and forest soils. Several techniques have been devised to reduce the effects and increase production on water repellent soils.

1.5.1 Cultivation

Cultivation is the traditional method for managing water repellent soils, and works in a number of ways. Tilling during and immediately after rain mixes the patches of dry soil with the wet patches, creating a uniformly moist soil (King, 1974), which is easily wet by subsequent rain (Van't Woudt, 1954). However, if the soil dries after the cultivation, water repellence returns (McGhie, 1979).

Jamison (1942, 1945, 1946) suggested that cultivation mixed the water repellent topsoil with wettable subsoil, creating a more wettable soil. He also recognised that the rough soil surface after cultivation allowed water to collect in the small depressions. When this water soaked in, the soil became more evenly wet than if the surface was smooth. Bond (1972) used the rough surface principle to demonstrate the advantages of sowing seed in the bottom of furrows. On a water repellent soil, rain collects in the furrows, and soaks in straight to the seed. Bond (1972) showed that in a field trial, furrow-sown barley yielded over 1200 kg ha^{-1}, whereas ridge-sown barley yielded only 500 kg ha^{-1}. This difference was due to increased and earlier germination of the furrow sown seed.

Abrasion (i.e. shaking) has been shown to decrease repellence of sandy soils in the laboratory (Bond, 1968; King, 1981), presumably by the removal of the organic coatings. The abrasive effects of cultivation probably also act to reduce repellence in the field, although this has not been measured.

Although the effects of a single cultivation are short term (Roberts and Carbon, 1972), long term agricultural use has been shown to decrease repellence. McFarlane *et al.* (1992) measured repellence in paddocks which had been cultivated for crop production for 30 years, and in adjacent uncleared areas. In the agriculturally developed soils, repellence was generally much lower and less variable than in the uncleared soils.

1.5.2 Wetting agents

Wetting agents (surfactants) can be applied to the soil, and act by reducing the surface tension of water as it comes into contact with the soil, thereby reducing the soil/water contact angle. Jamison (1946) found that wetting agents were effective in a water repellent orchard soil, and since then many workers have proposed wetting agents as a means of overcoming water repellence (e.g. Letey *et al.*, 1962b; Mustafa and Letey, 1969, 1971; Wilkinson and Miller, 1978; Miyamoto, 1985; Sawada *et al.*, 1989). Miyamoto (1985) showed that wetting agents increased the rate of infiltration into soils with contact angles of 56, 63 and 81°. Osborn *et al.* (1964) found that wetting agents reduced runoff and debris removal from a steeply sloping water repellent soil. When applied to a wettable soil, however, wetting agents can decrease the rate of infiltration (Letey *et al.*, 1961; Pelishek *et al.*, 1962).

Wetting agents may also be phytotoxic to some plants. Valoras *et al.* (1974) showed that the surfactant 'Soil Penetrant' was taken up by barley, and accumulated in the old leaves. As the concentration of surfactant increased, dry matter production decreased. Parr and Norman (1964), Roberts and Lage (1965), Osborn *et al.* (1967), Endo *et al.* (1969), and DeBano and Conrad (1974) also found evidence of phytotoxicity of wetting agents, although most of these were on plants grown in solution culture. Phytotoxicity of wetting agents applied to soils has not been demonstrated.

McGhie and Tipping (1983) stated that wetting agents must effectively reduce water repellence for a period of at least one year to be economic. Some of the surfactants they tested were able to achieve this, and they concluded that wetting agents may be economically viable in high value crops. Recent research has investigated application of wetting agents in the bottom of furrows in combination with press wheels and furrow sowing, and the reduced rates of wetting agent required (about 1 l ha^{-1}, compared with 50 l ha^{-1} for broadacre application) make this method even more economically attractive (W.L. Crabtree, personal communication).

1.5.3 Stimulating microbial degradation

Many micro-organisms in soils are capable of degrading long chain aliphatic compounds (Fehl and Lange, 1965; Braids and Miller, 1975; Vecchioli *et al.*, 1990) similar to those that cause water repellence. In water repellent soils, however, microbial degradation does not proceed fast enough, and the hydrophobic compounds accumulate to cause water repellence. Therefore, if the microbial community in a water repellent soil could be stimulated, repellence may be overcome. This may be difficult, however, because Chae and Lowe (1980) and Dinel *et al.* (1991) showed that relatively high lipid concentrations may be directly phytotoxic to micro-organisms, as well as the effects on water availability. In other words, water repellent soils are naturally low in terms of microbial activity, and low microbial activity leads to water repellence.

Sandy soils are traditionally low in most nutrients, and this could be one factor limiting microbial activity. Moucawi *et al.* (1981) demonstrated that in iron deficient soils, the addition of iron fertiliser increased microbial degradation of lipids. Similarly, Jambu *et al.* (1991) showed that N or NPK fertiliser resulted in a decrease in linear long chain (>27 carbon atoms) hydrocarbons in the soil. However, Tucker *et al.* (1990) compared water repellent patches in a golf green with adjacent wettable soil patches and could not find any link between soil nutrients and water repellence.

In general, the microbial community of water repellent soils has been largely and seriously ignored. This area requires further investigation, particularly as there is the possibility of reducing the incidence of water repellence by manipulating the natural micro-organisms.

1.5.4 Fine particle amendment

As discussed earlier, water repellence is most common in sandy soils because of their large particles and small specific surface area. For example, spherical particles with an average diameter of 0.2 mm (i.e. sand particles) have a surface area of 0.011 m^2 g^{-1}, whereas clays (<2 μm) commonly have measured surface areas of over 100 m^2 g^{-1}. Therefore, addition of fine particles (e.g. clays) to a sandy soil can dramatically increase the surface area available for adsorption, with the result that much more hydrophobic organic material is required to coat the surfaces and induce significant repellence. Jamison (1945, 1946) was probably the first to add clay to a water repellent sand. He concluded that although clays reduced repellence, cultivation was cheaper and just as effective.

Several other studies have shown that the addition of fine particles reduces water repellence in sands (Roberts, 1966; Roberts and Carbon, 1972; King, 1974; Bond, 1978; McGhie, 1979; Ward, 1984). However, only Ma'shum (1988) and Ma'shum *et al.* (1989) have investigated the interactions of fine particles with water repellent sands in any detail. They found that in general, the efficacy of a finely particulate material was related to its surface area. However, within the clay minerals, kaolinite and illite were more effective than montmorillonite, and sodium saturated clays were more effective than calcium saturated clays. They concluded that clay dispersibility was the major factor influencing the efficiency of clays in reducing water repellence. Clays which easily dispersed would expose a greater ‘available’ surface area to interact with the hydrophobic organics. Oades (1986) suggested that kaolinite and illite particles, because of their blocky geometry, would be more easily dispersed than platy montmorillonite particles, and Ma'shum *et al.* (1989) used this to explain the greater efficacy of kaolinite and illite over montmorillonite in reducing water repellence. However, Velasco-Molina *et al.* (1971) found that in the absence of electrolyte, montmorillonite was more dispersive than kaolinite and halloysite for any given ESP, and Ali *et al.* (1987) concluded that kaolinite, clay mica, montmorillonite, and vermiculite clay minerals dispersed equally from arid soil aggregates. Clearly, the role of dispersibility in the clay induced reduction of water repellence in sandy soils requires further attention.

Brindley *et al.* (1963) and Hedges (1977) investigated the adsorption of uncharged aliphatic compounds onto clay minerals. They found that on a surface area basis, kaolinite adsorbed more than montmorillonite, and this may help to explain why kaolinite clays appear to be more effective than montmorillonite clays in reducing repellence. These effects also require investigation. The occurrence and interactions of aliphatic compounds with soils will be discussed in greater detail in section 1.6.

Microbial activity can be increased by clay addition to sandy soils (Martin and Haider, 1986). Marshall and Roberts (1963), Heijnen and Van Veen (1991) and Heijnen *et al.* (1992, 1993) also showed that clay addition increased *Rhizobium* spp. or *Pseudomonas fluorescens* survival, by providing protective habitats for the bacteria. In a bentonite-amended sandy soil, Amblès *et al.* (1989) found that the increased microbial activity resulted in the stimulation of oxidation processes and production of short-chain hydrocarbons. However, Kunc and Stotsky (1974) found that clay addition had no consistent effect on CO_2 evolution, and that kaolinite and montmorillonite appeared to behave differently. Therefore, clay addition to a water repellent soil may reduce repellence by stimulating microbial degradation of the hydrophobic organic compounds, but this requires further investigation.

Clay minerals are also known to catalyse the decarboxylation of fatty acids to form alkanes in one of the processes of oil formation (Almon and Johns, 1975). In a water repellent soil, decarboxylation would remove the part of the molecule that attaches to the soil particle, allowing it to be removed from the system. However, catalytic activity of clays is usually referred to in terms of geologic time, temperature and pressure, and so is unlikely to have any noticeable effect on water repellence in a topsoil in the short to medium term.

The addition of clays to a sandy soil can have a direct influence on wind erosion, independent of any effects on water repellence. Diouf *et al.* (1990) showed that addition of a montmorillonite clay to a sand reduced erosion in a wind tunnel. The clay effectively bound the sand into aggregates too large to be moved by wind. However, this effect is likely to be reduced by cultivation, and clay applied at the rate required to reduce erosion may also cause the formation of a hard crust on the soil surface.

1.6 Aliphatic compounds in soils

1.6.1 Occurrence of aliphatic materials in soils

Historically, soil organic matter has been extracted as humic and fulvic acids, and humin, based on its solubility in alkali and acid. Subsequent chemical characterisation showed that these fractions were dominated by aromatic compounds, with only minor amounts of aliphatic materials. However, recent advances in spectroscopic techniques (particularly NMR and IR) have revealed the importance of uncharged aliphatic and polymethylenic compounds in whole soils (Hatcher *et al.*, 1981; Farmer and Pisaniello, 1985; Oades *et al.*, 1987; Krosshaven *et al.*, 1990; Schulten and Schnitzer, 1992). For example, Oades *et al.* (1987) found that nearly two-thirds of the organic matter in the clay fraction of an alfisol was aliphatic. Schulten and Schnitzer (1992) suggested that aliphatics may be covalently bound to phenolic compounds to form the backbone of soil humic substances.

Many workers have tried to extract soil lipids and determine the chemical nature of the compounds. For example, Ashworth (1942), Fridland (1976) and Solinas *et al.* (1988) used a mixture of benzene and ethanol to extract soil lipids. Solinas *et al.* (1988) found that benzene/ethanol soluble lipids constituted up to one third of soil organic matter, and were composed mainly of saturated long carbon chains. However, few other investigators have been able to extract this quantity of lipids from a soil.

Stevenson (1966) found that most soil waxes were esters of long chain saturated *n*-alcohols and *n*-acids. Similarly, Schnitzer and Neyroud (1975) found that up to 10% of soil organic matter was fatty acids, mostly C_{16} and C_{18}, linked by an ester bond to phenolic compounds. Grimalt and Saiz-Jimenez (1989) and Grimalt *et al.* (1989) separated soil lipids into ethanol-soluble and ethanol-insoluble fractions, and found, by gas chromatography, appreciable quantities of C_{16} fatty acids in both fractions.

However, as Dinel *et al.* (1990) stated, soil lipids are generally very difficult to extract. Few lipid extracts contain more than 10% of the total soil carbon, even though evidence from NMR, IR, and MS shows that polymethylene compounds (including *n*-acids and *n*-alcohols, and their esters) are common in soils (Ma'shum *et al.*, 1988; Krosshaven *et al.*, 1990, Hempfling and Schulten, 1991). Therefore, characterisation of soil extracts often ignores substantial quantities of aliphatic organic matter.

The origin of the aliphatic material in soil is a subject of some debate. Dinel *et al.* (1990) stated that algae and fungi tend to synthesise odd-numbered carbon chains (e.g. C_{15}, C_{17}, etc.), whereas plants tend to synthesise even-numbered carbon chains. They concluded that the majority of soil lipids were partially decomposed plant and animal products. Many other studies have found a predominance of even-numbered carbon chains (e.g. Ma'shum *et al.*, 1988; Grimalt and Saiz-Jimenez, 1989), which suggests plant origin. However, Schnitzer and Neyroud (1975) and Capriel *et al.* (1990) concluded that soil aliphatics were mostly of microbial origin. Recently, Tegelaar *et al.* (1989) proposed that soil aliphatics may be derived from 'insoluble non-hydrolysable aliphatic biopolymers' (polysaccharide bonded to polymethylene materials), found in most algae and higher plants.

The soil environment can play a significant role in the type and amount of aliphatic material in soils. For example, Arshad *et al.* (1990) found after ten years continuous barley, no-till soils contained relatively more aliphatic and less aromatic organic matter than conventionally cultivated soil. Conversely, Schulten *et al.* (1990) suggested that the quantity of aromatic organic matter declined under intense management. However, Capriel *et al.* (1990, 1992) used several spectroscopic techniques to show that intensity of agricultural management (e.g. cultivation) had no qualitative effect on the soil organic matter. In a study looking exclusively at soil lipids, Fridland (1982) demonstrated a link between vegetation and lipid type and quantity. However, Krosshaven *et al.* (1990) examined soils under 11 different vegetation types, and using NMR, found no differences in the types of aliphatic compounds present.

Clearly, the origin and reactions of polymethylene material in soils require further research. New spectroscopic techniques should be useful in elucidating these questions.

1.6.2 Interactions of aliphatic compounds with soil minerals

Because extraction of aliphatic compounds from soils has proved difficult, it is reasonable to assume that they strongly interact with the inorganic soil matrix (Dinel *et al.*, 1990). However, few studies have investigated these interactions. Brindley and Ray (1964) and Brindley and Moll (1965) investigated the adsorption of aliphatic alcohols and carboxylic acids respectively with carbon chain lengths up to 18 atoms onto Ca^{2+}-montmorillonite. For both types of compound, interlayer complexes were only formed under very specialised conditions. The longer chain alcohols formed complexes consistent with the carbon chain extended at an angle of about 70° to the clay surface. Similar complexes were formed with long chain acids, but only at temperatures above the melting point of the free acid. Interlayer adsorption in montmorillonite was also observed by Yariv and Shoval (1982) and Sidheswaran *et al.* (1990) for fatty acids, and Theng *et al.* (1986) for polymethylene compounds, but in most cases, the formation of the interlayer complex was only achieved under carefully controlled conditions..

Brindley *et al.* (1963) measured the adsorption of water soluble uncharged aliphatics onto clay minerals, and showed that on a surface area basis, gibbsite adsorbed most, followed by kaolinite and finally montmorillonite. They concluded that the OH- surface of gibbsite and one face of kaolinite was a stronger adsorbent than the O- surface of montmorillonite and the other kaolinite face. Hedges (1977) measured adsorption of stearic acid onto kaolinite and montmorillonite from water, up to a concentration of 1 mg l^{-1}. Kaolinite again adsorbed more than montmorillonite on a surface area basis, and both followed linear isotherms, probably as a result of the low solubility of stearic acid in water. Meyers and Quinn (1971, 1973) also observed linear adsorption isotherms for a fatty acid onto clay from sea water. These results suggest that kaolinite clay applied to a water repellent sand may be effective because it adsorbs the hydrophobic compounds more strongly than montmorillonite.

Hoffmann and Brindley (1960) observed that for neutral molecules, such as long chain acids, alcohols and esters, a chain length of at least 5 carbon atoms was required before adsorption occurred. However, German and Harding (1969) measured appreciable adsorption of all alcohols from ethanol to *n*-decanol onto montmorillonite. Sansone *et al.* (1987) showed that 99% of added stearate was adsorbed by clay minerals from water, but this was only measured at concentrations well below that required to form a monolayer. Rao *et al.* (1991) found maximum adsorption of oleate (a C_{18} chain) on fluorite at about 10 μmol m^{-2}, and concluded that adsorption occurred in a bilayer. Using data from Brindley and Moll (1965), Ma'shum *et al.* (1988) calculated that a close packed monolayer of straight carbon chains extended at 70° to the clay surface should contain 7.74 μmol m^{-2}. The orientation and mechanism of clay interaction with aliphatic chains requires more investigation, particularly in ‘real’ soil situations.

1.7 Introduction to experimental work

In this literature review, several aspects of water repellence have been highlighted as requiring further research. The most basic of these is in the induction of water repellence. Until we know how water repellence is generated in the field, we cannot hope to prevent its occurrence. This is addressed in chapter 2.

Of more immediate concern to the southern Australian farmer is the treatment of existing water repellence. Although some (but not all) clays have been shown to effectively reduce repellence, the mechanism by which they achieve this is not known.

The interactions of clays with model hydrophobic compounds known to occur in water repellent soils is investigated in chapters 3 and 4. The laboratory application of clays directly to a natural water repellent sand, and a comparison with the model system, is described in chapter 5 . A simple test designed for farmers to determine the effectiveness of a given field clay sample is developed in chapter 6.

CHAPTER 2. INDUCTION OF WATER REPELLENCE

2.1 Introduction

Water repellence in soils is caused by hydrophobic organic matter, probably derived from plant waxes. The organic matter forms a coating on the soil particles (Bond, 1969a; Ma'shum, 1988), which renders the sand particles hydrophobic. High temperatures (e.g fires) can cause repellence by 'distilling' hydrophobic compounds into the soil, forming a water repellent layer where they condense (Scholl, 1975). In the absence of high temperatutes, water repellence has been experimentally induced in sandy soils by adding ground plant remains. Bournemisza (1964; cited by Wallis and Horne, 1992) generated repellence by adding ground citrus leaves to a wettable sand. Similarly, Roberts and Carbon (1972) and McGhie and Posner (1981) induced repellence with leaves from several plant genera including *Eucalyptus*. However, the mechanism by which organic materials are transferred from plant fragments to the surfaces of sand grains in the absence of high temperatures (>100°C) is not known. An understanding of this process is vital in our efforts to reduce the effects and incidence of water repellence.

Field soils are exposed to a number of factors that may be involved in inducing water repellence. One of these is water, and the process of wetting and drying. The organic materials responsible are, by definition, insoluble in water. The action of water alone is therefore not sufficient to bring hydrophobic organic molecules and soil particles into close enough contact to allow the organics to coat the sand particles. However, Kemper *et al.* (1974) demonstrated that surface tension forces as water evaporates brings clay particles into close contact with the sand grains. A similar mechanism may bring plant fragments and sand grains into close enough contact to allow hydrophobic molecules to coat the sand grains. Water may also affect hydrophobicity by leaching the water soluble organic materials through the sand, leaving an excess of hydrophobic organic compounds behind (Chen and Schnitzer, 1978).

Another factor acting on soils is heat. On a hot sunny day in southern Australia, temperatures at the soil surface can reach more than 70°C. Ma'shum *et al.* (1988) found that compounds like palmitic acid, cetyl alcohol, and cetyl palmitate were major constituents of the material which caused water repellence, and these compounds all have melting points between 50 and 60°C. Therefore, these compounds may become much more mobile within the soil on hot days, and become evenly distributed in the soil. Many studies in the U.S.A. (e.g. Savage, 1974) have shown that fire (i.e. temperatures > 150°C) can induce repellence, but moderate temperatures (70°C) have not been investigated.

Microbial activity may also play a role in generating water repellence. Scott and Van Wyk (1990) found that in the absence of fire, water repellence was only measurable where fungi were visually present. Jex *et al.* (1985) demonstrated that repellence became more severe when slightly water repellent soils were incubated at 100% relative humidity. However, repellence was not induced in wettable soils. This suggests that the micro-organisms do not directly produce the hydrophobic compounds which cause repellence, but indirectly bring plant fragments and soil particles into contact.

In this chapter, the roles of temperature, water and micro-organisms in the generation of water repellence were investigated, using both single compounds and natural soil organic matter.

2.2 Materials and Methods

2.2.1 Measurement of repellence

Throughout this thesis, water repellence was measured using the M.E.D. (Molarity of Ethanol Droplet) test developed by King (1981). Solutions of ethanol in water were prepared at 0.2 M intervals from 0.0 to 7.0, and stored in glass dropper bottles at 20°C. In all cases, sand samples were brought to 20°C in a desiccator before measurement. Two droplets (100 μl) of various ethanol solutions were placed on the sand surface until an ethanol concentration was found which just soaked into the surface in 10±1 sec. This concentration was then recorded as the M.E.D. value of the soil. In situations when no solutions soaked in within 10±1 sec, the M.E.D. value was recorded as the value between the two closest concentrations. For example, if the 2.4 M solution droplets penetrated in 12 seconds, and the 2.6 M solution droplets penetrated in 7 seconds, the M.E.D. value would be 2.5 M. The M.E.D. method was chosen because it is quick, easy, and highly correlated with other more difficult methods of measuring water repellence (King, 1981). Values for field soils range from 0.0 (readily wettable) to about 4 (severely water repellent). With cetyl alcohol and acid-washed sand, M.E.D. values up to 7.0 can be obtained (Ma'shum *et al.*, 1989).

2.2.2 Sands

A *model* water repellent sand was prepared with cetyl alcohol (hexadecan-1-ol – $C_{16}H_{33}OH$ (supplied by British Drug Houses Ltd.)) and acid-washed sand (also BDH) using a procedure similar to that described by Ma'shum *et al.* (1989). Briefly, cetyl alcohol (400 mg per kg acid-washed sand) was dissolved in enough chloroform (trichloromethane) to saturate the sand. The cetyl alcohol solution was poured onto the sand, and allowed to evaporate in a fume hood.

Natural water repellent sand was collected from Western Flat in the south east of South Australia. This soil is a deep siliceous sand, and is part of an old coastal dune formation. The soil sample was air-dried, sieved < 2 mm and stored at room temperature. It contained approximately 97% sand, 2% clay and 1% organic matter. Its M.E.D. value after oven drying at 105°C, was 3.1± 0.1.

2.2.3 Role of water

The ability of wetting and drying to induce repellence by bringing natural organic matter and sand into close contact was determined with an organic rich fraction separated from the Western Flat sand by repeated washing with reverse osmosis (RO - <5 μS cm^{-1}) water. The sand was shaken in RO water, allowed to settle (approx. 30 seconds), and the free organic matter (and any clay and silt) was decanted. The solution was concentrated by rotary evaporation in a water bath at 50°C, and finally freeze dried. This was then added to acid-washed sand to give the same amount as present in the natural sand (i.e. about 5%). Duplicate samples of the acid-washed sand/organic mix (20 g) were wetted with 8 ml RO water, and dried at 70°C.

The ability of water to induce repellence by leaching water soluble organics was tested by placing 40 g of the acid-washed sand/organic mix into two glass columns (19 mm inside diameter) with fine cotton mesh stretched over the bottom. A 200 ml volumetric flask filled with RO water was inverted over the sand, and allowed to flow through the sand column. The leached sand was dried at 70°C, and measured for repellence. Other experiments showed that 70°C alone did not induce repellence in this sand (table 2.1).

2.2.4 Role of temperature

A sample of the cetyl alcohol-amended acid-washed sand was placed in a glass vial and heated at 35,40,45,...,70°C ±1°C for 1,2,4,8, or 24 hours in three replicates. This examined the role of heat in driving off adsorbed water and allowing the molecules to orient on the sand grains so that their hydrophobic chains became the exposed surface. A similar experiment was performed using cetyl alcohol added directly to the sand as chunks of about 0.5 mg, without first dissolving in chloroform. This was to test whether heat could also be involved in evenly distributing the hydrophobic materials throughout the sand sample.

The role of temperature in generation of water repellence by natural organic compounds was also investigated. Duplicate samples of the Western Flat sand were treated at either 20, 50, 70 or 105°C for 24h, cooled to 20°C in a desiccator, and M.E.D. values were measured. Similarly, the acid-washed sand/organic mix described previously was heated at either 70°C or 105°C for 48 hours, and measured for repellence.

2.2.5 Role of micro-organisms

Natural organic particles were extracted from a water repellent sand and mixed with an acid-washed sand as described above. Some of the sand/organic mix was sterilized by either autoclaving or chloroform fumigation. Another sand/organic mix was prepared with water-soluble (i.e. hydrophilic) natural organic matter, to determine whether micro-organisms were directly responsible for the production of hydrophobic compounds. Samples were incubated either air dry, or at 100% relative humidity (0.6% w/w), or near saturation (20% w/w) for 3 weeks. Samples were subsequently dried at 70°C, and M.E.D. values were measured.

2.3 Results

2.3.1 Effect of water

Wetting and slow drying (70°C), and leaching, did not induce measurable repellence (M.E.D. 0.0) in acid-washed sand amended with natural organic matter.

2.3.2 Effect of temperature

No repellence could be measured after treatment of acid-washed sand with cetyl alcohol dissolved in chloroform when the sample was not heated above 20±2°C (room temperature). However, a temperature of 35°C was sufficient to induce measurable repellence (Fig. 2.1a). A temperature of 50°C for 24 hours generated maximum repellence, and higher temperatures induced maximum repellence more quickly.

Where chloroform was not used to distribute the cetyl alcohol throughout the sand, a heat treatment of 50°C for 24 hours was required before any repellence could be measured (Fig. 2.1b). Temperatures over 60°C generated intense repellence after 4 hours. Variation in the results was greater than when chloroform was used, probably as a result of the variable initial distribution of the cetyl alcohol.

In the natural water repellent sand from Western Flat, temperatures of 20, 50 and 70°C had little effect on the level of water repellence. However, at 105°C, the M.E.D. value rose from 1.5 to 3.1 (Figure 2.2). Similarly, when the natural organics

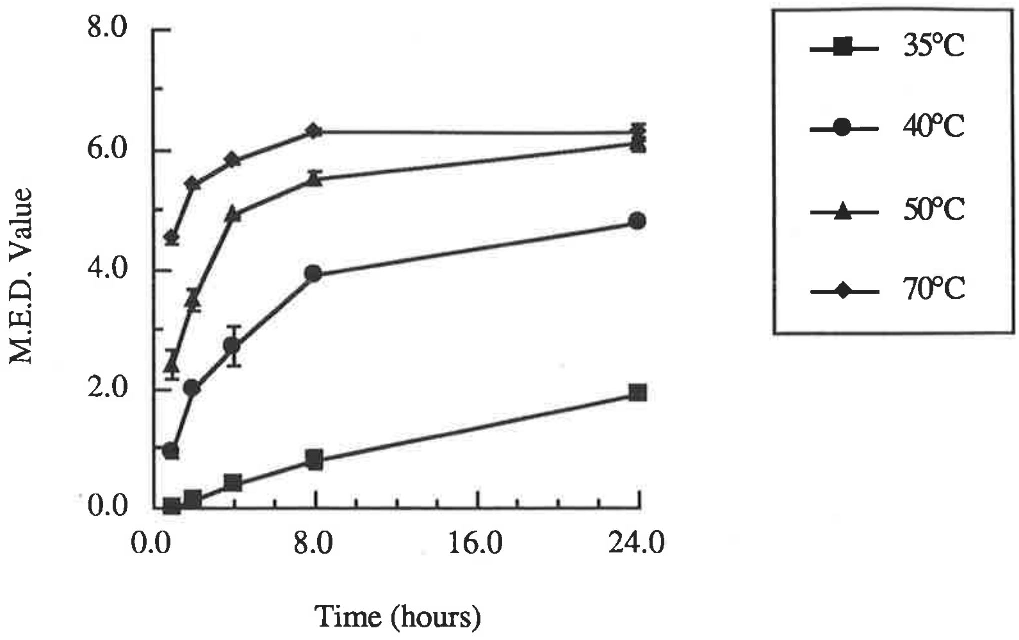


Figure 2.1a. *Effect of drying temperature on water repellence induced by evenly distributed cetyl alcohol.*

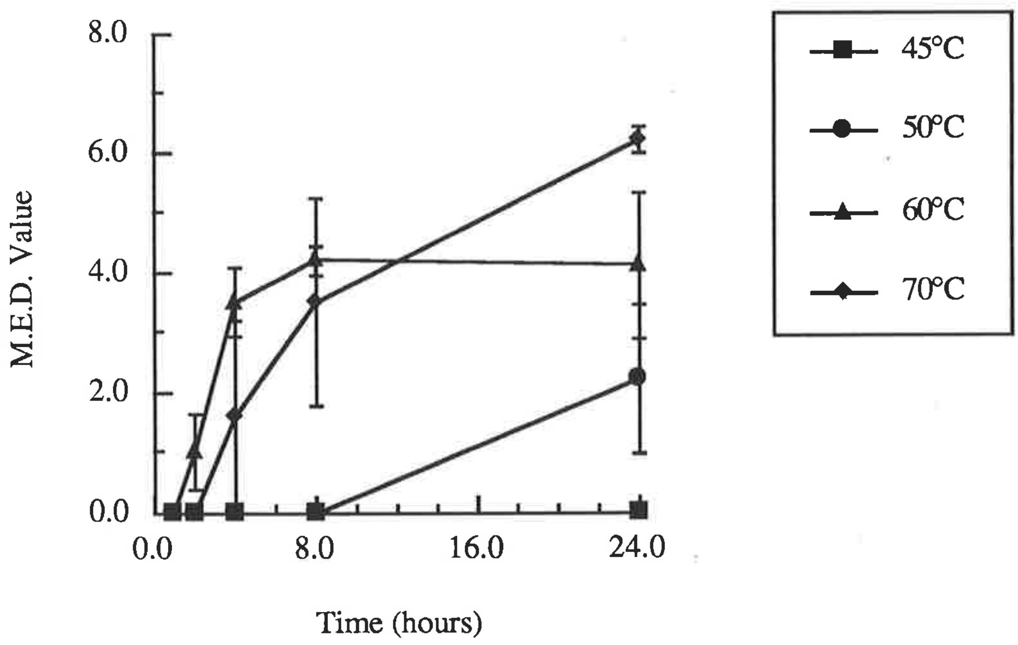


Figure 2.1b. *Effect of drying temperature on water repellence induced by unevenly distributed cetyl alcohol.*

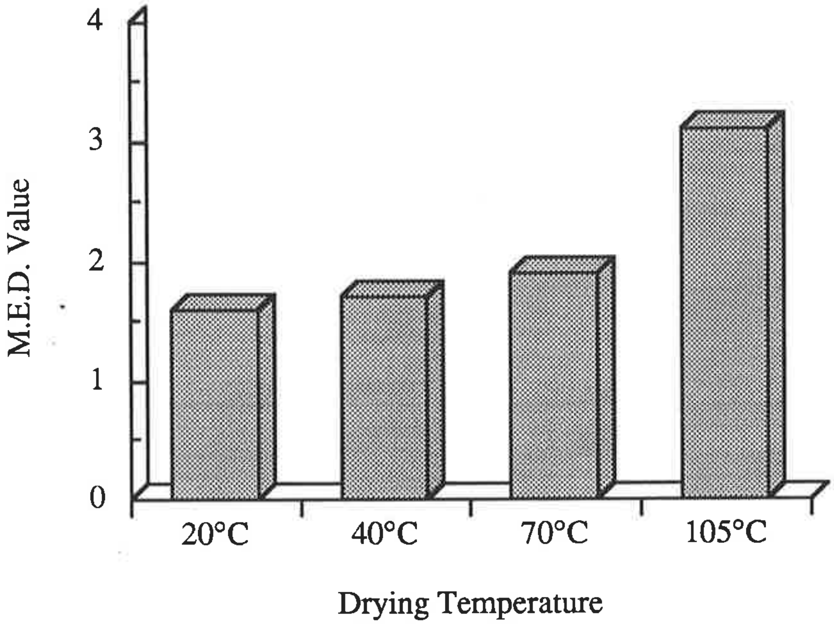


Figure 2.2. *Effect of drying temperature on water repellence in Western Flat sand. The Tukey-Kramer Least Significant Diference (LSD) value was 0.21.*

were added to an acid-washed sand (initial M.E.D. 0.0), a temperature of 70°C was not sufficient to induce repellence, but 105°C generated an M.E.D. value of 1.3 (Table 2.1).

2.3.3 Effect of microbial activity

When the acid-washed sand/natural organic mix was incubated at 100% R.H. (water content 0.6% w/w) for three weeks, microbial activity increased the M.E.D. value from 0.0 to 3.2, which was similar to the original water repellent sand (Table 2.1). However, at a water content of 20%, the M.E.D. value only increased to 0.2. There was no change in repellence in either of the sterilised sands, or the sand kept air-dry. Similarly, repellence did not increase in the sand amended with water soluble organic matter.

Treatment description	M.E.D. Value
No treatment	0.0
Heated 70°C	0.0
Heated 105°C	1.3
21 days air dry	0.0
21 days at 100% RH (w=0.6%)	3.2
21 days 100%RH, fumigated	0.0
21 days at w=20%	0.2
21 days at w=20%, autoclaved	0.0
21 days at w=20%, fumigated	0.0
21 days 100%RH; sand + water soluble OM	0.0

Table 2.1 *Effect of various treatments on water repellence in acid-washed sand mixed with organic matter washed from a natural water repellent sand..*

2.4 Discussion

Water alone, through wetting and drying and leaching processes, was not sufficient to generate repellence. Therefore, other factors must operate in the induction of repellence in the field.

2.4.1 Role of temperature

For repellence induced by cetyl alcohol, the chloroform treatment distributed cetyl alcohol evenly throughout the sand sample. Relatively low temperatures of 35-40°C (below the melting point of cetyl alcohol) removed some of the water adsorbed on the sand grains and allowed orientation of the cetyl alcohol molecules so that their hydrophobic chains were exposed. Higher temperatures allowed this to proceed at a faster rate. In the absence of a chloroform treatment, temperatures of greater than the melting point of cetyl alcohol were required to induce repellence. Above this temperature, the cetyl alcohol was mobile in the sand matrix, and coated the sand surfaces. After this had occurred, the high temperatures also allowed exposure of hydrophobic portions of the molecules.

Therefore, moderately high temperatures affected water repellence in two ways. Firstly, heat drove off adsorbed water molecules and allowed orientation of the hydrophobic molecules on the sand grains so that their aliphatic chains were exposed. Heat also was involved in the distribution of hydrophobic molecules, and at 70°C, the hydrophobic molecules were able to move relatively large distances to cover the sand grains evenly.

However, the situation was more complex with natural soil organics. The organic matter extracted from a natural water repellent sand consisted of virtually undecomposed plant litter as well as humified material. Although C_{16} compounds such as cetyl alcohol are a significant component (Ma'shum *et al.*, 1988), the organic material is a mixture of hundreds of different compounds. When this mixture was added to an acid-washed sand, a temperature of 70°C did not induce repellence. The natural hydrophobic compounds were possibly trapped within particulate organic 'aggregates', and more severe treatments were required. A temperature of 105°C did induce an M.E.D. value of 1.3. This treatment presumably freed the hydrophobic compounds from the plant litter, and allowed them to spread throughout the sand. In situations where water repellence has been observed after a fire, this mechanism is probably responsible. However, this temperature is too high to explain the generation of water repellence in the absence of fire, as occurs throughout southern Australia.

2.4.2 Role of micro-organisms

Severe repellence was generated within three weeks by microbial activity at 100% RH and subsequent drying at 70°C. This level of repellence was similar to that of the initial natural water repellent sand. Therefore, micro-organisms appear to play a vital role in the induction of repellence. At 100% RH, the water content was approximately 0.6%. At this water content, fungi and actinomycetes were probably the most active microbes (Dommergues *et al.*, 1978; Kieft, 1991), and are therefore the most likely causes. Bond (1969b) concluded that basidiomycete fungi were responsible for the induction of water repellence in the south east of South Australia. Similarly, Scott and Van Wyk (1990) noted that in the absence of fire, water repellence only occurred where fungi were present. Chan (1992) described the development of water repellence under direct drilling, and concluded that repellence was associated with conspicuous fungal growth in the organic-rich surface soil.

Water repellence did not increase markedly when the sand was incubated at higher water contents. It appears that microbial communities active at the different water contents have vastly different effects on the generation of water repellence. This may help to explain why water repellence is more common in sandy soils. Because sandy soils have large pores, they drain very quickly after being wetted, and consequently dry out. However, the RH in a sandy soil only falls below 99% near wilting point (Hillel, 1980), and so sandy soils are frequently exposed to low water contents and high humidities, which generated water repellence in this experiment.

Although fungi and actinomycetes can synthesise hydrophobic compounds directly (Dinel *et al.* 1990), they may not be the direct cause of water repellence. It is possible that microbial activity reduces the quantity of water soluble organic compounds (as these are the most readily used as a food source), and leaves an excess of hydrophobic compounds. Normally, these polymethylene compounds may be 'tangled up' with the more polar compounds, and as discussed earlier, need high temperatures before they can coat the sand surfaces. However, after microbial activity and degradation of water soluble compounds, they may become free to coat the sand surfaces upon exposure to moderate temperatures. In this case, the development of natural water repellence would rely on microbial activity at high relative humidity and low water content, and moderately high temperatures. This agrees with the general observations of water repellence in the field. For example, King (1974) and Chan (1992) stated that water repellence was most severe after the first summer or autumn rains. At this time, the soil would have a low water content, high humidity, and temperatures at the soil surface would be sufficient to induce repellence.

This theory is supported in that microbial activity using water-soluble organic compounds alone did not generate significant water repellence (table 2.1). In other words, hydrophobic compounds must be present initially for water repellence to be induced by subsequent microbial action. However, different organic substrates would almost certainly favour different microbial communities. Further research is required to determine the role of fungi and actinomycetes in the development of natural water repellence.

2.5 Conclusions

In systems where a single compound is responsible for water repellence, moderate heat alone is sufficient to induce water repellence. However, in natural systems, microbial activity or high temperatures (> 100°C) are required for the generation of water repellence. Micro-organisms may directly synthesise the causal hydrophobic compounds, or alternatively they may degrade water soluble organic materials, and render the native hydrophobic compounds more readily distributed by subsequent moderate temperatures. Temperatures >100°C may act in a similar way, by liberating the hydrophobic organic compounds from a multi-compound organic 'aggregate'.

Sandy soils may be prone to the development of repellence at moderate temperatures because their water relations favour a specific microbial community, probably largely consisting of fungi or actinomycetes, or both.

The induction of water repellence appears to be a function of organic matter derived from plants, and microbial activity. In a sandy soil, organic matter acts as the major source of nutrient retention by cation exchange, and microbial activity is generally regarded as beneficial to plant growth. Therefore, arresting the development of water repellency in sandy soils by decreasing the organic inputs and the microbial activity of the soil is likely to render the soil less productive, and expose it to greater risk of erosion. Because of this, a cure for water repellence which does not rely on reducing organic carbon and microbial activity is essential.

CHAPTER 3. INTERACTIONS OF PALMITIC ACID AND CETYL ALCOHOL WITH CLAY MINERALS

3.1 Introduction

Ma'shum *et al.* (1988) extracted and characterised the compounds responsible for water repellence. They found that cetyl alcohol, palmitic acid (hexadecanoic acid – $C_{15}H_{31}COOH$) and long chain esters of palmitic acid were major components. Although these types of compounds have often been observed in soils (e.g. Dinel *et al.*, 1990), their interactions with soil components have not been extensively studied. These interactions are of particular interest because clay particles have been proposed as a potential ameliorant for water repellence in sandy soils (Ma'shum *et al.*, 1989).

Most studies of mineral/organic interactions have focussed on either aromatics, water soluble compounds, or compounds of biological interest (e.g. pesticides). However, recent advances in spectroscopic techniques (especially NMR and MS) have highlighted the importance of uncharged aliphatic and polymethylenic compounds (Hatcher *et al.*, 1981; Farmer and Pisaniello, 1985; Oades *et al.*, 1987; Krosshaven *et al.*, 1990). For example, Oades *et al.* (1987) found that nearly two thirds of the organic matter in the clay fraction of an alfisol was aliphatic. Although the interactions of aliphatic cations (e.g. alkylammonium) with clays have been investigated (Weiss, 1963), non-ionic aliphatic compounds have not been extensively studied, because the traditional extracts of humic acid, fulvic acid and humin indicated that soil organic matter was dominated by aromatic rather than aliphatic compounds.

Brindley and Ray (1964) and Brindley and Moll (1965) investigated the adsorption of aliphatic alcohols and carboxylic acids with carbon chain lengths up to 18 carbon atoms in the interlayer spaces of Ca^{2+}-montmorillonite. For both types of compound, interlayer complexes were only formed under very specialised conditions. The longer chain alcohols formed complexes consistent with the carbon chain extended at an angle of about 70° to the clay surface. Similar complexes were formed with long chain acids, but only at temperatures above the melting point of the free acid. According to their calculations, and Weiss (1963), a monolayer of long chain aliphatics should contain 7.74 µmol m^{-2}.

However, several studies have found that interlayer complexes are not common in soils. For example, Theng *et al.* (1986) concluded that most soil organic matter was confined to the external surfaces of clay micro-aggregates. Similarly, Greenland (1963), Parfitt and Greenland (1970), and Ben-Hur *et al.* (1992) showed that the aliphatic polymers PVA and PAM were adsorbed primarily on external surfaces of clay tactoids.

Hedges (1977) measured adsorption of stearic acid ($CH_3(CH_2)_{16}COOH$) onto kaolinite and montmorillonite from water, up to a maximum concentration of 1 mg l^{-1}. Kaolinite adsorbed much more than montmorillonite on a surface area basis, and both followed linear isotherms. He concluded that stearic acid was not actually adsorbed by the clays, but precipitated on the clays because of the low solubility of stearic acid in water. Sansone *et al.* (1987) described similar results for the adsorption of stearic acid onto marine sediments, using similar concentrations to those used by Hedges (1977). However, the maximum adsorption measured in the above studies was about 0.02 µmol m^{-2}, which is much less than the coverage required to form a monolayer.

In this study, the adsorption and desorption of cetyl alcohol and palmitic acid (both straight chain saturated C_{16} compounds) on sodium and calcium saturated montmorillonite and kaolinite was investigated. A non-polar organic solvent (hexane) was used, to determine adsorption at relatively high concentrations. Adsorption isotherms were measured using ^{14}C labelled compounds.

3.2 Materials and Methods

3.2.1 Clays

The <2 µm fraction was separated from the Kent Sand kaolinite (from the pallid zone of a laterite at Rocky Gully, in the south west of Western Australia; Muljadi *et al.* 1966), the Redhill montmorillonite (Fullers Earth Union Ltd., Surrey; Ma'shum *et al.*

1989) and Mundulla clays (B horizon of a water repellent soil; Ma'shum *et al.* 1989) by sedimentation from reverse osmosis (RO) water. X-Ray Diffraction showed that the montmorillonite was free from impurities, and the kaolinite contained a small amount of gibbsite. The Mundulla clay was mainly kaolinite with some illite. Na^+- and Ca^{2+}-saturated forms were prepared by washing the clay three times with the appropriate M chloride solutions. Ca^{2+} clays were washed with RO water (<5 μS cm^{-1}) and centrifuged five times, and then freeze dried. Na^+ clays were washed once with RO water, dialysed against RO water until free from salt, and then freeze dried. The surface areas of these clays (and other clays used in this thesis) were measured by nitrogen adsorption and application of the BET equation (Brunauer *et al.*, 1938), and are given in table 3.1.

Clay	Na^+-saturated (m^2 g^{-1})	Ca^{2+}-saturated (m^2 g^{-1})
Redhill montmorillonite[a]	107	98
Blackpool kaolinite[b]	12	12
Kent kaolinite[b]	42	42
Mundulla kaolinite[a]	159	150

Table 3.1 *Surface areas of clays as measured by nitrogen adsorption*

[a] - Ma'shum *et al.*, 1989

[b] - A.G. Waters, personal communication

3.2.2 Organic compounds

Cetyl alcohol (LR grade) was obtained from B.D.H., and palmitic acid (LR grade) from Ajax. 1-^{14}C cetyl alcohol and U-^{14}C palmitic acid were obtained from Amersham. All chemicals were used as supplied.

3.2.3 Adsorption

Solutions of the unlabelled compounds were prepared in *iso*-propanol with concentrations ranging from 0.7 to 30 mM. ^{14}C compounds were added to *iso*-propanol to generate an activity of 9.25 kBq ml^{-1}. Clay suspensions were prepared in *iso*-propanol to contain 25 g l^{-1} Mundulla kaolinite, 50 g l^{-1} montmorillonite or 75 g l^{-1} Kent kaolinite, so that each suspension contained approximately equal clay surface areas. Glass scintillation vials were used for adsorption. Each 20 ml vial received 15 ml unlabelled cetyl alcohol or palmitic acid solution, 1 ml labelled solution and 4 ml clay suspension. Vials were shaken for 24 hours, evaporated to dryness in a fume hood, heated to 70°C for 24 hours, and left to equilibrate at 20°C for 24 hours. These treatments were necessary to generate measurable adsorption. Hexane (20 ml) was added to each vial and shaken for two hours to dissolve the free organic compounds. The hexane extract (1 ml) was added to 10 ml Amersham Phase Combining Solution in a plastic scintillation vial, and the concentration of free (unadsorbed) cetyl alcohol or palmitic acid was measured by scintillation in a Beckman scintillation counter LS 3801. Results were compared with measurements from glass vials treated without clay (no adsorption) to determine the quantity of cetyl alcohol or palmitic acid adsorbed. There were three replicates for the adsorption of cetyl alcohol, and two replicates for palmitic acid.

Another two vials of montmorillonite clay were prepared at the highest concentrations of cetyl alcohol and palmitic acid as described above, except that the ^{14}C label was not applied. These samples were examined by XRD to determine the extent of interlayer adsorption.

3.2.4 Desorption

Supernatant was decanted from samples of Kent kaolinite and Redhill montmorillonite exposed to the highest concentration of aliphatics, and the amount of liquid remaining in the vial was determined by weighing before and after drying. AR grade hexane (20 ml) was added and the vials were shaken end over end for ten minutes, as preliminary experiments indicated that further shaking did not increase the amount of desorption. After the clay had settled (about ten minutes), a 1 ml aliquot was removed to determine the concentration of cetyl alcohol or palmitic acid as described above. The amount of aliphatic compound desorbed was calculated allowing for the quantity retained after decanting the supernatant. This process was repeated four times with each sample.

3.3 Results

3.3.1 Adsorption

Both cetyl alcohol and palmitic acid adsorbed onto all clays with L-type isotherms (Giles *et al.*, 1960). The isotherms are shown in figures 3.1 and 3.2. Adsorption per square metre of clay surface (measured by nitrogen adsorption to exclude interlayer surfaces) was very similar for the different clay minerals and saturating cations, and reached a maximum of approximately 3 μmol m^{-2}. This suggests that interlayer adsorption of aliphatics by montmorillonite did not occur to a significant degree and was supported by XRD measurements, which showed no evidence of expanded interlayers.

Ca^{2+}-saturated kaolinite and montmorillonite both adsorbed more cetyl alcohol and palmitic acid than the Na^{+}- saturated forms. However, this effect was only extreme in the montmorillonite/palmitic acid case, where Ca^{2+}-saturated montmorillonite was very efficient in adsorbing palmitic acid at low concentrations.

3.3.2 Desorption

Palmitic acid was adsorbed more strongly than cetyl alcohol by all the clays (table 3.2). After four washes with hexane, over two thirds of the initially adsorbed palmitic acid remained on all clay types, whereas only half of the adsorbed cetyl alcohol was retained by Na^{+}-montmorillonite, and less for the other clays. There was little difference between the clays, except that Na^{+}-saturated montmorillonite tended to retain more aliphatic material than other clays, suggesting that a little interlayer adsorption may have occurred. Close to three quarters of the total desorbed cetyl alcohol and palmitic acid was removed in the first two washes with hexane, indicating that there were at least two different adsorption sites on the clays.

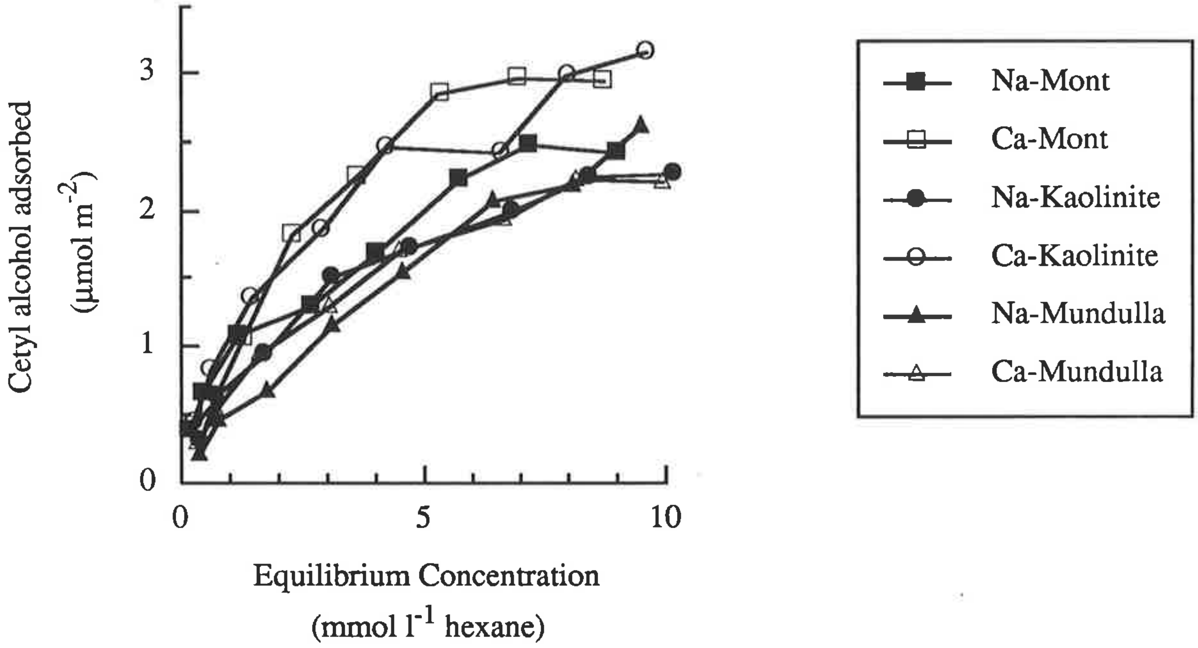


Figure 3.1. *Adsorption isotherm of cetyl alcohol on clays.*

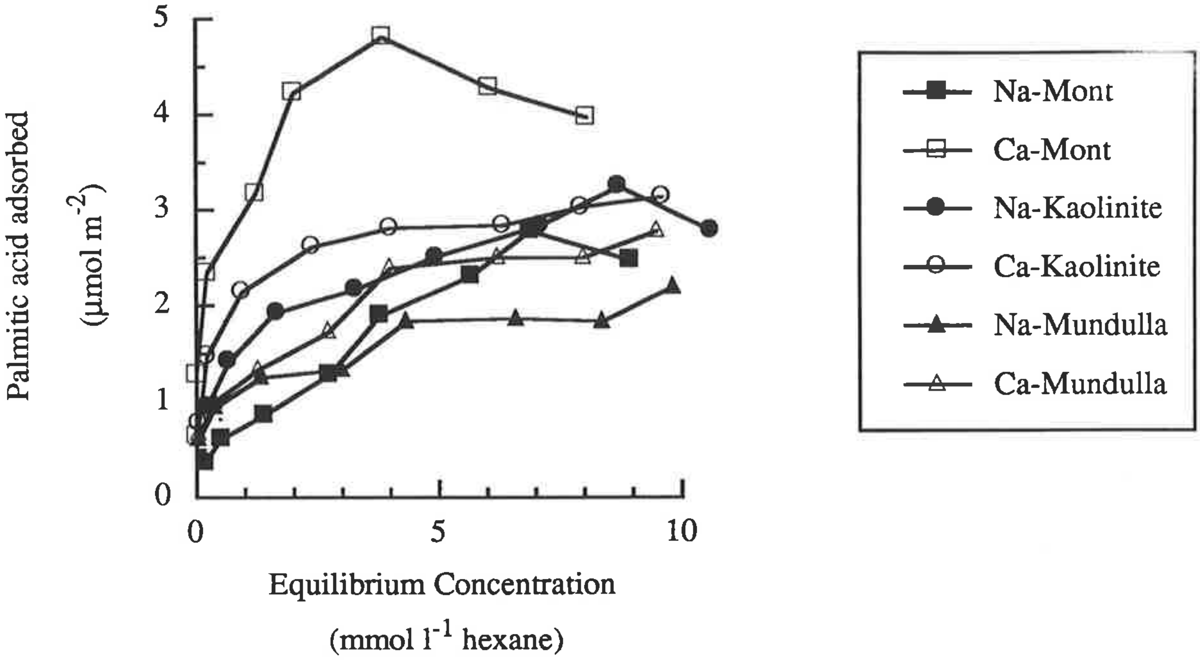


Figure 3.2. *Adsorption isotherm of palmitic acid on clays.*

Clay	Washings	CA desorbed (%)	PA desorbed (%)
Ca-Kaolin	1	47.2	12.2
Ca-Kaolin	2	15.0	5.7
Ca-Kaolin	3	7.0	2.7
Ca-Kaolin	4	4.1	3.0
Ca-Mont	1	39.2	10.4
Ca-Mont	2	16.9	7.0
Ca-Mont	3	9.8	4.0
Ca-Mont	4	6.0	2.5
Na-Kaolin	1	46.1	16.7
Na-Kaolin	2	13.9	10.1
Na-Kaolin	3	6.2	5.1
Na-Kaolin	4	3.4	3.1
Na-Mont	1	25.6	5.6
Na-Mont	2	11.8	3.8
Na-Mont	3	5.7	3.7
Na-Mont	4	4.0	1.8

Table 3.2. *Percentage of originally adsorbed cetyl alcohol (CA) and palmitic acid (PA) desorbed from clays by washing with hexane.*

3.4 Discussion

Total adsorption of aliphatics by both montmorillonite and kaolinite was similar when expressed in terms of external clay surface area. This, and the XRD results, suggest that interlayer adsorption in the montmorillonite did not occur to a large extent, which is not surprising given the non-polar nature of the solvents used. Theng *et al.* (1986) also observed that polymethylene materials in soils were mostly confined to external surfaces. Brindley and Ray (1964) and Brindley and Moll (1965) were able to demonstrate interlayer adsorption of palmitic acid and cetyl alcohol respectively on Ca^{2+}-saturated montmorillonite, but only after treatment with other compounds to 'prop open' the interlayers, and with careful temperature control.

There is a distinct plateau on the adsorption isotherms at about 3 μmol m^{-2}. Previously calculated values for monolayers of aliphatics adsorbed onto clays (Weiss, 1963; Brindley and Moll, 1965) give values of about 7.7 μmol m^{-2}. However, these values were calculated assuming close packing of carbon chains extended at about 70° to the clay surface, based on XRD measurements of interlayer expansion. Theng *et al.* (1986) concluded that polymethylene compounds in soils were adsorbed parallel to the clay surface, and Derjaguin *et al.* (1992) showed cetyl alcohol adsorbed parallel to a silica surface. The close-packed longitudinal cross-sectional area of palmitic acid and cetyl alcohol molecules is approximately 110 $Å^2$, which equates to a monolayer of about 1.5 μmol m^{-2}. Therefore, the observed adsorption plateau at 3 μmol m^{-2} agrees closely with a bilayer of adsorbed molecules oriented with the carbon chain parallel to the clay surface. However, this could also be due to adsorption of a single layer of molecules with their carbon chains extended at a low angle to the clay surface (Weiss, 1963).

Brindley *et al.* (1963) and Hedges (1977) measured greater adsorption by kaolinite than montmorillonite on a surface area basis for water soluble uncharged aliphatics and stearic acid respectively. Brindley *et al.* (1963) concluded that the OH-surface of one face of kaolinite was a better adsorbent than the O-surface of montmorillonite particles. However, in this study, there was no difference between kaolinite and montmorillonite in their adsorption of cetyl alcohol and palmitic acid. This may be due to the drying phase incorporated in the adsorption procedure. Drying allowed the aliphatic molecules to interact with the clay particles in the absence of a competing solvent, and this must affect the adsorption process (Nayak *et al.*, 1990; Varadachari *et al.*, 1991). Because drying occurs under natural conditions, these interactions may also be important in real soils.

In soils, aliphatics tend to be closely associated with clay minerals, but how they are brought into contact is still unknown. Although appreciable quantities of aliphatic compounds were adsorbed by the clays in this experiment, relatively complex pre-treatments with organic solvents and heat were required. The use of *iso*-propanol and hexane, in particular, is not likely to have a natural parallel! However, heating to 70°C is possible in nature, especially close to the soil surface, and therefore relatively high temperatures may be involved in the interaction of aliphatic compounds and clay minerals.

In chapter 2, the relationship between temperature and the mobility of pure cetyl alcohol was investigated, and temperatures greater that 50°C (the melting point of cetyl alcohol) were shown to allow the compound to spread throughout the sand matrix. However, in natural organic matter, compounds such as cetyl alcohol and palmitic acid appeared to be trapped by less volatile organic matter, and temperatures greater than 70°C were required to initiate movement. Therefore, in soils, pure aliphatics would rarely be able to interact directly with the inorganic soil fraction. For this reason, the study of the interaction of pure aliphatic compounds with clays may be of limited use in terms of understanding the processes involved in natural systems. However, there is no doubt that polymethylene compounds do interact with clay particles in natural soils (Theng *et al.*, 1986), and these interactions need to be investigated. A study of pure compounds appears to be a reasonable starting point.

The desorption experiment showed that about half the cetyl alcohol, and 10-20% of the palmitic acid was readily desorbed, but the remaining aliphatic material was more strongly held. If adsorption occurred as a bilayer with the carbon chain oriented parallel to the clay surface, the desorbed cetyl alcohol was probably the second adsorbed layer, which would be weakly held by hydrophobic interactive forces. The palmitic acid was less susceptible to desorption in hexane because it is slightly more polar, and therefore less soluble in hexane. In soils, desorption in hexane is not a common occurrence. Therefore, a bilayer of aliphatic compounds on the external surfaces of soil clay domains can be expected in dry soils.

Ma'shum *et al.* (1988) showed that water repellence in sandy soils was caused by compounds similar to cetyl alcohol and palmitic acid. These results suggest that the amelioration of water repellence by clay application should be related to the available (external) surface area of the clay applied. All clays adsorbed similar quantities of aliphatic material per unit surface area, and so clays with high available surface areas regardless of mineralogy should be effective in reducing repellence.

3.5 Conclusions

Adsorption of cetyl alcohol and palmitic acid was dependent on the external surface area of the clays. There was no evidence of interlayer adsorption by montmorillonite or kaolinite. Ca^{2+}-saturated clays appeared to adsorb slightly more than Na^{+}-saturated clays. The quantity adsorbed for all clays agreed closely with calculations for a close packed bilayer adsorbed with the carbon chains parallel to the clay surface. Desorption studies showed that at least the first layer of cetyl alcohol or palmitic acid was strongly held by the clay.

The implication for water repellence is that clays with the highest specific surface area should be the most effective in reducing repellence, if clays act by adsorbing the hydrophobic materials.

CHAPTER 4. CLAY ADDITIONS TO A MODEL WATER REPELLENT SAND

4.1 Introduction

Addition of fine particles (e.g. clays) has been shown to reduce repellence in water repellent sands (Roberts, 1966; Bond, 1978; Ma'shum *et al.*, 1989), but the mechanism responsible for this reduction is not known. One explanation is a 'dilution' of the hydrophobic compounds over the high surface area provided by the fine particles. Addition of small amounts of clay to a sandy soil can dramatically increase the surface area available for adsorption, with the result that when clays and sands interact, the hydrophobic organic materials become spread so thinly that repellence is reduced. This theory, however, appears not to apply universally because the efficacy of clays applied to a water repellent sand is not always related to their external surface areas. Ma'shum *et al.* (1989), using a 'model' water repellent sand prepared from acid-washed sand and cetyl alcohol, showed that a low surface area kaolinite was significantly more effective than a higher surface area montmorillonite.

Ma'shum *et al.* (1989) concluded that clay dispersibility was the major factor influencing the efficiency of clays in reducing water repellence, because clays which easily disperse expose a greater available surface area. Kaolinite and illite were more effective because they may be more easily dispersed, due to their blocky geometry (Oades, 1986). However, Velasco-Molina *et al.* (1971) found that in the absence of electrolyte, montmorillonite was more dispersive than kaolinite and halloysite for any given exchangeable sodium percentage, and Ali *et al.* (1987) concluded that kaolinite, clay mica, montmorillonite, and vermiculite clay minerals dispersed equally from arid soil aggregates. The apparent discrepancies in clay dispersibility and the role of available surface area therefore require further attention.

Wetting and drying occurs naturally in the field, and is likely to affect the interactions of clay particles with sand grains. Wetting will allow clay particles to disperse throughout the sand matrix, and drying forces clays into intimate contact with sand grains (Kemper *et al.*, 1974). However, these processes have not been studied for clay additions to water repellent sands. Similarly, clay application in a farm situation will be expensive, and will only be economical if the effects are long term. The leaching of clays through sandy soils therefore should also be investigated. If clays are rapidly washed through water repellent sands, their effects will only be temporary. Anecdotal evidence (C. Obst, personal communication) suggests that clays remain in the top 10 cm for over 20 years, but this has not been studied scientifically.

4.2 Materials and Methods

4.2.1 Sands

A water repellent sand (called *model* sand) was prepared from acid-washed sand (May and Baker) and cetyl alcohol ($C_{16}H_{33}OH$; BDH) using the procedure described in section 2.2.2, and also by Ma'shum *et al.* (1989). The sand was oven dried (105°C) before use. This produced a sand with an M.E.D. value of 4.5.

4.2.2 Clays

Clays used were Na^+- and Ca^{2+}-saturated forms of the Blackpool kaolinite (English Clays, Lovering; Oades, 1984), Redhill montmorillonite, and Mundulla clay, all prepared as described previously (section 3.2.1).

4.2.3 Clay application

Duplicate samples of air-dry *model* water repellent sand (20.0 g) was placed in a glass vial, and the relevant clay (0.100 g) was added. This corrresponded to an application rate of 0.5%, as used by Ma'shum *et al.* (1989). The vials were gently shaken end-over-end (13 rpm) for 2 minutes to mix the clay with the sand. The mixtures were oven dried at 105°C and then cooled in a desiccator over silica gel before M.E.D. values were measured at 20°C. Oven drying at 105°C allowed maximum expression of water repellence (see chapter 2).

4.2.4 Wetting/drying cycle

Clays were added and mixed as described above. RO water (9 ml) was added to each vial. The sand was wetted by placing the vials in a vacuum desiccator, evacuating and allowing air to rapidly re-enter the desiccator. This technique wetted the sand with minimal disturbance (Ma'shum and Farmer, 1985). The vials were then oven dried at 105°C, cooled, and M.E.D. values were measured at 20°C.

4.2.5 Clay transport through sand columns

Clays (Na^+- or Ca^{2+}-saturated Redhill montmorillonite or Blackpool kaolinite) were applied to either clean acid-washed sand or *model* water repellent sand either mixed with the sand, added to the surface of the sand, or poured on as a suspension. Dry mix samples were prepared by adding 0.5 g clay to 100 g acid-washed or *model* sand, and shaking end over end for two minutes. Glass columns (19 mm internal diameter) were treated with a silicone solution to render them hydrophobic, and sealed at one end with a piece of cotton gauze. Acid-washed sand or *model* water repellent sand (100 g + dry mix clay where appropriate) was poured in. Surface clays were then applied to the appropriate columns, and clays to be applied as suspension were placed in a 250 ml volumetric flask. For each column, water was added to a 250 ml volumetric flask, shaken to suspend clay where necessary, and the flask was inverted over the column to maintain a constant head of about 10 mm. Infiltration was allowed to proceed until the volumetric flask was empty (about 7 pore volumes), and the time taken was recorded. The leachate was collected in a conical flask, and transferred to a measuring cylinder to measure the volume collected. The clay content of the leachate was measured by evaporating a 20 ml aliquot in a pre-weighed vial.

4.3 Results

4.3.1 Wetting and drying

Clay applied as a dry mix to *model* water repellent sand had no significant effect on water repellence as measured by the M.E.D. value. After a wetting and drying cycle, however, all clays significantly reduced repellence (Fig. 4.1). The montmorillonite and Mundulla clays proved to be particularly effective, but the low surface area Blackpool kaolinite clays were not as efficient. Exchangeable cation had little effect.

4.3.2 Clay transport

In general, Na^+-saturated clays were much more mobile than Ca^{2+}-saturated clays (Table 4.1). Clays applied as a suspension were the most easily leached from the sand, and surface applied clays were also readily transported. However, clays applied as a dry mix appeared to be held more tightly by the sand matrix. Trends in clay transport were the same for both wettable and repellent sands, although there was a slight but significant decrease in transport associated with the addition of cetyl alcohol to the acid-washed sand.

	Wettable sand			*Model* sand		
Clay	Surface	Susp.[c]	Dry Mix	Surface	Susp.	Dry Mix
Na-R[a]	59.9	79.3	10.9	51.4	73.4	4.9
Ca-R	0.2	0.3	0.0	0.0	0.0	0.0
Na-B[b]	53.4	72.6	2.7	44.2	67.5	0.0
Ca-B	1.0	11.5	1.7	0.0	10.4	0.1

Table 4.1. *Effect of method of application on percentage of added clay recovered in the leachate from a column of wettable or* model *water repellent sand.*

[a] - *Redhill montmorillonite.* [b] - *Blackpool kaolinite*

[c] - *Clay added as suspension*

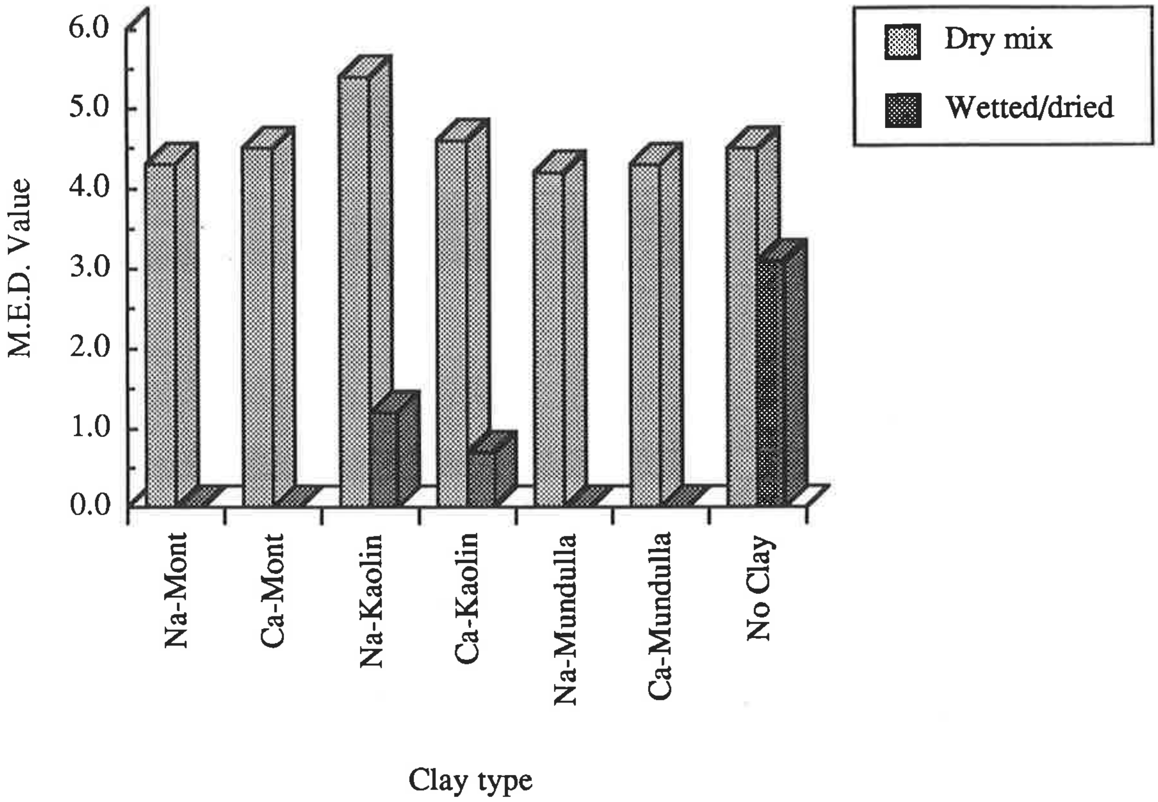


Figure 4.1. *Effect of various clays and a wetting and drying cycle on water repellence in cetyl alcohol-treated acid-washed sand. The Tukey-Kramer least significant difference (LSD) values were 0.87 and 0.80 for dry mix and wetted/dried treatments respectively.*

There was only a small effect of water repellence on flow rate through the sand column, and clays did not increase the flow rate (results not shown). Clays were ineffective because the sand/clay system had not been exposed to wetting and drying before infiltration. However, repellence itself did not markedly affect infiltration rate. After a short initial delay (approximately 2 minutes), infiltration proceeded at the same rate as in the wettable sand.

4.4 Discussion

For *model* water repellent sands, clay application had virtually no effect on water repellence until the sand was exposed to a wetting and drying cycle, after which significant reductions in repellence were observed. These results contradict the work of Ma'shum *et al.* (1989), who found that mixing clay with dry sand was effective in reducing repellence in *model* water repellent sands. In their work, the rate of 0.5% clay addition, as used here, rendered illite- and kaolinite-model sand mixtures completely wettable (M.E.D. value 0.0) without any wetting and drying. Despite several experimental attempts and correspondence with the author, the reasons for this discrepancy could not be determined.

The amelioration of cetyl alcohol-induced repellence by clays was related to the external surface area of the applied clay. Montmorillonite and Mundulla clays, with surface areas of approximately 100 and 150 $m^2\ g^{-1}$ respectively, left the *model* sand completely wettable. Blackpool kaolinite clay, with a surface area of only 12 $m^2\ g^{-1}$, left the sand with an M.E.D. value of about one. The higher the surface area of the clay, the more scope there is for dilution of the hydrophobic molecules in the soil. Under the conditions of this experiment, the total surface area of sand (20.0 g) was approximately 0.23 m^2 (assuming spheres of average diameter 0.2 mm), and the surface area of clay added (0.100 g) was approximately 1.2, 10.0 and 15.0 m^2 for kaolinite, montmorillonite and Mundulla clay respectively. Therefore, the surface area of clay added far exceeded the original surface area of the sand for montmorillonite and Mundulla clays, but was similar for the Blackpool kaolinite. Before clay addition, there was the equivalent of about 40 monolayers of cetyl alcohol on the sand surfaces, but less than one monolayer after the addition of the Mundulla clay. Clay dispersibility, as influenced by saturating cation, did not appear to affect the reduction in water repellence.

Clay transport through the sand was reduced by mixing the clay with the sand. In situations where the infiltrating water dispersed and suspended the clay before entering the sand matrix (i.e. surface and suspension applied clay), it carried the clay particles through the sand. However, if the clay particles were previously mixed with the dry sand, water flowing through the pores was not able to dislodge them, and they remained in the sand. Also, cetyl alcohol appeared to trap a small amount of clay, and therefore hydrophobic compounds may act as a bridge between sand and clay. Ma'shum (1988) also noted this effect. However, the 'hydrophobic bridge' appears to have at best a small effect on clay movement. Mixing clay with the sand will significantly reduce clay leaching in field soils, and so clay application to a water repellent soil should act to reduce repellence for a period of several years. It should be pointed out that the sand columns were exposed to the leaching power of approximately two years' rainfall in about 30 minutes. In the field, clay applied to the surface of a water repellent soil may be washed into the soil by rainfall, but when the soil dries out, a 'dry mix' situation is created, which will prevent further leaching losses.

The maintenance of a 10 mm water head reduced the effects of repellence on water infiltration. This has implications in the field, in that rainfall can be collected in furrows created by press wheels. A small ridge across the furrow can be easily created by putting a small dent in the rim of the press wheel, and this 'dams' the water in the furrow, allowing infiltration to proceed. However, the problem of uneven soil wetting will persist, and application of clay has the potential to overcome this.

4.5 Conclusions

A wetting and drying cycle was required before the application of clay had any effect on *model* water repellence. Wetting helped to distribute clays evenly, and surface tension forces during drying brought the clay particles and sand grains into intimate contact. After a wetting and drying cycle, high external surface area clays were more effective than low surface area clays. The greater surface allowed more of a ‘dilution’ of the hydrophobic compounds. Clay transport through a sand was reduced by first mixing the clay evenly with the sand. If this can be easily accomplished in the field, clay application should remain active in reducing water repellence for several years.

CHAPTER 5. CLAY ADDITIONS TO A NATURAL WATER REPELLENT SAND

5.1 Introduction

In the previous chapter, high surface area clays were shown to be more effective in reducing *model* water repellence than low surface area clays. A wetting and drying treatment was required before any effects could be observed. Wetting and drying also increased the retention of clay in the sand. However, although cetyl alcohol is a constituent of waxes isolated from water repellent sands, several differences between cetyl alcohol and natural organic materials in terms of their behaviour in sands have already been discussed (Chapter 2). It is important therefore to determine the effects of various clays in reducing water repellence of sands from the field.

The mechanism of the clay-induced reduction of water repellence also needs to be investigated. Hydrophobic materials may be adsorbed preferentially by the added clays, leaving the sand grains (i.e. most of the soil volume) wettable. In this case, the clays that adsorbed the greatest quantity of hydrophobic compounds would be the most effective in reducing water repellence. This would depend on the surface properties of the clay minerals, and may explain why kaolinite clays are more effective than montmorillonite (Ma'shum *et al.*, 1989). Alternatively, the clay particles may spread over the organic-coated sand grains, masking the hydrophobic sand surface and exposing a hydrophilic clay surface. This hypothesis requires that the clay particles interact more strongly with the organic/sand surface than with each other, and would be a function of both the surface properties and available surface area of the clays.

This investigation aimed to compare the effects of clays on a natural water repellent sand with the model cetyl alcohol system proposed by Ma'shum *et al.* (1989) and discussed in Chapter 4, and also with another artificial sand prepared from natural organic matter extracted from a water repellent sand. For each sand, clay mineralogy, exchangeable cation, and the influence of a wetting and drying cycle on repellence and clay retention were studied. The possible mechanisms of clay interaction with the sand were investigated.

5.2 Materials and Methods

5.2.1 Sands and clays

The Western Flat natural water repellent sand and cetyl alcohol *model* sand have been described previously (section 2.2.2). The Badgingarra sand was collected from near Geraldton, north of Perth, Western Australia. Another water repellent sand (called *artificial* sand) was prepared from natural hydrophobic materials extracted from the Western Flat sand, and subsequently added to an acid-washed sand. Hydrophobic compounds were extracted in a Soxhlet apparatus with a mixture of *iso*-propanol and ammonia solution (7:3 v:v) (Ma'shum *et al.*, 1989). The methanol soluble portion of this extract contains most of the hydrophobic compounds (C.M. Franco, personal communication), and this was obtained by repeated washing with methanol and filtering. The extract was then applied to an acid-washed sand at the rate of 0.10%. The sand was subsequently washed twice with reverse osmosis (RO) water to remove water soluble compounds, and finally oven dried (105°C).

Clays used were Na^+ and Ca^{2+} forms of the Blackpool kaolinite, Redhill montmorillonite, and Mundulla clay, all as described previously (section 3.2.1). To study the effects of clay surface charge on repellence, samples of the Redhill montmorillonite and Blackpool kaolinite (<2 µm fractions) were washed with 1 M LiCl solution three times, and then rinsed with ethanol four times. The clays were subsequently freeze dried, and heated at either 250°C (montmorillonite) or 130 °C (kaolinite) for 24 hours. This procedure created charge-reduced clays by incorporating Li^+ ions into the clay lattice, in what is called the Hofmann-Klemen effect (Hofmann and Klemen, 1950; Jaynes and Bigham, 1987; Pennell *et al.*, 1991). Jaynes and Bigham (1987) showed that the montmorillonite charge (CEC) was reduced by 90-95%, and Pennell *et al.* (1991) measured a 50% reduction in kaolinite charge.

The <2 µm fractions of the Tumut illite (Mackintosh, 1969) and a commercial gibbsite sample (supplied by Merck) were obtained by sedimentation, concentrated by rotary evaporation, and finally freeze dried. These clays were also assessed for their effects on water repellence.

5.2.2 Clay application

Clays were mixed with the natural water repellent sand using the procedure described in section 4.2.3.

5.2.3 Wetting/drying cycle

Clay/sand mixtures were wetted and dried as described previously (section 4.2.4).

5.2.4 Clay retention

The retention of Na^+- and Ca^{2+}- saturated Redhill montmorillonite and Blackpool kaolinite by ignited (wettable) and normal Western Flat sand was investigated using the procedure described in section 4.2.5, except that the 'suspended clay' application treatment was not included. For the natural water repellent sand, the effect of a drying cycle on clay retention was also studied. Clays were mixed with the sands and wetted either in the glass column or in a beaker. The wetted glass columns were dried for 2 weeks at 70°C, and the leaching studies were performed on the undisturbed dry sands. Sands wetted in beakers were dried at 70°C for 24 hours, gently stirred to crush any aggregates, and poured into a glass column for measurement of the leaching of clay.

Clay loss by leaching in the field over an extended period was also assessed. A water repellent sand from Mundulla in the south east of South Australia was exposed to a large but unmeasured amount of clay (100-200 t ha^{-1}) applied *c.*1968 to the top 5 cm. The sand was sampled in April 1990 at 5 cm intervals, and clay contents were measured by sedimentation after removal of organic matter by peroxide treatment.

5.2.5 Adsorption of extracted hydrophobic compounds by clays

The methanol soluble portion of the *iso*-propanol/ammonia extract was dissolved in methanol (2.5 g l^{-1}). The appropriate clay (0.100 g) was placed in a vial and the methanol solution (8 ml) was added. Each vial was shaken end over end for 16 h. Contents of the vials were transferred to centrifuge tubes and centrifuged at 940 g for 5 min. The supernatant from each centrifuge tube was poured onto acid-washed sand (20.0 g) in a glass vial, and the methanol was allowed to evaporate before further drying at 70°C. To remove water soluble organic compounds, the sand was washed twice with RO water (20 ml), as described for the preparation of the *artificial* water repellent sand. Sands were then oven dried (105°C), and M.E.D values were measured at 20°C. A low M.E.D. value indicated that hydrophobic compounds were adsorbed by the clay, and not transferred to the sand. The complex mixture of compounds contained in the organic extract simulated natural soil conditions, where there is competition for the adsorption sites on the clay surface.

5.2.6 Separation of clays from sand

If added clays reduced water repellence by adsorbing the causal compounds, subsequent separation of the clay from the sand should also remove the hydrophobic compounds, leaving the sand wettable. If the clays acted by covering the sand surface, clay separation may not remove the causal compounds, leaving the sand repellent. Clays (0.100 g) were added to either natural or *artificial* water repellent sand (20.0 g) and wetted and dried using the procedure described above. M.E.D. values were determined on all samples. The sand/clay mixtures were then stirred with RO water (100 ml), sonified with a Branson Sonifier 250 (80% power) for one minute, and the supernatant decanted through a 53 µm sieve to separate sand from clay. Material remaining on the sieve was returned to the sand, which was oven dried (105°C) and M.E.D. values were measured at 20°C. Clay recovery in the supernatant was measured after oven drying (105°C) and heating at 600°C to remove organic matter.

5.2.7 Distribution of clays in sand

Clays were added to water repellent sands which were wetted and dried as described above. Samples were then examined with a scanning electron microscope (Cambridge S250 Mk.3) to observe the distribution of clay within the sand.

5.2.8 Effect of clay addition on soil organic matter

Solid-state ^{13}C CP/MAS NMR (^{13}C Cross-Polarisation/Magic Angle Spinning Nuclear Magnetic Resonance) and DRIFT (Diffuse Reflectance Infra-red Fourier Transform) spectra of samples of the Keith water repellent sand with clay added 2 years previously were obtained. These spectra were compared with spectra from samples of the same sand without clay or with clay added (and wetted and dried) one week previously and subsequently kept air dry . ^{13}C NMR spectra were collected at 50.309 MHz on a Varian Unity 200 with wide-bore Oxford magnet and 7 mm Doty probe. Samples were packed into zirconia rotors with Kel-F caps and spun at 5000 Hz. For the IR spectra, samples were poured into 10 mm diameter stainless steel cups, and the top surfaces were levelled. Mid-infrared spectra were recorded and signal-averaged over 64 scans on a Bio-Rad FTS-80 FT-IR spectrometer using a high-intensity ceramic water cooled source, a wide-band mercury-cadmium telluride liquid nitrogen-cooled detector, and an off-axis DRIFT accessory (Harrick DRA-3SO). The full spectral data range covered the frequency region from 4000-450 cm^{-1}, at a resolution of 4 cm^{-1} and a sampling interval of 1.92 cm^{-1}.

5.3 Results

5.3.1 Effects of clays on repellence

Natural sand and *artificial* sand treated with extracted organics behaved similarly to the *model* sand when treated with clays without wetting and drying – there was effectively no reduction of repellence as measured by the M.E.D. value. However,

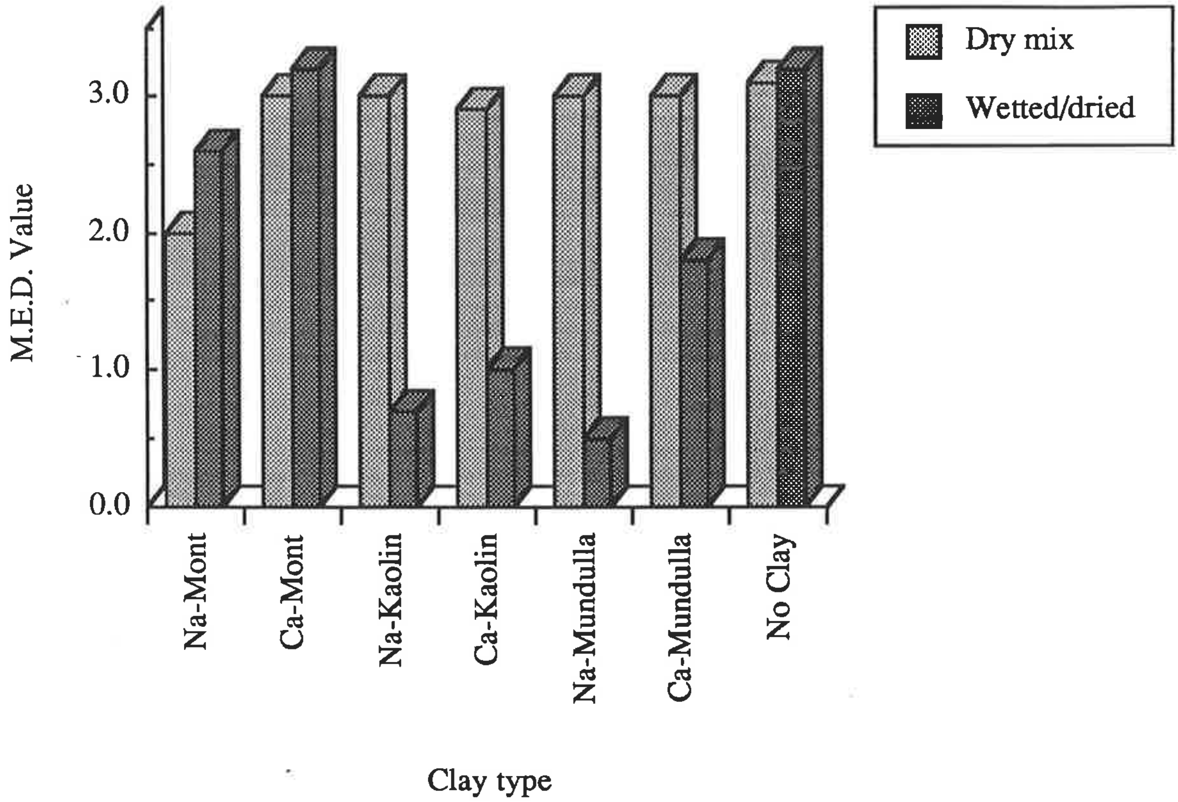


Figure 5.1. *Effect of various clays and a wetting and drying cycle on water repellence in Western Flat soil. The Tukey-Kramer LSD values were 0.30 and 0.62 for dry mix and wetted/dried treatments respectively.*

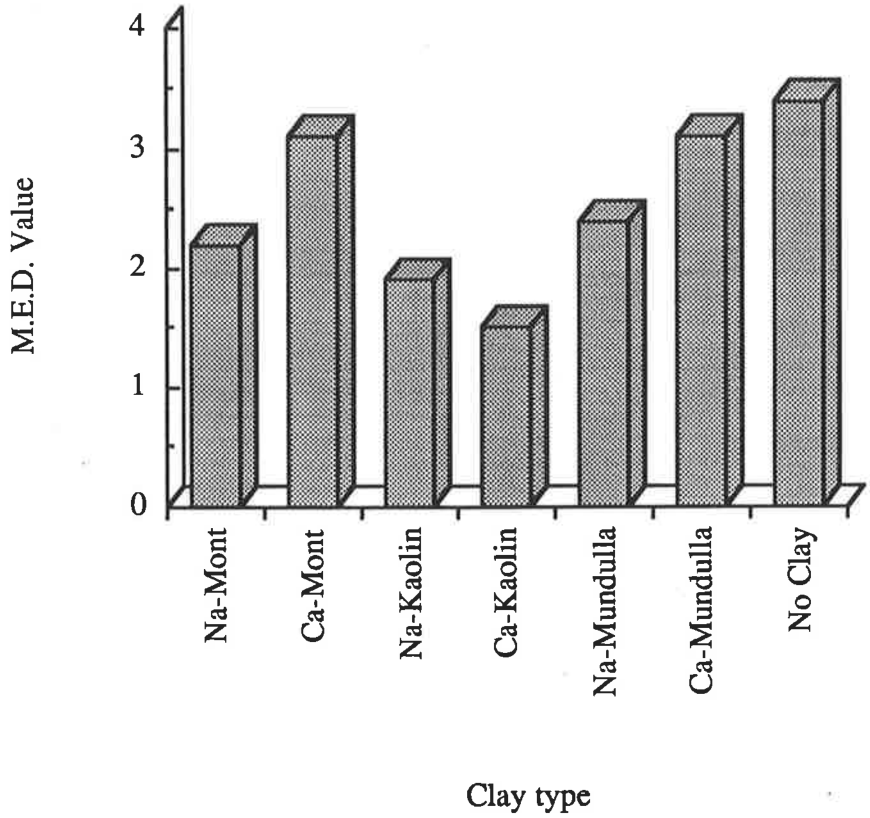


Figure 5.2. *Effect of various clays after a wetting and drying cycle on water repellence in artificial sand treated with extracted organics. The Tukey-Kramer LSD value was 0.64.*

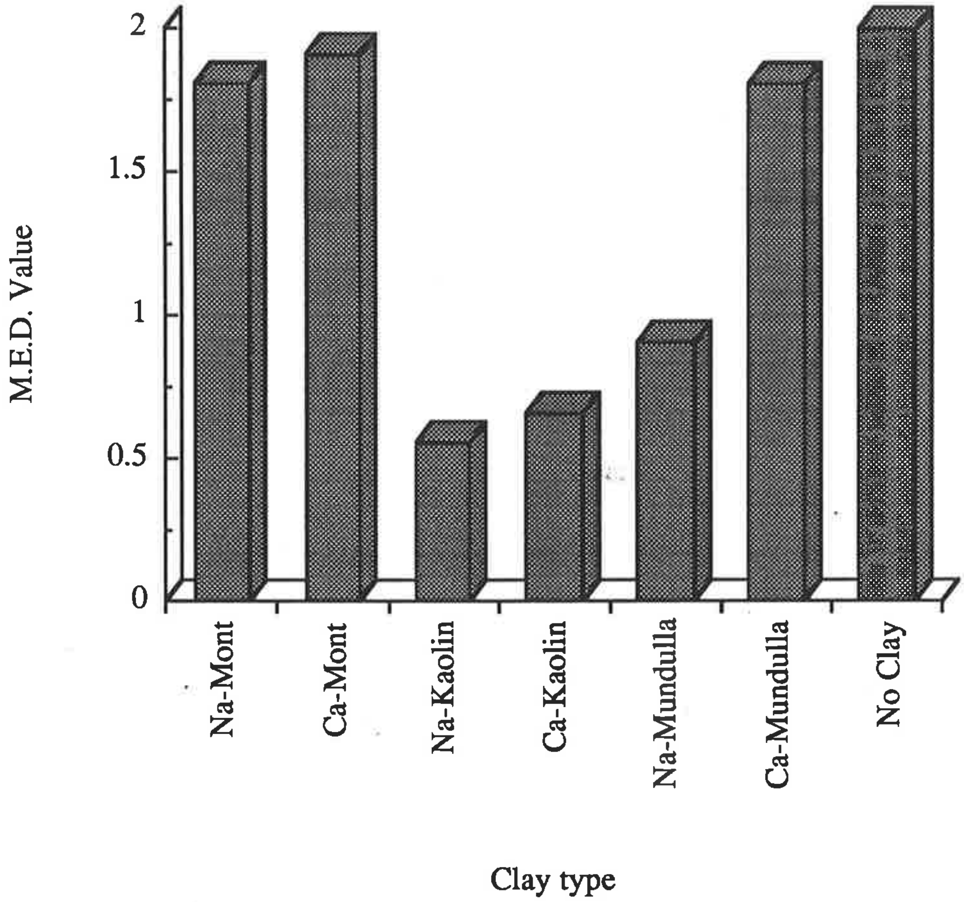


Figure 5.3. *Effect of various clays after a wetting and drying cycle on water repellence in the Badgingarra soil. The Tukey-Kramer LSD value was 1.19.*

after a wetting and drying cycle, both Blackpool and Mundulla kaolinite clays caused a dramatic and significant decrease in repellence, whereas the montmorillonite clays had almost no effect compared with the "no clay" control (Figs. 5.1 and 5.2). For Na^+-montmorillonite in the natural sand, a wetting/drying cycle actually increased the M.E.D. value from 2.0 to 2.6. The M.E.D. value induced by kaolinite of about 1.0 is rated as slightly repellent by King (1981), and is considered to cause no agronomic problems to crops or pastures. Na^+ saturated clays were consistently more effective than the corresponding Ca^{2+} saturated clays. After a wetting and drying cycle, clays were found to have a similar effect on water repellence in the Badgingarra sand (from Western Australia – Figure 5.3).

The effects of gibbsite, illite, and the charge reduced kaolinite and montmorillonite on water repellence can be seen in table 5.1. The charge reduced montmorillonite was more effective than the Na^+- or Ca^{2+}-saturated montmorillonite, but the charge reduced kaolinite and the Tumut illite were equally as effective as the other kaolinite clays. The virtually uncharged gibbsite was not as effective as the kaolinites.

Clay	M.E.D. value
Na^+-Mont	2.6
Ca^{2+}-Mont	3.0
Li^+-Mont (250°C)	2.1
Na^+-Kaolinite	0.9
Ca^{2+}-kaolinite	1.1
Li^+-kaolinite (130°C)	1.1
Illite	1.0
Gibbsite	1.6
No clay	3.1

Table 5.1. *Effect of various clay treatments on natural water repellence.*

5.3.2 Clay transport

In the wettable (ignited) sand, only Na^+-saturated montmorillonite surface-applied was leached through the sand to a significant degree (table 5.2). However, the rate of flow through the ignited sand was only about half of the flow rate through the untreated sand, and so the results are not directly comparable.

In the natural sand, applied clays were much more mobile. Only the Ca^{2+}-saturated montmorillonite was held within the sand matrix. Dry mixing reduced clay transport for the Na^{+}-saturated montmorillonite, but not for the kaolinite. More than 80% of the Na^{+}-saturated kaolinite was lost by leaching for both surface and dry mix applications. After a wetting and drying cycle, clay transport was reduced to less than 5% for all clays, and there was no difference between the two methods of drying.

SAND	Western Flat (Ignited)		Western Flat (Repellent)			
TMT.	Surface	Dry mix	Surface	Dry mix	Wet & Dried	Wet & Dried & Stirred
Na-R	18.8	1.4	63.6	14.2	0.6	2.4
Ca-R	0.0	0.3	0.0	0.0	0.4	0.0
Na-B	0.9	0.2	81.7	81.0	4.4	3.9
Ca-B	1.8	0.0	17.2	39.2	1.3	3.3

Table 5.2. *Effect of method of application on percentage of applied clay recovered in the leachate from ignited and natural water repellent sand. R - Redhill montmorillonite; B - Blackpool kaolinite.*

Depth (cm)	Clay content (%)	M.E.D. value
0–5	5.6	0.3
5–10	2.1	0.0
10–15	1.6	0.1
15–20	1.3	0.0
20–25	1.1	0.0

Table 5.3. Clay content and M.E.D. value of a water repellent sand with depth approximately 20 years after surface clay application.

Clay contents and M.E.D. values of the Mundulla water repellent sand approximately 20 years after clay application are presented in table 5.3. The majority of the clay appeared to be retained near the soil surface, and was active in reducing repellence. A nearby untreated sand had an M.E.D. value of 4.0. However, an untreated sand sample was not available for comparison in terms of clay content.

5.3.3 Adsorption of hydrophobic compounds from methanol

The methods used do not permit an absolute determination of the amount of hydrophobic organic material adsorbed by the clays. However, the various clays can be compared with respect to their ability to adsorb hydrophobic materials preferentially over other natural organic compounds (Fig. 5.4). When Ca^{2+}-saturated, the montmorillonite and Mundulla clays significantly reduced M.E.D. values (i.e. adsorbed more hydrophobic material) compared with the no clay treatment.. However, the Na^{+}-saturated forms, and the low surface area Na^{+}- and Ca^{2+}-saturated kaolinite clays, had no significant effect on repellence.

5.3.4 Repellence after clay addition and removal

Figure 5.5 shows M.E.D. values of Western Flat sand after clay addition as well as after clay removal. After clay removal, all sands except those treated with Na^{+}-saturated Mundulla clay regained most of their original repellence, although the Na^{+}- and Ca^{2+}-saturated kaolinites were also significantly different to the control. However, the amount of clay actually removed from the Na^{+}-saturated Mundulla and kaolinite treatments was very low (Table 5.4). Therefore, these low residual M.E.D values were probably due to a lot of the clay remaining in the sand after the sonication treatment, possibly trapped by the free organic matter in the soil.

In the artificial water repellent sand (no free organic matter), the amount of clay removed from the sand/clay mixtures was much more consistent . Virtually all the applied clay was recovered in the supernatant for all treatments (Table 5.4). Before clay removal, M.E.D. values were similar to those for the natural sand. However, clay

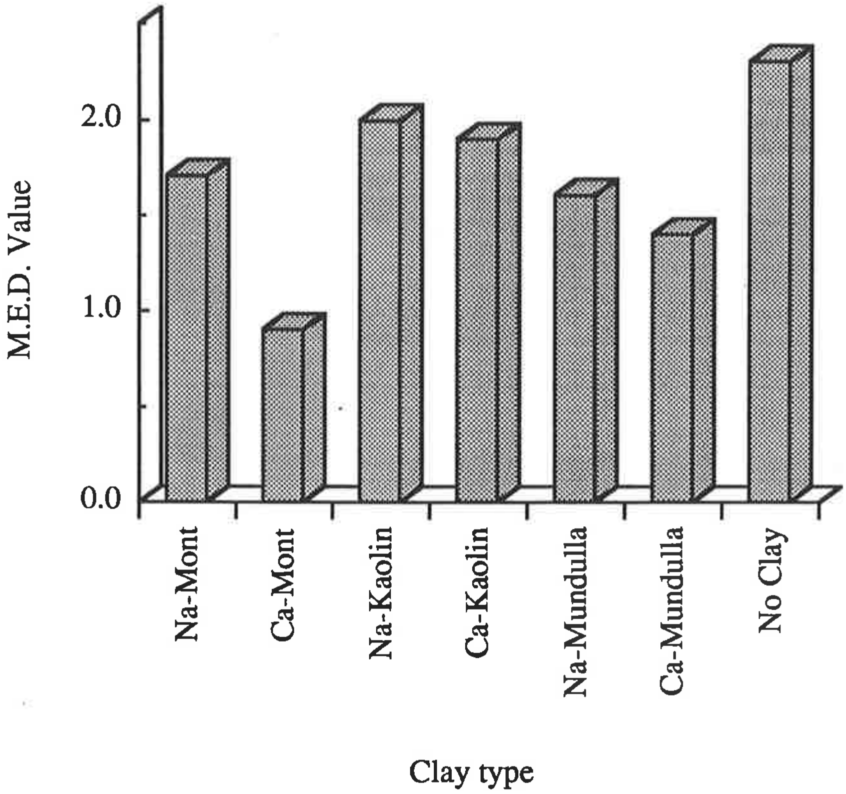
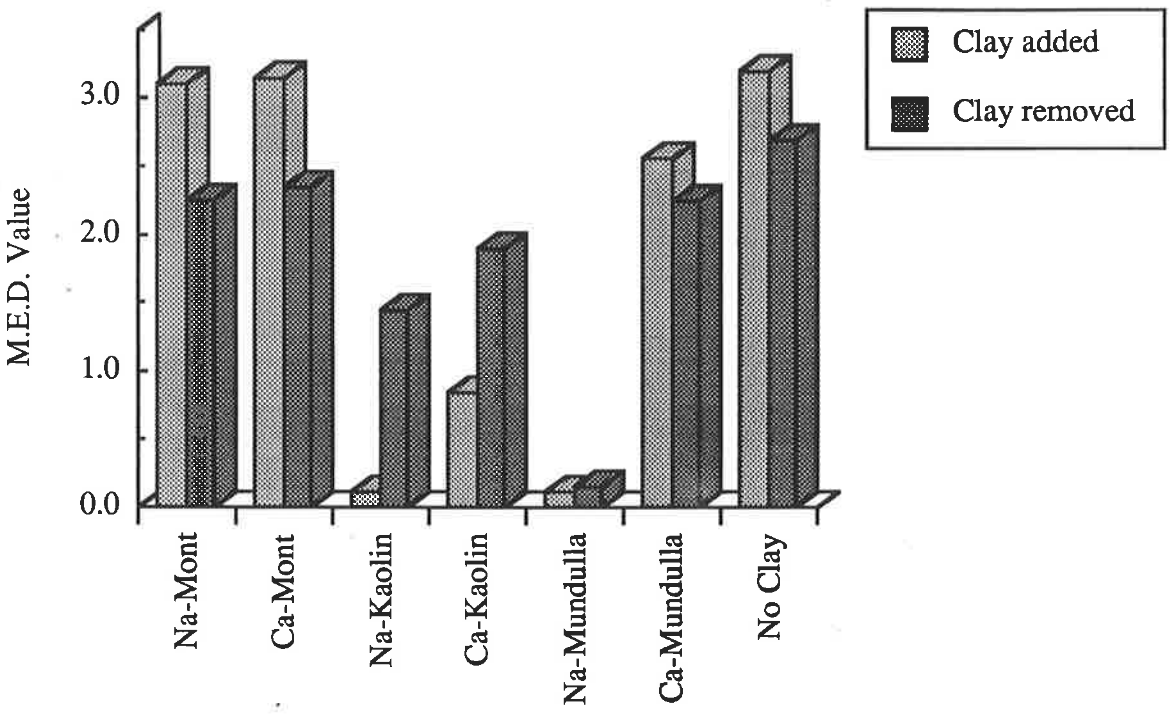


Figure 5.4. *Water repellence induced on acid-washed sand by extracted organic compounds* not *adsorbed by the indicated clays. The Tukey-Kramer LSD value was 0.76.*



Clay type

Figure 5.5. *Water repellence of Western Flat sand after clay addition and removal. The Tukey-Kramer LSD values were 0.55 and 0.53 for 'clay added' and 'clay removed' treatments respectively.*

removal resulted in almost complete restoration of the original water repellence for all clay treatments (Figure 5.6). Na^+-saturated Mundulla and Na^+-saturated montmorillonite clays did significantly reduce the M.E.D. value of the residual sand compared with the no clay treatment, but these M.E.D. values were still greater than 2.0.

Clay	Western Flat	Artificial
Na-Mont	0.071	0.112
Ca-Mont	0.068	0.106
Na-Kaolin	0.002	0.109
Ca-Kaolin	0.055	0.099
Na-Mundulla	0.012	0.110
Ca-Mundulla	0.083	0.121
No Clay	0.000	0.000

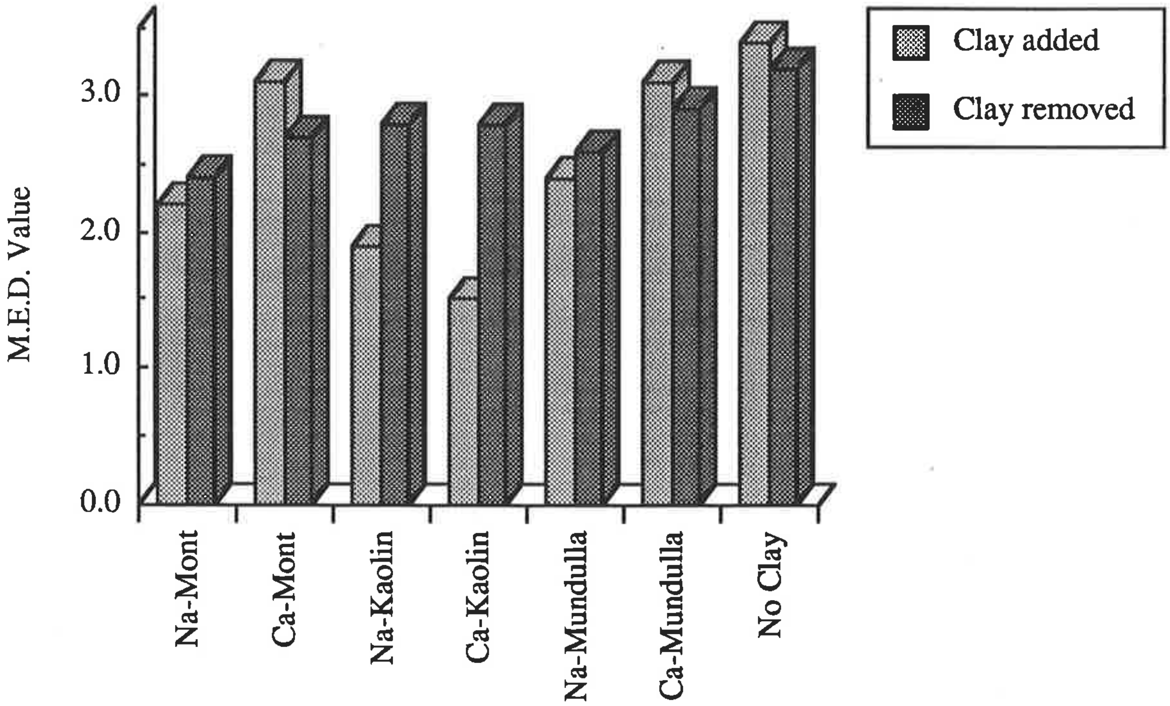
Table 5.4 *The amount of clay recovered (g) from Western Flat and* artificial *water repellent sand, after initial addition of 0.100g.*

5.3.5 Distribution of clay in sand

The scanning electron micrographs (Figures 5.7 and 5.8) show respectively Na^+-saturated Blackpool kaolinite and Na^+-saturated montmorillonite on a water repellent sand particle after wetting and drying. The kaolinite particles have spread over the surface of the sand grain, whereas montmorillonite formed clay 'strings' across the sand grain, probably at points of contact between sand grains. Ca^{2+}- and Na^+-saturated kaolinite behaved similarly, but the Ca^{2+}-saturated montmorillonite did not appear to interact with the sand grains, and remained in the sand as discrete aggregates.

5.3.6 Effects of clay on soil organic matter

Close inspection of the NMR spectra (figure 5.9) revealed some subtle differences between the soil with clay added two years previously and the other two samples. In the 'two year old' soil, there appeared to be a small reduction in the quantity



Clay type

Figure 5.6. *Water repellence of* artificial *sand after clay addition and removal. The Tukey-Kramer LSD values were 0.64 and 0.49 for 'clay added' and 'clay removed' treatments respectively.*

Figure 5.7. *Kaolinite particles on the surface of a sand grain from a natural water repellent sand.*

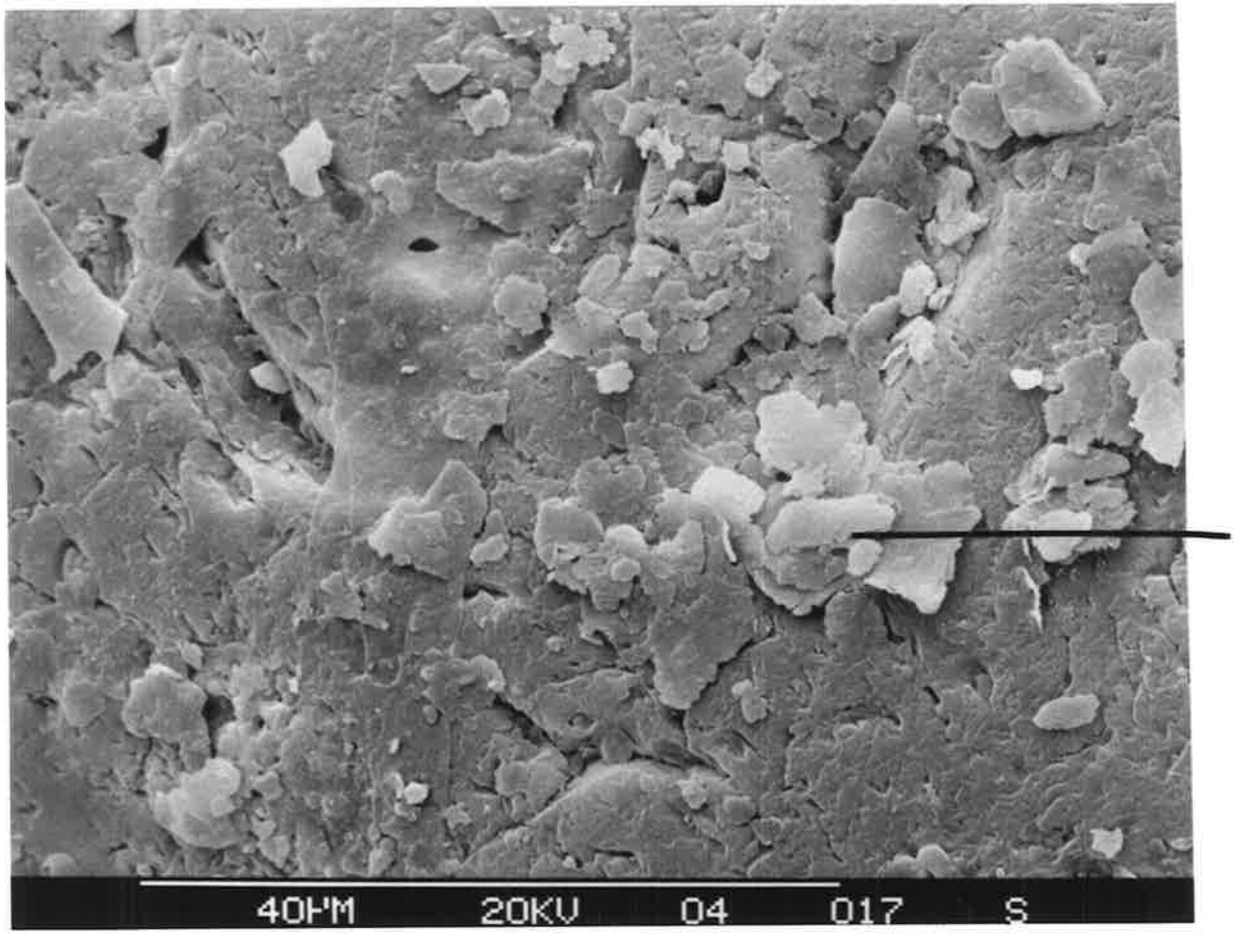
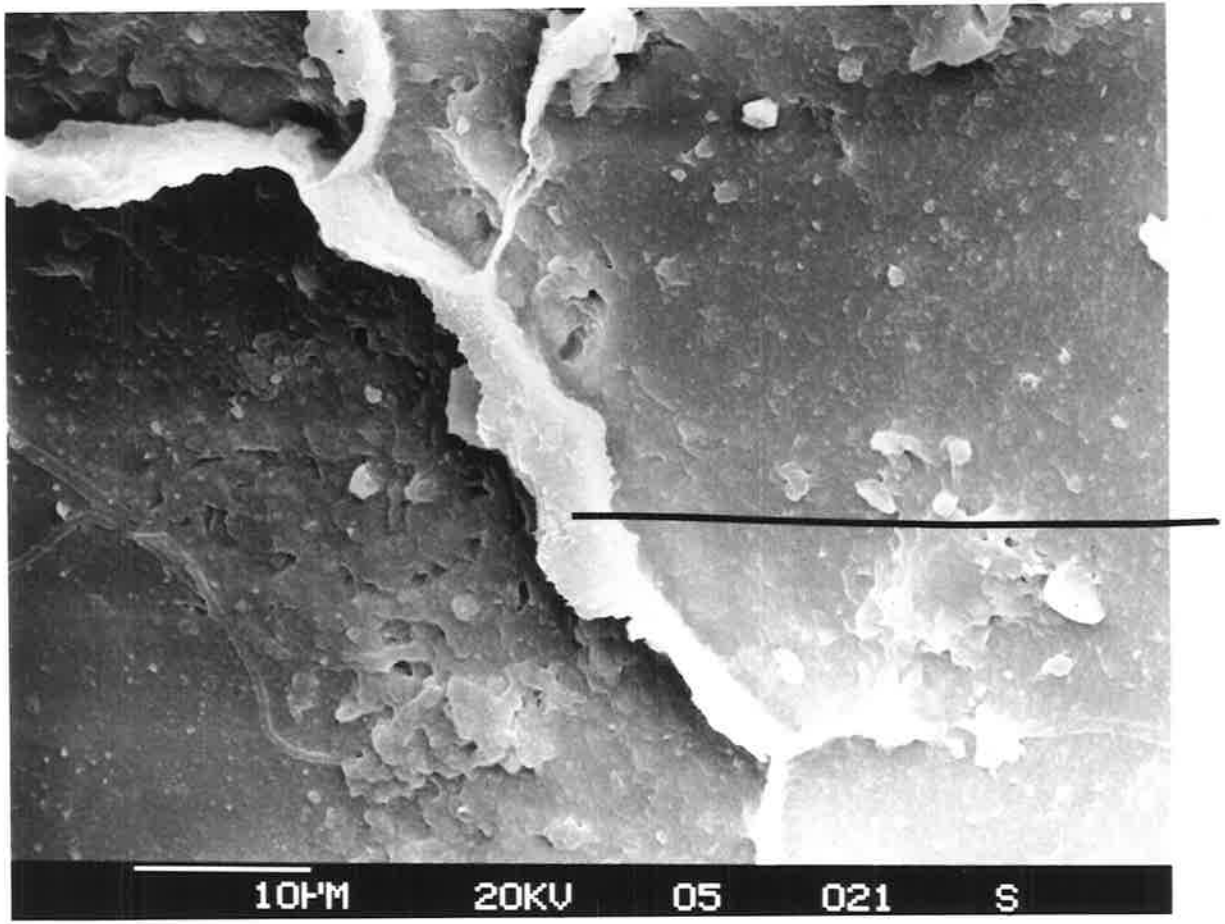

40ΜΜ 20KV 04 017 S
Kaolinite particles

Figure 5.8. *Montmorillonite particles on the surface of a sand grain from a natural water repellent sand.*



Montmorillonite particles

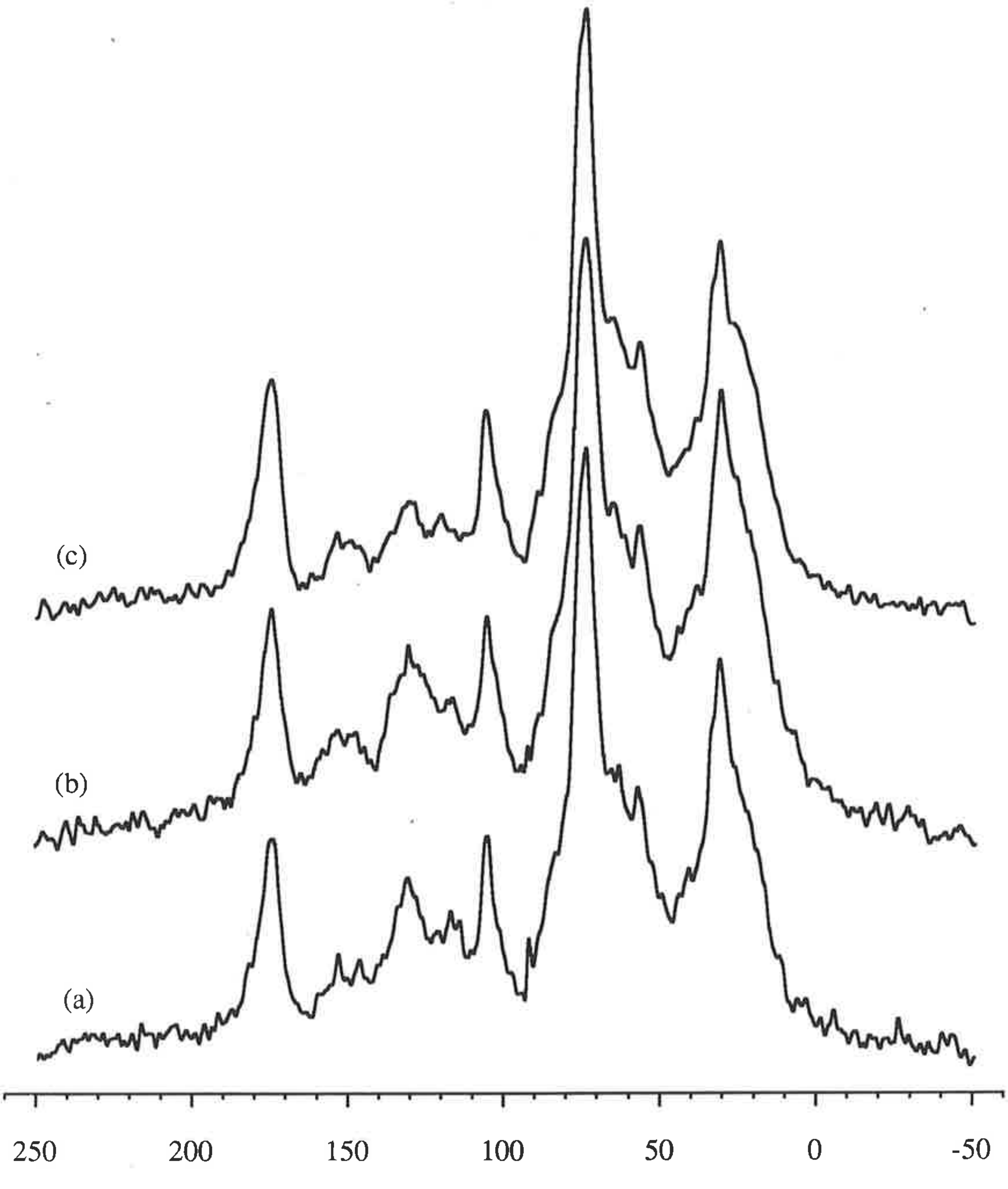


Figure 5.9. *^{13}C NMR spectra of Keith water repellent sand with (a) no clay; (b) clay applied recently in the laboratory; (c) clay applied two years previously in the field.*

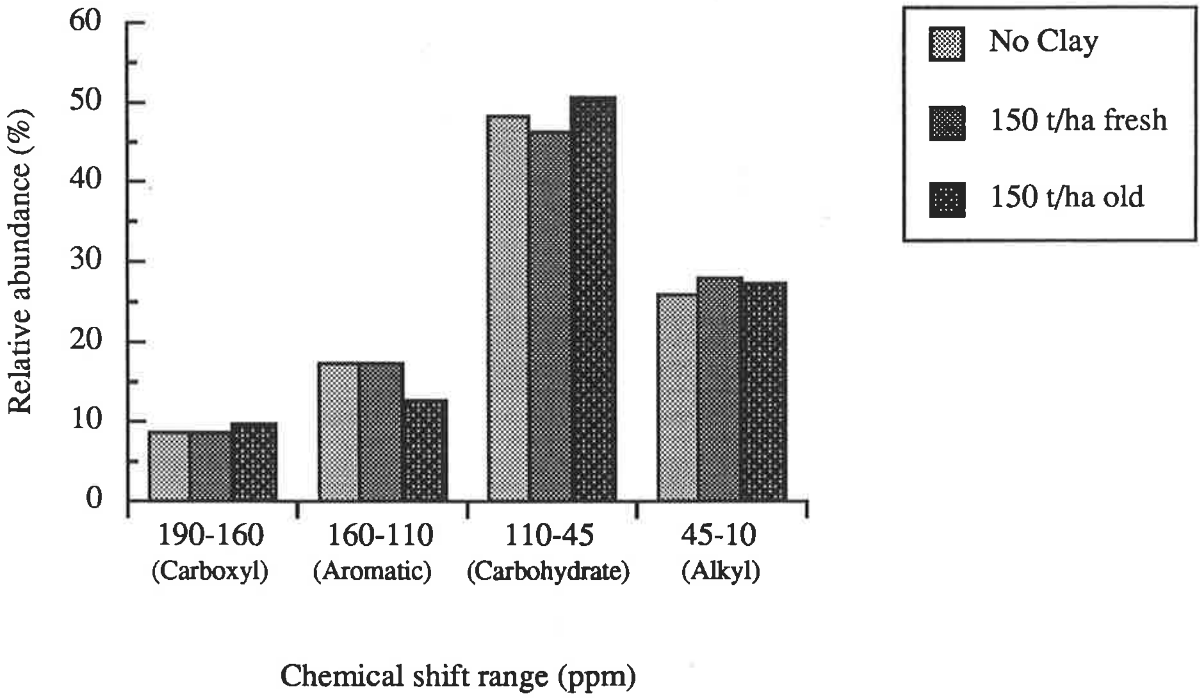


Figure 5.10. *Realtive abundance of different chemical types of carbon in the Keith sand with either no clay, clay applied recently in the laboratory, or clay applied two years previously in the field. Percentages were calculated from integrations of the NMR spectra (Figure 5.8) within the given chemical shift ranges (after Baldock* et al., *1992).*

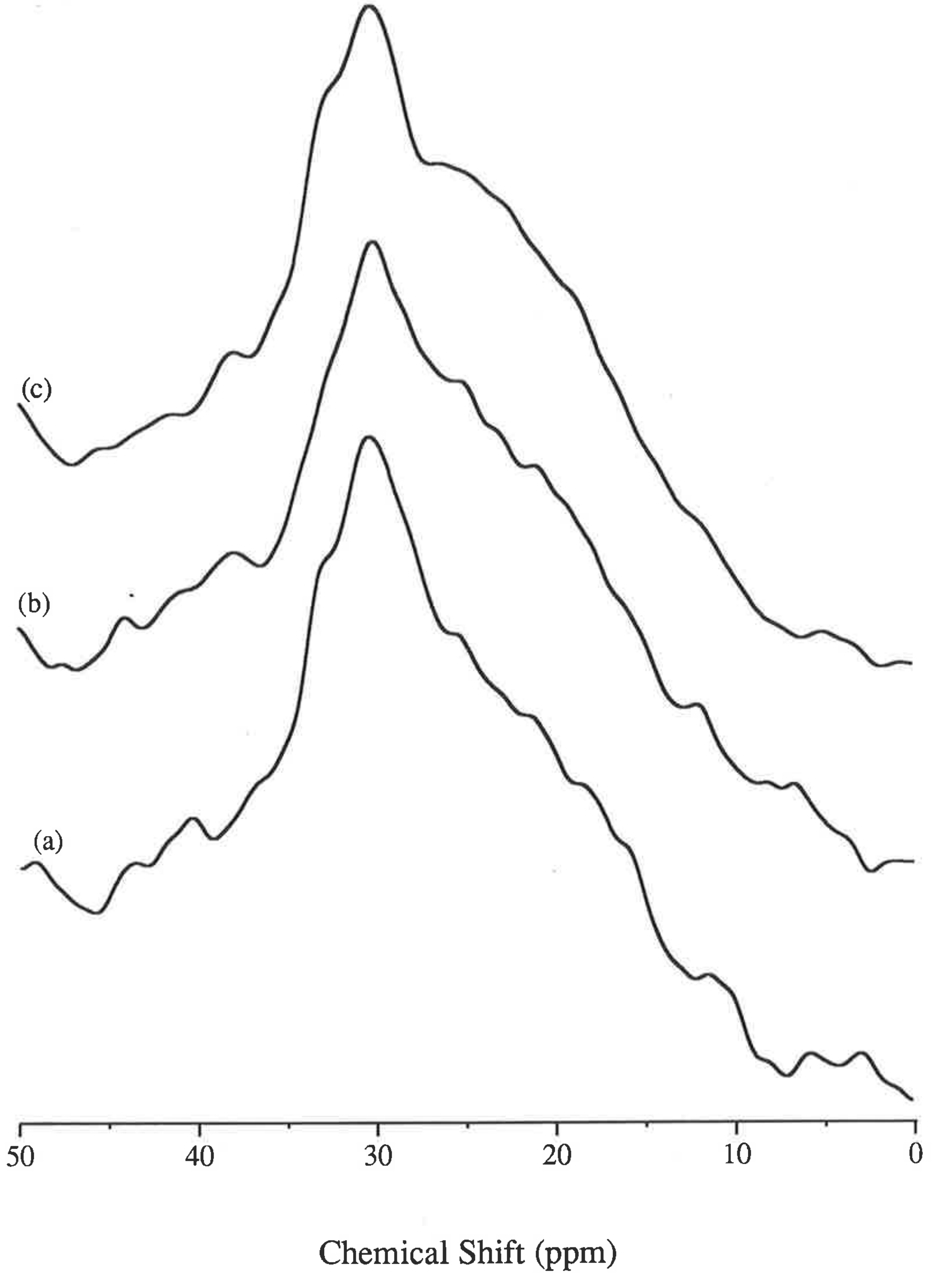


Figure 5.11. *The alkyl peak of the ^{13}C NMR spectra of Keith water repellent sand with (a) no clay; (b) clay applied recently in the laboratory; and (c) clay applied two years previously in the field.*

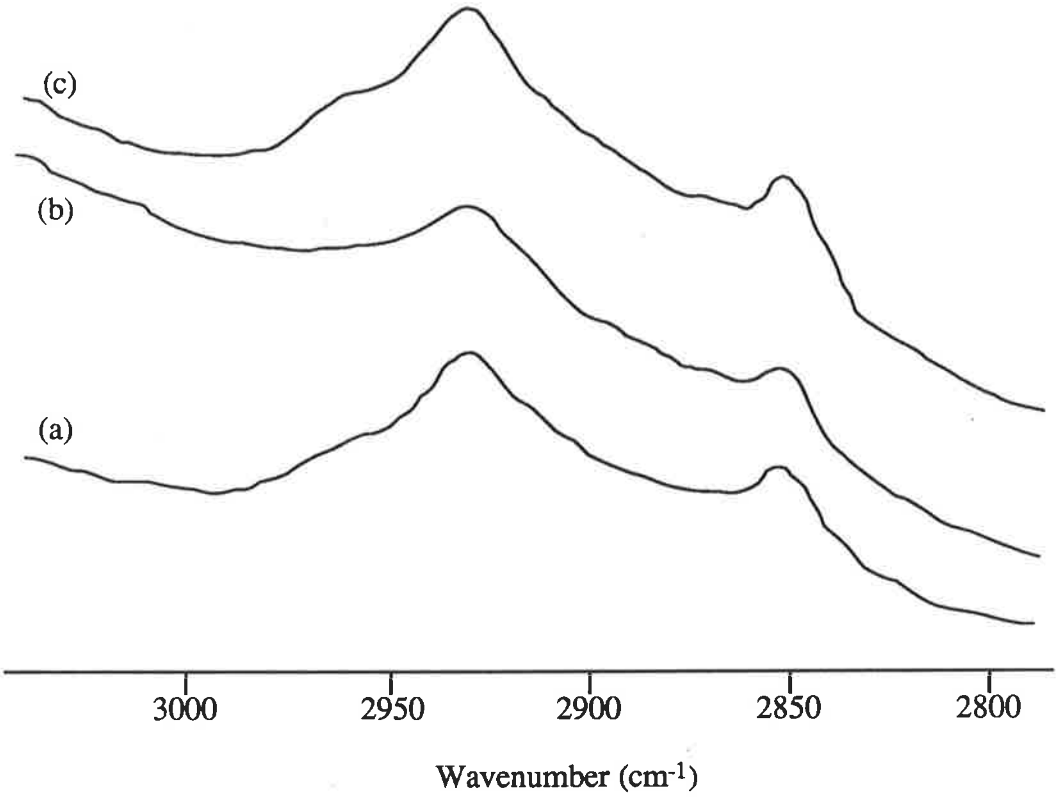


Figure 5.12. *The alkyl peaks of the IR spectra of Keith water repellent sand with (a) no clay; (b) clay applied recently in the laboratory; (c) clay applied two years previously in the field.*

of aromatic carbon, shown by the smaller peaks in the 110-160 ppm range (also figure 5.10). Figure 5.11 shows a magnification of the alkyl peaks of the three soils, and the exaggerated shoulder at 26 ppm for the 'two year old' soil indicates a slight increase in CH_3 groups, implying either more branching of aliphatic chains, or a decrease in average chain length. The alkyl sections of the IR spectra, and in particular the small peak at 2960 cm^{-1} (figure 5.12), also indicate an increase in CH_3 groups in this soil.

5.4 Discussion

5.4.1 Clay additions to natural and artificial sand

Clay applied as a dry mix did not appear to interact closely with the sand grains before wetting. Wetting, particularly for the Na^+-saturated clays, allowed the clays to interact with more of the sand surface, and the process of drying forced both Na^+- and Ca^{2+}-saturated clay particles into intimate contact with the sand grains (Kemper *et al.*, 1974), allowing the observed reduction in water repellence. King (1981) concluded that soils with an M.E.D. value less than 1.2 caused few problems in farm management, and this was achieved by several different types of clay after wetting and drying.

Although water repellent sands are very difficult to wet in the field, they almost always wet up at some stage of the season (Wetherby, 1984). The requirement of a wetting and drying cycle should therefore not pose a problem for the amelioration of water repellence by clay additions in the field, even if the full effects of clay addition are not seen immediately.

Additions of kaolinite to the natural (Western Flat and Badgingarra) and artificial sands proved to be more effective than montmorillonite, and independent of surface area. The Blackpool kaolinite was at least as effective as the Mundulla kaolinite, and both were more effective than the Redhill montmorillonite. Furthermore, clay dispersibility also appeared to be a factor in the reduction of natural and artificial repellence, the Na^+-saturated clays being consistently more effective than Ca^{2+}-clays, particularly for the Mundulla clay. During the wetting phase, the Na^+-saturated clays spontaneously dispersed, and on drying, were able to interact with more of the sand surface. Ma'shum *et al.* (1989) also found that dispersibility was a factor in the reduction of repellence by clays.

The Redhill montmorillonite clay was made more effective by reducing the surface charge of the clay particles. The reduced charge clay, and the naturally low charge kaolinite clays, may have been able to interact more strongly with the low charge silica sand particles coated with uncharged non-polar hydrophobic compounds. This is discussed further in section 5.4.5.

5.4.2 Clay transport

In the *model* water repellent sand, the presence of hydrophobic organic compounds reduced clay transport. However, any similar effect in the natural sand was hidden by the differences in flow rate between the two sands. This supports the argument of Bahrani *et al.* (1973), who concluded that the measurement of contact angle by comparing capillary rise in ignited and untreated water repellent sand columns (Emerson and Bond, 1963) was questionable because ignition may change the pore size distribution of the sand sample. This appeared to be the case here.

Wetting and drying reduced clay transport in a similar way to the way it reduced repellence. The drying process forced clay particles into contact with the sand grains, and subsequent infiltration could not dislodge the clay particles. The amount of water (250 ml) in the 19 mm column used here represents approximately 880 mm of rain, or about 2 years average rainfall. Therefore, clay applied to a water repellent sand should remain in the topsoil for an extended period of time..

5.4.3 Natural versus model and artificial water repellent sands

Ma'shum *et al.* (1989) proposed the cetyl alcohol model used in this investigation. The *model* system's advantages were seen as it being of consistent, predictable repellence free from small amounts of natural clay and free organic matter which occur in natural sand. They found that the *model* and natural sands behaved similarly, but the greater repellence of the *model* system allowed a more rigorous assessment of potential ameliorants. In this study the *model* and natural sands behaved very differently in their reactions to clay additions. This becomes obvious by comparing figures 4.1 and 5.1. In the natural water repellent sand, kaolinite was the most effective clay in reducing repellence, and montmorillonite had very little effect. In the model sand, however, the montmorillonite clay was much more effective than the low surface area kaolinite.

There were also differences between the *model* sand and natural sand in terms of clay transport through the sands. In the *model* sand, mixing the clay with the sand prior to infiltration virtually eliminated clay leaching. In the natural sand, however, mixing did not affect the mobility of Na^+-saturated kaolinite, and actually increased the leaching of Ca^{2+}-saturated kaolinite.

Overall, despite the advantages of the *model* water repellent system, its inability to mimic natural water repellence in its reaction to clay additions suggests that it should not be used in studies of amelioration of water repellence by clay amendments.

The *artificial* sand used in this study, prepared from extracted hydrophobic organic compounds, was a much better model. The pure kaolinite and montmorillonite clays produced similar results compared with the natural sand, but the Mundulla clay was slightly less effective in the *artificial* sand. For this reason, the use of the *artificial* system as a model can only be justified where free organic matter and native clay in the natural sand pose an insurmountable problem.

5.4.4 Adsorption of hydrophobic compounds by clays

Adsorption of hydrophobic organics by clays was the only process affecting water repellence when the supernatant from the clay/extracted organic/methanol suspension was added to acid-washed sand. Any compounds adsorbed by the clays were not transferred to the sand, and therefore could not contribute to repellence. Ca^{2+}-saturated montmorillonite was the most effective clay in reducing water repellence, followed by the Ca^{2+}-saturated Mundulla clay. The least effective clay was the low surface area Blackpool kaolinite, which had no significant effect on repellence. In general, Ca^{2+}-saturated clays adsorbed more hydrophobic organic materials than the corresponding Na^{+}-saturated clays. The Ca^{2+} ion is known to provide a better bridge between clays and many organic molecules (Theng, 1974), and this appears to be the case for methanol soluble hydrophobic compounds. The data for adsorption from methanol cannot be used to derive an adsorption isotherm, and gave no indication of the mechanism for adsorption of hydrophobic organic compounds onto clay surfaces. However, it did allow a relative comparison of the various clays with regard to their ability to reduce water repellence by adsorbing the causal compounds.

These results contrast with the reduction of water repellence caused by addition of clay to a water repellent sand. The clay that adsorbed the most hydrophobic materials from methanol solution (montmorillonite) was the least effective when added directly to a water repellent sand (see figure 5.1; also Ma'shum *et al.*, 1989). Conversely, the low surface area kaolinite clay was very effective when added to a water repellent sand, but did not adsorb significantly more hydrophobic material than the 'no clay' treatment. This indicates that the reduction in water repellence generated by clay addition to a water repellent sand is not principally due to adsorption of hydrophobic organic materials by the clay minerals. However, the differences could also be due to the presence of methanol in the adsorption system, because in the natural system, the only solvent available is water.

The amount of hydrophobic materials adsorbed by clay in the presence of water was estimated by clay addition and subsequent separation from a water repellent sand after a wetting and drying cycle. The proportions of clay, organic materials and sand were the same as for the adsorption experiment discussed above, and so the results can be directly compared. If clays reduced repellence by adsorbing hydrophobic organic molecules from the sand surfaces, removal of the clay would also remove the hydrophobic compounds, leaving the sand wettable. For most natural and all *artificial* water repellent sand treatments, however, clay removal did not significantly decrease water repellence in the residual sand, indicating that the clays did not strongly adsorb appreciable quantities of hydrophobic material. This agreed with the results discussed above, and confirmed that adsorption was not the major mechanism by which clays reduced water repellence.

In the situations where clay 'removal' did not leave a high level of residual repellence, most of the clay appeared to be retained by the sand and not separated by sonication. The low residual repellency was therefore due to incomplete removal of the clay, rather than the removal of hydrophobic compounds adsorbed by the clay. As this only occurred in the natural water repellent sand, it seems possible that some clays (particularly kaolinite) were physically trapped by free organic matter, which was common in natural sand but absent in the artificial sand. As free organic matter also contributes to water repellence in natural sand (Ma'shum, 1988), the possible interaction of kaolinite with these materials may help to explain the greater efficacy of kaolinite clay.

5.4.5 Masking of hydrophobic compounds by clays

Examination of the clay/sand mixtures, after a wetting and drying cycle, by scanning electron microscopy revealed that kaolinite was distributed evenly over the surface of the sand grains, whereas montmorillonite tended to form clay micro-aggregates either on the sand surface or independent of the sand grain. This implies that on drying, kaolinite had a higher affinity for the hydrophobic sand surface than for other kaolinite particles, and so formed 'face-to-sand' associations. However montmorillonite, even when dispersed, preferentially associated with other montmorillonite particles on drying, and formed mostly 'edge-to-sand' contacts at points of contact between sand grains, which only covered a small proportion of the sand surface. These distribution patterns of kaolinite and montmorillonite on sand grains have also been described by Peterson (1944). Brewer and Haldane (1957) noted that the exchangeable cation (Ca^{2+}, Mg^{2+}, K^+, Na^+, or H^+) in a 60% illite/30% kaolinite clay had no effect on the spreading of the clay over a sand surface. This confirms the results described here, in which exchangeable cation had little effect on the ability of a clay to reduce water repellence. Therefore, the main factor in determining the effectiveness of a clay sample in reducing water repellence was not dispersibility as such (Ma'shum *et al.*, 1989), but the ability of the clays to remain 'dispersed' over the sand surface during the drying process. The low surface charge of kaolinite (Peterson, 1944) and blocky geometry of kaolinite and illite particles were possibly responsible for this effect. However, when gibbsite (virtually uncharged) particles with similar geometry and the same surface area as the Blackpool kaolinite were added to a water repellent sand, they were not as effective. Therefore, clay particles with low but significant charge and blocky geometry appeared to be the most effective to coat the sand surfaces and reduce water repellence.

5.4.6 Long term effects of clay addition

Although clay addition is unlikely to directly affect soil organic matter, it can affect the microbial community in the soil (Kunc and Stotsky, 1974), and it is the microbial community which largely determines the chemical composition of soil organic matter (Oades *et al.*, 1988). The NMR and IR spectra showed that clay addition to a water repellent sand may cause a decrease in the quantity of aromatic carbon, and increase the number of CH_3 groups over a two year period. The increase in CH_3 groups is particularly interesting, as this may be due to a decrease in the average chain length of the aliphatic materials. Shorter chains are less hydrophobic, and so may generate less severe water repellence. However, the differences observed were very small, and further research is required to confirm any effects clay addition may have on soil organic matter. It should be remembered that two years is a short time in the life of soil organic matter (particularly the lipid fraction), and more time may be required before any differences due to clay addition become readily measureable.

Furthermore, about 90% of the organic matter in the soil was in the form of relatively large and mostly undecomposed plant fragments (C.M. Franco, personal communication). Clay content has been shown to influence microbial decomposition of various substrates (Kunc and Stotsky 1974; Amato and Ladd 1992) but has little effect on large particulate organic matter. Therefore, clay application only affects a small proportion of the total organic pool, and its effect in these experiments was overshadowed by the bulk soil organic matter. Nevertheless, microbial activity can be important in water repellent sands, because the development of water repellence was linked to the action of micro-organisms in Chapter 2. Clay application, although it may affect only a small proportion of the soil organic matter, may have a big effect on water repellence in sandy soils.

Overall, the differences observed between the 'two year old' soil and the other soils were too small to draw any firm conclusions. Further research, involving removal of undecomposed plant fragments before using spectroscopic techniques, may help to quantify any effects of clay addition on the compounds that cause water repellence.

5.4.7 Implications for field use of clays

In South Australia, many water repellent sands have a B horizon dominated by kaolinite and illite clays within 50 cm of the soil surface. This is an ideal source of clay for the amelioration of water repellence, because it is very close to where it is needed, thereby minimising transport costs. In this study, the rate of 0.5% pure clay was used, corresponding to a rate of approximately 7 t ha^{-1} to a depth of 10 cm. B horizon clays under sands are usually only 30-50% clay, and so a rate of at least 20 t ha^{-1} would be required to achieve comparable results in the field. As masking of the hydrophobic sand surface appeared to be the mechanism of action at low rates of clay addition, the total surface area of the sandy soil was not significantly increased. In the field, further organic additions are likely to coat the exposed clay layer on the sand grains, and possibly return the soil to its water repellent state. Because of this, higher rates of clay than used in this experiment may be required for long-term amelioration of water repellence. Field trials (M. Cann and D. Lewis, personal communication) show that a rate of 25 t ha^{-1} is sufficient to substantially improve plant emergence. Rates of 50-100 t ha^{-1} significantly improved plant growth, probably through the effects of the added clay on nutrient and water availability, in addition to the effects on water repellence.

The clay transport results reported here suggest that clays applied to a water repellent sand will remain in the topsoil (the zone where water repellence is severe) for an extended period of time. Van Dam *et al.* (1990) noted that clay applied to a water repellent sand 30 years previously was still predominantly located near the surface, and anecdotal evidence (C. Obst, personal communication) suggests that clays remain active in reducing water repellence for over 20 years. Given this time frame, clay additions to water repellent sands should be economically viable in the medium term.

5.5 Conclusions

Naturally occurring water repellence was overcome by the addition of kaolinite clay. However, montmorillonite clay was not effective. Wetting and drying was necessary before clay affected repellence, and this process also drastically reduced the amount of clay lost by leaching. Clay application appears to be a long term solution for water repellence, but the expense involved in transporting the clay means that only local clay can be economically added. Clays reduce repellence by masking the hydrophobic sand surface, but do not appear to strongly adsorb appreciable quantities of the causal hydrophobic organic matter in the short term.

Clay application in the field appears to have some effects on the qualitative nature of the soil organic matter. These effects require further investigation.

The inability of the *model* water repellent sand to mimic natural sand in its reactions to clay additions suggests that the *model* should not be used in investigations into water repellency.

CHAPTER 6. A SIMPLE TEST OF CLAY EFFICACY

6.1 Introduction

The previous chapter showed that kaolinitic clays were more effective than smectitic clays in reducing natural water repellence, and that the technique of clay application appeared promising for the long term amelioration of this problem. However, on a broad-acre scale the quantities of clay required are very large, and so clay application will only be economical if transport costs can be kept to a minimum. In practice, this means that clay must be found within about one kilometre of where it is to be applied (C. Obst, personal communication). Most farms have ready access to a clay B horizon within this distance, and the effectiveness of a given sample of field clay can be estimated by determining its clay mineralogy. However, it is often difficult to distinguish between the various types of clay. The only sure way is by X-Ray Diffraction, which is expensive and of limited availability.

Therefore, if clay application is to be widely practiced by farmers, a simple test of clay efficacy is required. The test should be able to be performed by a person not scientifically trained (e.g. a farmer) with commonly available materials. The test must also reduce variation due to differences in clay sampling e.g. water content and aggregate size and shape.

Experiments of clay application to water repellent sands described earlier in this thesis used a finely powdered <2 μm clay sample. However, field clay samples are usually only 30 to 60% <2 μm, and aggregated rather than powdered. Because of these differences, the rate used previously (0.5% w/w) is probably too low to generate substantial effects on water repellence with field clay samples. Therefore, the rate of field clay addition needs to be investigated. The method of mixing the clay with the sand is also important due to the aggregated nature of field clay samples. The mixing must be vigorous enough to distribute the clay throughout the sand sample, but King

(1981), Ma'shum *et al.* (1989) and others have shown that excessive agitation can reduce repellence.

Most of the experiments described previously used quantities of sand and clay too small to be readily performed in a home environment. The actual test (described in section 6.5) uses larger samples, and therefore it is important to verify that the results achieved on small samples also hold for large samples. Furthermore, larger samples require longer drying times (more than twelve hours at 105°C), which may be impractical. A microwave oven can reduce the drying time, but it is not known what effects this method may have on water repellence.

The method of measurement of water repellence also requires some attention. Few farmers will have access to a range of ethanol solutions prepared at 0.2 M intervals, and so the M.E.D. method is not a practical alternative. However, the Water Drop Penetration Time (W.D.P.T.) method is simple, and only requires water and a soil. King (1981) showed that over 25 water repellent soils, M.E.D. and log(W.D.P.T.) were both closely correlated with contact angle, and therefore, with each other. The correlation between M.E.D. and W.D.P.T. after clay addition should also be investigated, because it may be affected by the incorporation of clay into the sand.

Experiments were performed to determine an appropriate rate of field clay addition, to compare various techniques of clay/sand mixing and drying, and to attempt to reduce variability caused by variation in aggregate size. The relationship between M.E.D. and W.D.P.T. after clay addition was also determined.

6.2 Materials and Methods

6.2.1 Soils and clays

The water repellent sand used was the Western Flat water repellent sand, as described earlier. The clay was a field sample of the Mundulla clay, containing about 38% <2 μm and 60% > 20 μm. The <2 μm fraction of this clay was shown to be effective in reducing water repellence of natural sands in the previous chapter. A sample of Redhill montmorillonite (about 60% <2 µm) was also used as a clay known to have little effect on natural water repellence.

To measure the relationship between M.E.D and W.D.P.T., different levels of repellence for a sand were generated by adding various amounts of clays. Kaolinite/illite clays from Mundulla and Keith (also in South Australia) and Kojaneerup (Western Australia) were added to water repellent sands from Western Flat and Keith. The Keith sand contained similar amounts of clay and organic matter compared with the Western Flat sand, and its M.E.D. value was 2.1.

6.2.2 Clay application rate and mixing

A field sample of the Mundulla clay was sieved < 1 mm, and added to 4 vials containing 20 g Western Flat sand at one of the following rates: 0, 0.5, 1.0, 2.5, 5.0, 7.5, and 10% w/w. The vials were sealed and shaken end over end for two minutes. RO water (8 ml) was added. Half the vials were wetted with minimal disturbance by evacuation as described previously (section 4.2.4), and the other vials were wetted by stirring with a glass rod for 15 seconds. All vials were dried at 105°C, and cooled to 20°C for M.E.D. measurement. The samples wetted with minimum disturbance were re-wetted with the same technique, to determine the effect of a second wetting and drying cycle.

The effect of time of stirring was determined on samples of Western Flat water repellent sand (20 g and 175 g samples) mixed with 2.5% Mundulla clay (<1 mm) as described above, in two replicates. RO water (8 ml or 65 ml) was added, and the sand was stirred for 5, 10, 15, or 20 seconds. The sand was oven dried (105°C) and M.E.D. values were determined on the cooled samples.

6.2.3 Clay Aggregate Size

Field clay samples can have a wide range of aggregate sizes, depending on how they are collected and treated. To determine the effect of aggregate size on the effectiveness of clays in reducing water repellence, the Mundulla field clay sample was sieved into the following size fractions: 4000-2000, 2000-1000, 1000-500, 500-250, 250-150, 150-90, and <90 µm. Each fraction was added at 2.0% w/w to duplicate samples of the Western Flat sand, and either gently wetted or stirred (for 30 seconds) as described above. M.E.D. values were measured after drying at 105°C.

The actual clay content of each size fraction was measured by sedimentation. Aggregates (10.000 g) were placed in a 250 ml beaker, and RO water (200 ml) and sodium hexametaphosphate (40 mg) were added. The suspension was ultrasonically dispersed for 2 minutes, and transferred quantitatively to a 500 ml measuring cylinder. The volume was made up to 500 ml, and the cylinder was sealed and inverted several times. The suspension was allowed to settle for 7h 30 min, and then a 20 ml aliquot was removed from the top 5 cm and evaporated in a pre-weighed vial.

6.2.4 Method of drying

Water repellent sand (175g) was placed in glass beakers, and field samples of the Mundulla clay (3.5 g) were added to half the beakers. RO water (65 ml) was added to all the beakers, and the contents were stirred with a spoon for 30 seconds. The beakers were loosely covered with paper towel and placed two at a time (± clay) in a microwave oven (Samsung RE 727D; 700 watt) on 'medium' setting for either 10, 15, or 20 minutes. Beakers were weighed and then transferred to a conventional oven at 105°C, and weighed at hourly intervals to determine when drying was complete. Dried samples were cooled to 20°C and M.E.D. values were measured.

6.2.5 M.E.D./W.D.P.T. correlation

Soil clays from Mundulla, Keith or Kojaneerup were added to water repellent sands (10 g) from Western Flat or Keith at rates ranging from 0 to 2% w/w. Each mixture was wetted with 4 ml RO water, stirred for 20 seconds, dried at 105°C, and M.E.D. and W.D.P.T. values were measured at 20°C.

6.2.6 Verification of the test

The test (the procedure described in section 6.5.2) was verified in duplicate using field samples of the Mundulla kaolinite (an effective clay) and Redhill montmorillonite (an ineffective clay), added to the Western Flat water repellent sand.

6.3 Results

6.3.1 Clay application rate and mixing

The effect of clay rate and wet stirring of the clay/sand mix can be readily seen in Figure 6.1. For unstirred samples, clay rates up to 10% did not reduce the M.E.D. value to less than 1.0. A second wetting and drying cycle reduced repellence further, but still not to the level expected from previous experiments. However, after wet stirring, 5% clay reduced the M.E.D. value to 0.0.

Time of stirring effects are illustrated in figure 6.2. Near minimum repellence was obtained after 20 seconds stirring for both small and large samples. A time of 30 seconds was chosen for subsequent experiments.

6.3.2 Aggregate size

The effect of aggregate size on reduction of water repellence is shown in figure 6.3. As expected, the <90 μm fraction was most effective. The fractions between 90 and 500 μm were not very effective, but the 500 to 4000μm fractions were better. Subsequent analysis of clay contents of the fractions (also shown in figure 6.3) showed that the least effective fractions had the lowest clay contents, presumably due to a concentration of single sand grains during the sieving process. Nevertheless, wet stirring, by destroying the aggregates, reduced the effects of aggregate size, such that even the largest aggregate sizes reduced water repellence to an acceptable level.

6.3.3 Method of drying

Sand samples the same size as those used in the test (section 6.5) took more than twelve hours to dry at 105°C. This was reduced to 2 hours at 105°C after 20 minutes in

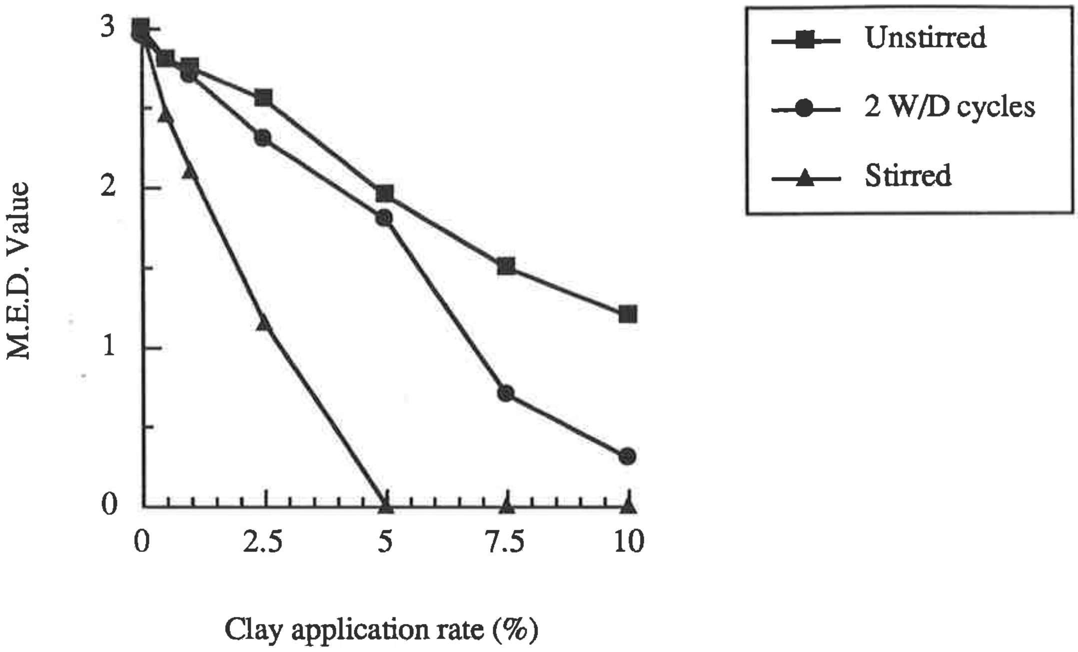


Figure 6.1. *Effect of wet stirring and a second wetting and drying cycle on water repellence after field clay addition.*

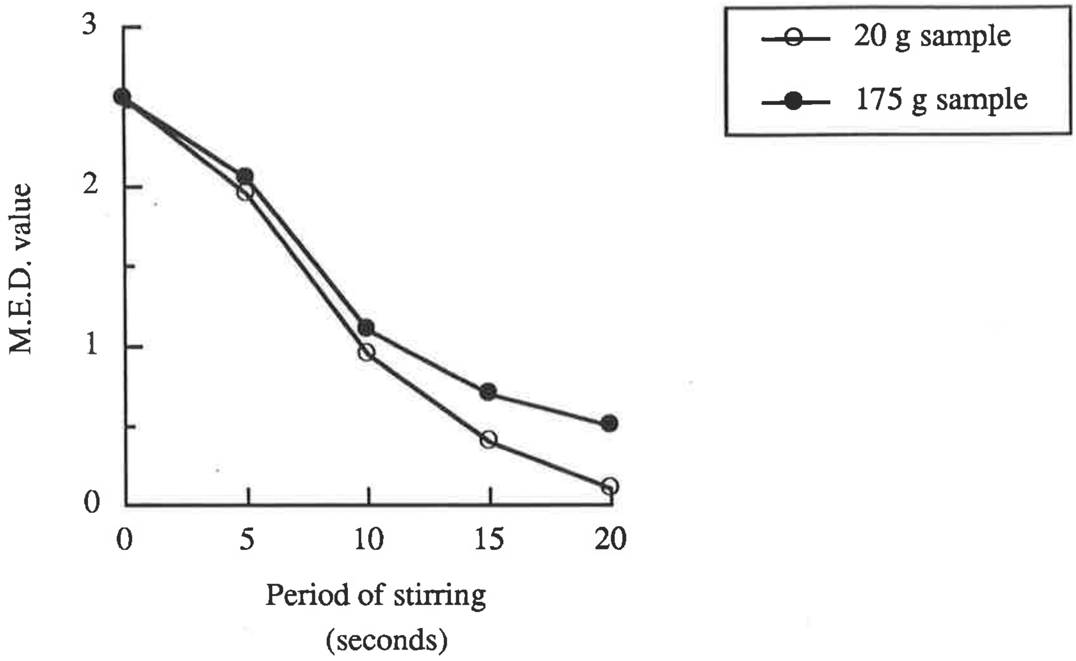


Figure 6.2. *Effect of period of stirring on water repellence after addition of 2.5% Mundulla field clay.*

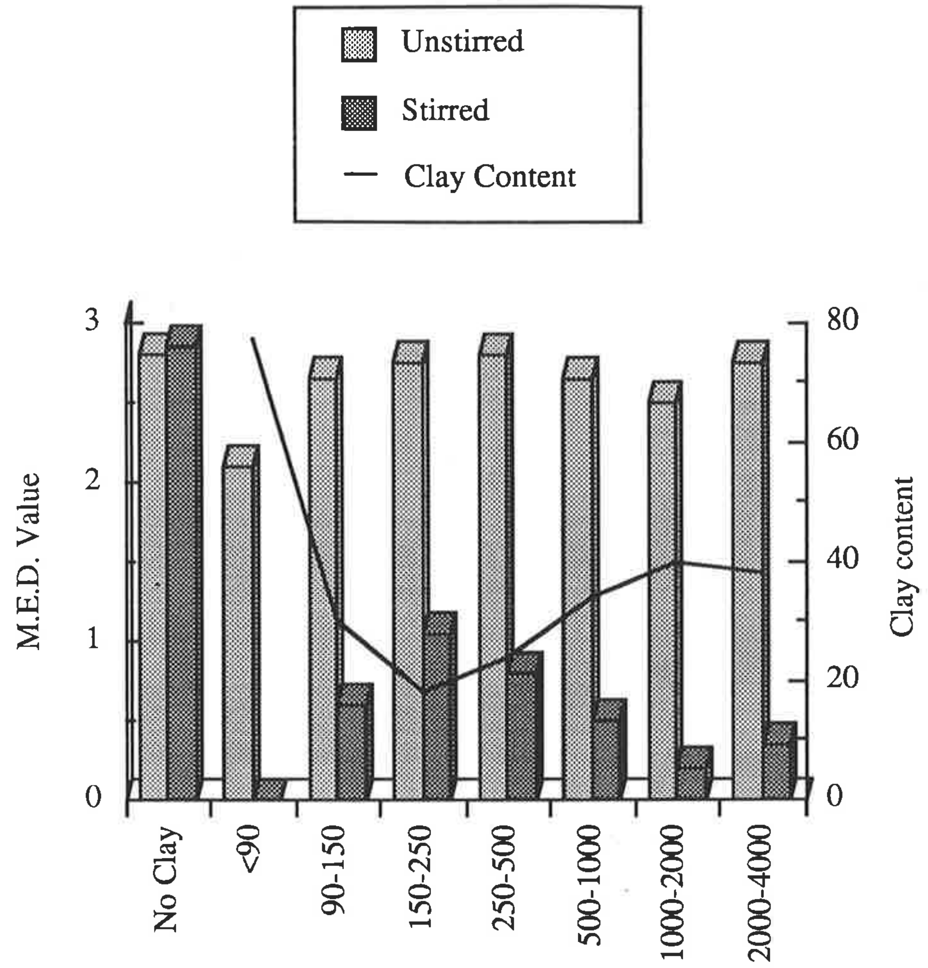


Figure 6.3. *Effect of aggregate size and wet stirring on water repellence after Mundulla field clay addition to the Western Flat soil. The clay content of each aggregate size range has also been plotted.*

a microwave oven on 'medium' setting (figure 6.4). The combination of microwave and conventional drying had no effect on M.E.D. values compared with drying in a conventional oven alone (table 6.1).

Drying Method	2% Mundulla Clay	No clay
16h @ 105°C	0.3	3.6
10 min mw[a], 8h @ 105°C	0.2	3.4
15 min mw, 6h @ 105°C	0.4	3.4
20 min mw, 2h @ 105°C	0.3	3.5

Table 6.1. *Effect of method of drying on water repellence (M.E.D. value).*

[a] - microwave oven, medium setting.

6.3.3 Correlation of M.E.D. with W.D.P.T.

Figure 6.5 shows the correlation between W.D.P.T. and M.E.D. values. Below W.D.P.T. of 60 seconds, all points lie on the same exponential curve, regardless of the sand or clay origin. This correlation agrees closely with the correlation obtained by King (1981). However, variation increases above this value.

6.3.4 Verification of the test

When the test procedure (section 6.5.2) was followed exactly, the two replicates of the Mundulla kaolinite (effective clay) gave water drop penetration times of 12 and 13 seconds; and >180 and >180 seconds for plus and minus clay treatments respectively. In contrast, the Redhill montmorillonte (ineffective clay) gave water drop penetration times of >180 seconds for both plus and minus clay treatments.

6.4 Discussion

As expected, the actual rates of field clay addition in the laboratory need to be higher than for pure clay (<2 µm) addition. Application rates in the field are probably higher again, due to the effects of continual organic addition and the natural variability always encountered in real life. The rate found to be effective (2%) corresponds to an application rate of 28 t ha^{-1}, assuming a soil density of 1.4 g cm^{-3} in the top 10 cm. Department of Agriculture trials showed that a clay application rate of 50 t ha^{-1} reduced water repellence, but 100 t ha^{-1} produced better results in terms of reduction of water repellence and germination and growth of a clover pasture (M. Cann, personal communication).

Stirring the wet soil clay mix for 30 seconds eliminated variation caused by aggregate size. Although this magnitude of energy input is unlikely to occur in the field, there is more time and many more wetting and drying cycles to distribute the clay throughout the sand. Wet cultivation will also help to perform this function. Therefore, with time the effects of stirring can be imitated in the field, and so the test is not unrealistic in terms of the field situation.

Drying the sample at 105°C required more than twelve hours, which is impractical in most kitchens. Although this can be accelerated by using a higher temperature, high temperatures can also start to degrade the organic matter in the soil. However, microwave ovens are readily available, and for the sample sizes used in the test, reduced the drying time to 20 minutes in the microwave (medium setting), followed by 2 hours at 105°C in a conventional oven, without affecting water repellence. Different microwave ovens may dry at different rates, and so care must be exercised. Temperatures in a microwave may also exceed 105°C at some points in the sample. However, the time savings involved suggest that mivrowave ovens are worthy of serious consideration.

The correlation between M.E.D. values and Water Drop Penetration Time showed that an M.E.D. value of 1.0 corresponds approximately with a W.D.P.T. of 60 seconds. The exponential relationship held for M.E.D. values less than 1.0, regardless of the source of sand or clay used to decrease repellence, and agrees closely with King (1981). At higher M.E.D values, the relationship becomes more variable, because W.D.P.T. involves a long contact time between sand and water, whereas M.E.D. solutions are in contact with the sand for only 10 seconds. Because the contact angle

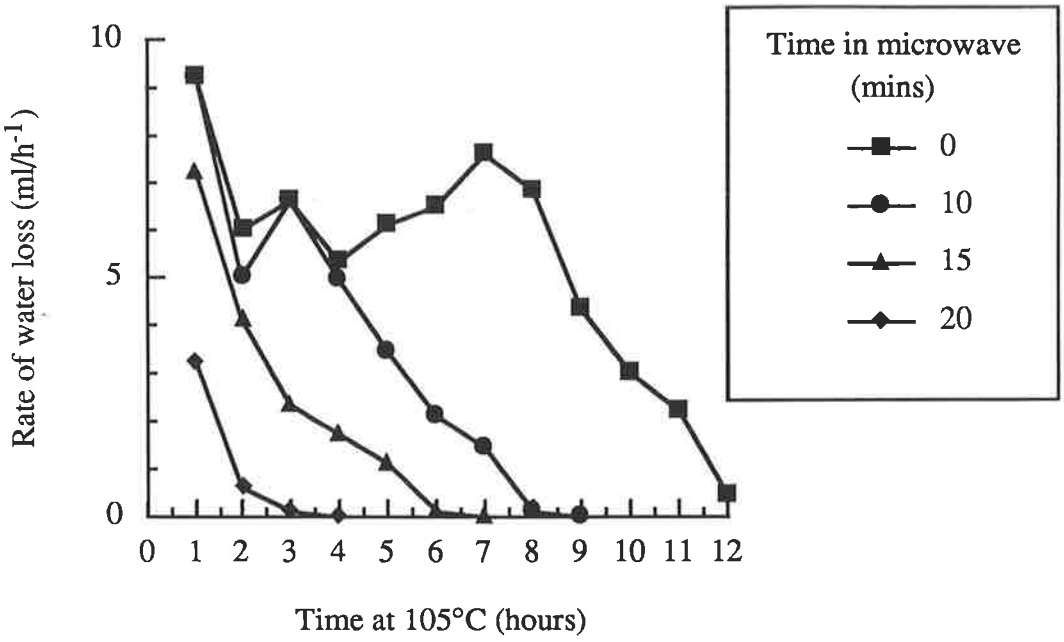


Figure 6.4. *Influence of time in a microwave oven on drying time for the quantity of sand and water required in the test of clay efficacy.*

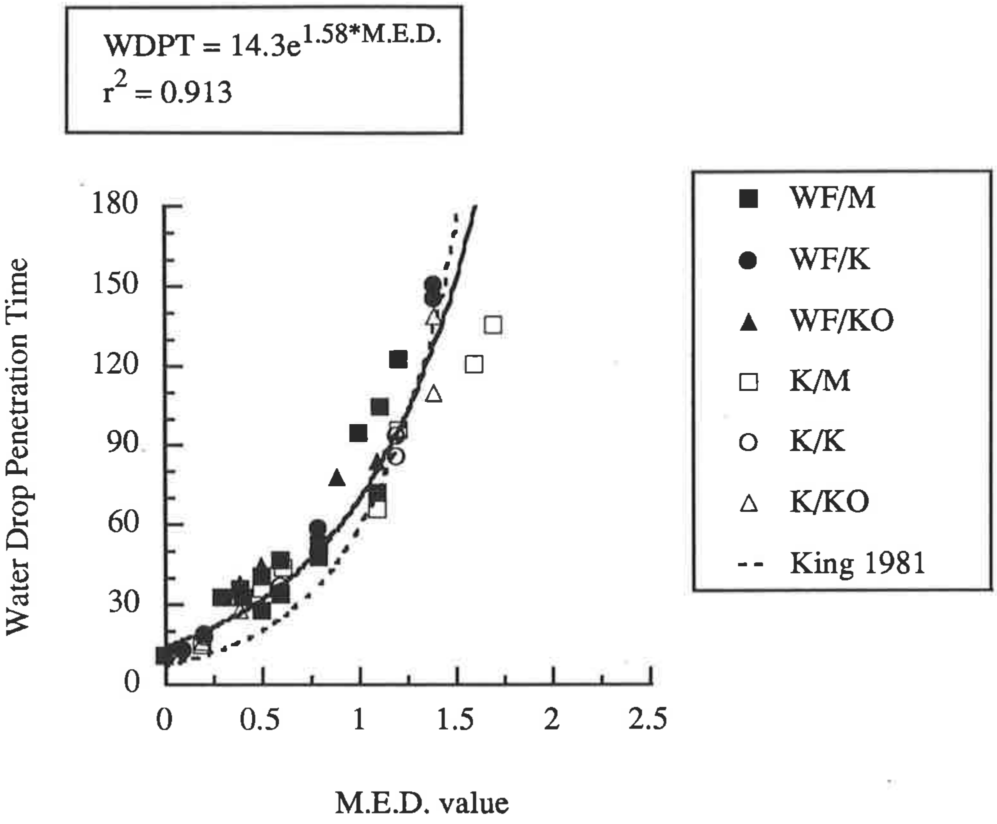


Figure 6.5. *Correlation between M.E.D. and W.D.P.T. values. The correlation calculated by King (1981) has also been plotted for comparison. WF - Western Flat sand; K - Keith sand; /M - Mundulla clay; /K - Keith clay; /KO - Kojaneerup clay.*

tends to change with time (Hammond and Yuan, 1969), W.D.P.T. is a measure of persistence of repellence, whereas M.E.D. is a measure of the initial repellence. Nevertheless, the relationship appears to hold for the first 60 seconds, which is the zone of interest in terms of the reduction of repellence by clay addition. King (1981) concluded that an M.E.D. value of 1.0 was equivalent to a W.D.P.T. of 53 seconds, and repellence became an agronomical problem above this level. Therefore, if clay can reduce the W.D.P.T. to less than 60 seconds, the clay will probably be effective in the field. In the actual test, a W.D.P.T. of 30 seconds was chosen to ensure a conservative test, although this value can be varied depending on the land use. For example, potatoes, because they are grown in mounds of soil and are very susceptible to water stress, may be adversely affected by very low levels of repellence (M. Heap, personal communication).

The test must also use a control sample, without clay addition. The W.D.P.T. value of this sample will give an indication of whether the repellence is severe enough to warrant clay addition. Although once again this will depend on the land use, a W.D.P.T. of over 180 seconds is capable of causing major problems in most agronomic situations, and these soils will gain the most benefit from clay addition. For higher value (e.g. horticultural) crops, clay addition may be economical at lower levels of water repellence.

In addition to the experiments described above, the initial water contents of the sand and clay will affect the performance of the clay. These effects can be largely overcome by simply air-drying the sand and clay before mixing them. Although air drying can lead to low and variable levels of repellence (see Chapter 2), oven drying the samples (105°C) after clay addition and wetting restores maximum and consistent repellence. A temperature of 105°C (220°F) is also about the lowest temperature able to be maintained by kitchen ovens, which is important in that it can be accomplished easily with readily available equipment.

Verification of the test procedure showed that the Mundulla clay would be effective in Western Flat sand, but the Redhill montmorillonite would not have an economical effect on water repellence. This agrees with the results presented in chapter 5, and also with observations of field trials with the Mundulla clay (M. Cann, personal communication). Field trials using a smectitic clay on water repellent sand (Ma'shum 1988) showed that the clay had no effect on water repellence, and this also agrees with the results generated by the test. Therefore, the test is correlated with results obtained on small samples in the laboratory, and also with the results observed in field trials. However, further field verification is required.

6.5 The Test

The test as described below reads more like a cake recipe than a scientific experiment. This is a deliberate attempt to use terms and equipment familiar to most people, and aims to make the test easier to use.

6.5.1 Sampling

The test of clay efficacy uses a sample of the same sand that the clay in question will be applied to if it is effective. The sand (about 500 g) should be taken from the top 10 cm in an area where the symptoms of water repellence (i.e. patchy plant growth and dry soil patches) are consistently severe. These are the areas that most need amelioration, and the clay must be effective against repellence of this severity. The sand should be allowed to air dry for at least one week. Sieve the sand through flywire or similar mesh, or alternatively, remove large plant fragments by hand.

Clay should be sampled from an area where it is close to the surface, and can be easily 'mined'. Depending on the land form, shallow clays can usually be found either on ridges or in depressions. Experience has shown that clays can vary considerably over a short distance, and so samples (approximately 25 g) should be collected from several different places within the same ridge or depression. The clay samples should be air dried for at least two weeks, and then crushed to clods of less than 5 mm and combined to generate an 'average' sample for the whole site.

6.5.2 Clay addition to sand

You will need: 350 g (1 cup) air-dry sieved water repellent sand
3.5 g (1 level tsp) air-dry crushed clay aggregates
130 ml ($^1/_2$ cup) water
2 glass jars (e.g. jam jars)

Place half the air dry water repellent sand in one of the jars, and add the air dry clay aggregates. Place the rest of the sand in the other jar. To both jars, add 65 ml water, and stir vigorously with a teaspoon for 30 seconds. Loosely cover the jars with paper towel, and put them both in a microwave oven. Heat on medium for 20 minutes, and then transfer to a conventional oven at 105°C (220F - very low heat) for at least 2 hours until dry. Allow to cool to room temperature, and then use a teaspoon to break up any aggregates. Smooth the sand surfaces by tapping the containers on a bench. Gently place a drop of water onto the sand surfaces, and measure the time taken for the drops to completely soak into the sand.

Important: Do not dry at temperatures higher than 105°C, as this can destroy the water repellency in the soil.

6.5.3 Interpretation

For the sand without added clay, the water drop should remain on the surface for more than three minutes. If the water drop penetrates in less than this time, water repellence may not be severe enough for clay application to produce an economical response. Although clay addition in a low-repellency situation may improve productivity through effects on water and nutrient retention, the response is unlikely to be economical.

If the water drop remains on the sand surface for more than three minutes, it is worth looking at the clay-amended sand sample. If the water drop on the clay-amended sand penetrates within 30 seconds, the clay will be effective in reducing water repellence and increasing production in the field. Water drop penetration times between

30 and 60 seconds indicate that clay addition may be economical, and small scale trials (e.g. one sandhill) are recommended before broad acre clay application is attempted.

These explanations are summarised in table 6.2.

W.D.P.T. Sand Only	W.D.P.T. Sand + Clay	Interpretation
<3 min		Water repellence not severe enough to justify clay addition
>3 min	>60 sec	Clay not effective enough
>3 min	30-60 sec	Clay may be economical - try on a small scale first
>3 min	<30 sec	Clay will economically reduce repellence and increase productivity

Table 6.2. *Interpretation of the clay test results.*

CHAPTER 7. GENERAL CONCLUSIONS.

Water repellence in soils causes major problems in agricultural production in southern Australia. It is caused by hydrophobic organic compounds which coat the sand surfaces and prevent water entry into the soil. In *model* water repellent systems, where repellence was induced by cetyl alcohol, the hydrophobic molecules were free to move within the sand matrix at temperatures above the melting point of the free alcohol (50°C). Temperatures of this magnitude induced severe repellence in acid-washed sand. However, with natural organic matter, although the hydrophobic compounds appear to be similar to cetyl alcohol, microbial activity or temperatures in excess of 100°C was necessary before repellence could be generated in acid-washed sand. The micro-organisms may degrade the easily decomposable water soluble compounds, leaving the hydrophobic compounds free. Only after this can moderately high temperatures, as occur on hot days, allow the molecules to move within the sand matrix and coat the sand surfaces. Because virtually all plants contain similar quantities of hydrophobic organic matter, most plant material is capable of inducing water repellence. However, there is a possibility that some plants or crops and their associated microbial communities may be more likely to generate water repellence than other species. Because water repellence was easily induced at low water contents, fungi or actinomycetes, or both, probably play a major role in this process. The growth of fungi and actinomycetes is particularly favoured in sandy soils due to their commonly low water contents, and this may help to explain why water repellence is such a problem in these soils.

Water repellence in sandy soils can be alleviated by clay addition. Adsorption studies showed that kaolinite and montmorillonite clays, regardless of exchangeable cation, were equally effective at adsorbing cetyl alcohol and palmitic acid. Both these compounds, and long chain esters such as cetyl palmitate, were found to be common in water repellent sands (Ma'shum *et al.*, 1989). The quantity of aliphatics adsorbed agreed closely with calculations for a bilayer on the external surfaces of clay domains, with the molecules oriented parallel to the clay surface. Interlayer adsorption did not occur to a significant extent. It is possible that given a sufficient quantity of hydrophobic compounds, clay particles in soils may also become hydrophobic. However, the vastly greater surface area, and the increased microbial activity associated with clays in soils means that the hydrophobic compounds will probably be degraded microbiologically before they can accumulate to the levels required to induce repellence.

The free movement of hydrophobic compounds observed in the *model* systems resulted in the clays with highest specific external surface area being the most effective in reducing repellence. There was no effect of mineralogy and little effect of exchangeable cation, which was consistent with the adsorption results. The clays were able to adsorb the free hydrophobic compounds, which therefore became diluted over a much larger surface area. As Ma'shum *et al.* (1989) showed, the larger the surface area, the greater the quantity of hydrophobic material required to induce repellence. A wetting and drying cycle was necessary before clay addition had any effect on water repellence. The wetting phase allowed dispersible clays to disperse, but more importantly, surface tension forces during the drying phase brought the sand and clay particles into intimate contact, allowing the observed reduction in water repellence.

However, the situation was more complex in the natural sand. The hydrophobic materials were not alone on the sand surfaces, but were also intermingled with hydrophilic material. Free organic matter and plant fragments were also present. The combination of these factors appeared to 'bind' the hydrophobic molecules so that they were not free to move within the sand matrix, as illustrated by the inability of moderate temperatures (70°C) to induce repellence in acid-washed sand amended with natural organic matter. For this reason, single compound model systems have proved inadequate for the study of water repellence.

When clay was added to a natural water repellent sand, the most effective clay was not necessarily the clay with the greatest available surface area, but rather the clay which spread most easily throughout the sand, and remained distributed throughout the sand after drying. Once again, clay addition had no effect on repellence until the mixture was exposed to wetting and drying. Adsorption of hydrophobic molecules was not the mechanism of reduction of water repellence, possibly due to competition between hydrophobic and hydrophilic molecules for adsorption sites on the clays. The low surface charge and blocky shape of kaolinite particles resulted in them forming a layer of clay particles around the sand grains, thereby masking the hydrophobic compounds. Both Ca^{2+}- and Na^{+}-saturated kaolinites were effective in reducing repellence.

However, the high surface charge and platy shape of montmorillonite particles resulted in them having a greater attraction for other montmorillonite particles than for the organic-coated sand surfaces. Although Na^{+}-saturated montmorillonite particles were able to disperse throughout the sand matrix, on drying they formed clay micro-aggregates at points of contact between sand grains, which covered only a small proportion of the surface. This resulted in a very stable soil, but had virtually no effect on water repellence.

The use of clay to ameliorate water repellence in sands appears to be a long term solution. Clay movement through a sand was drastically reduced by mixing the clay with the sand, and subsequent wetting and drying. Clay contents measured on a sand treated more than 20 years previously showed that the majority of clay was still retained in the top 10 cm, and M.E.D. values were still very low. In the long term, clay application also has the potential to change the microbial ecology and chemistry of the soil organic matter, which may help to prevent the recurrence of water repellence. This is an area for future research.

However, because of the costs involved with clay addition, it is only economical to the farmer if local clays can be used. As the suitability of clays can vary widely (for example, montmorillonite versus kaolinite), a simple test has been developed so that the efficacy of a given clay sample can be quickly and easily determined.

Clay application appears to be an economical and physically possible method of long term amelioration of water repellence in sands.

References

Adhikari, M. and Chakrabarti, G. (1976)."Contribution of natural and microbial humic acids to water repellency in soil." J. Ind. Soc. Soil Sci. **24** 217-219.

Albert, R. and Köhn, M. (1926)."Investigations into the resistance of sandy soils to wetting." Internat. Rev. Sci. and Practice Agric. **4** 312-318.

Ali, O. M., Yousaf, M. and Rhoades, J. D. (1987)."Effect of exchangeable cation and electrolyte on mineralogy of clay dispersed from aggregates." Soil Sci. Soc. Amer. Proc **51** 896-900.

Almendros, G., Gonzáles-Vila, F. J. and Martin, F. (1990)."Fire-induced transformation of soil organic matter from an oak forest: an experimental approach to the effects of fire on humic substances." Soil Sci. **149** 158-168.

Almon, W. R. and Johns, W. D. (1975)."Petroleum forming reactions: clay catalysed fatty acid decarboxylation." Int. Clay Conf. Proc. 399-409.

Amato, M. and Ladd, J. N. (1992)."Decomposition of ^{14}C-labelled glucose and legume material in soils: Properties influencing the accumulation of organic residue C and microbial biomass C." Soil Biol. Biochem. **24** 455-464.

Amblès, A., Magnoux, P., Jambu, P., Jacquesy, R. and Fustec, E. (1989)."Effects of addition of Bentonite on the hydrocarbon fraction of a podzol soil (A1horizon)." J. Soil. Sci. **40** 685-694.

Arshad, M. A., Schnitzer, M., Angers, D. A. and Ripmeester, J. A. (1990)."Effects of till versus no-till on the quality of soil organic matter." Soil Biol. Biochem. **22** 595-599.

Ashworth, M. R. F. (1942)."The fractionation of the organic matter, including nitrogen, of certain soils and its relation to their quality." J. Agric. Sci. **32** 349-359.

Bahrani, B., Mansell, R. S. and Hammond, L. C. (1973)."Using infiltrations of heptane and water into soil columns to determine soil water contact angles." Soil Sci. Soc. Amer. Proc. **37** 532-534.

Baldock, J. A., Oades, J. M., Waters, A. G., Peng, X., Vassallo, A. M. and Wilson, M. A. (1992)."Aspects of the chemical structure of soil organic materials as revealed by solid-state ^{13}C NMR spectroscopy." Biogeochem. **16** 1-42.

Barrett, G. and Slaymaker, O. (1989)."Identification, characterization, and hydrological implications of water repellency in mountain soils, southern British Columbia." Catena **16** 477-489.

Ben-Hur, M., Malik, M., Letey, J. and Mingelgrin, U. (1992)."Adsorption of polymers on clays as affected by clay charge and structure, polymer properties and water quality." Soil Sci **153** 349-356.

Biswell, H. H. (1974) "Effects of fire on chaparral." *in:* Fire and Ecosystems. Ed. Kozlowski, T. T. and Ahlgren, C. E. Academic Press pp 321-364

Bond, R. D. (1964)."The influence of the microflora on the physical properties of soils. II. Field studies on water repellent sands." Aust. J. Soil Res. **2** 123-131.

Bond, R. D. (1965)."Water repellent sands." Rural. Res. C.S.I.R.O. **51** 30-32.

Bond, R. D. (1968)."Water repellent sands." 9th Int. Congr. Soil Sci. Trans. **1** 339-347.

Bond, R. D. (1969a) "The occurrence of water repellent soils in Australia." *in:* Water Repellent Soils. Ed. DeBano, L. F. and Letey, J. University of California pp 1-6.

Bond, R. D. (1969b) "Factors responsible for water repellence of soils." *in:* Water Repellent Soils. Ed. DeBano, L. F. and Letey, J. University of California pp 259-263.

Bond, R. D. (1972)."Germination and yield of Barley when grown in a water repellent sand." Agron. J. **64** 402-403.

Bond, R. D. (1978) "Addition of cores of loam to overcome dry patch in turf on sandy soils." *in:* Modification of Soil Structure. Ed. Emerson, W. W., Bond, R. D. and Dexter, A. R. John Wiley and Sons pp 285-288.

Bond, R. D. and Hammond, L. C. (1970)."Effect of surface roughness and pore shape on water repellence of sandy soils." Soil Crop Sci. Soc. Fla. **30** 308-315.

Bond, R. D. and Harris, J. R. (1964)."The influence of the microflora on physical properties of soils. I. Effects associated with filamentous algae and fungi." Aust. J. Soil Res. **2** 111-122.

Bournemisza, E. (1964) "Wettability of soils in relation to their physico-chemical properties." Ph.D. Thesis. University of Florida

Bowers, S. A. and Hanks, R. J. (1961)."Effect of DDAC on evaporation and infiltration of soil moisture." Soil Sci. **92** 340-346.

Bozer, K. R., Brandt, G. H. and Hemwall, J. B. (1969)."Chemistry of materials that make soils hydrophobic." *in* Water repellent soils. Ed. DeBano, L.F., and Letey, J. University of California pp. 189-204.

Braids, O. C. and Miller, R. H. (1975) "Fats, waxes and resins in soils." *in:* Soil Components Vol.1:Organic Components. Ed. Gieseking, J. E. Springer-Verlag, Berlin pp 343-368.

Brewer, R. and Haldane, A. D. (1957)."Preliminary experiments in the development of clay orientation in soils." Soil Sci. **84** 301-309.

Brindley, G. W., Bender, R. and Ray, S. (1963)."Sorption of non-ionic aliphatic molecules from aqueous solutions on clay minerals. Clay-organic studies VII." Geochim. Cosmochim. Acta. **27** 1129-1137.

Brindley, G. W. and Moll, W. F. (1965)."Complexes of natural and synthetic Ca-Montmorillonites with fatty acids. Clay-organic studies IX." Amer. Mineralogist **50** 1355-1370.

Brindley, G. W. and Ray, S. (1964)."Complexes of Ca-montmorillonite with primary monohydric alcohols (Clay-organic studies – VIII)." Amer. Mineralogist **49** 106-115.

Brunauer, S., Emmett, P. H. and Teller, E. (1938)."Adsorption of gases in multimolecular layers." J. Amer. Chem. Soc. **60** 309-310.

Burch, G. J., Moore, I. D. and Burns, J. (1989)."Soil hydrophobic effects on infiltration and catchment runoff." Hydrological Processes **3** 211-222.

Capriel, P., Beck, T., Borchert, H. and Härter, P. (1990)."Relationship between soil aliphatic fraction extracted with supercritical hexane, soil microbial biomass, and soil aggregate stability." Soil Sci. Soc. Amer. J. **30** 415-420.

Capriel, P., Härter, P. and Stephenson, D. (1992)."Influence of management on the organic matter of a mineral soil." Soil Sci. **153** 122-128.

Chae, Y. M. and Lowe, L. E. (1980)."Distribution of lipid sulfur and total lipids in soils of British Columbia." Can. J. Soil Sci. **60** 633-640.

Chan, K. Y. (1992)."Development of seasonal water repellence under direct drilling." Soil Sci. Soc. Amer. J. **56** 326-329.

Chen, Y. and Schnitzer, M. (1978)."The surface tension of aqueous solutions of soil humic substances." Soil Sci. **125** 7-15.

DeBano, L. F. (1969a) "Observations on water repellent soils in western United States." *in:* Water Repellent Soils. Ed. DeBano, L. F. and Letey, J. University of California pp 17-29.

DeBano, L. F. (1969b) "Water movement in water repellent soils." *in:* Water Repellent Soils. Ed. DeBano, L. F. and Letey, J. University of California pp 61-89.

DeBano, L. F. (1971)."The effect of hydrophobic substances on water movement in soil during infiltration." Soil Sci. Soc. Amer. Proc. **35** 340-343.

DeBano, L. F. and Conrad, C. E. (1974)."Effect of a wetting agent and nitrogen fertilizer on establishment of ryegrass and mustard on a burned watershed." J. Range Management **27** 57-60.

DeBano, L. F., Mann, L. D. and Hamilton, D. A. (1970)."Translocation of hydrophobic substances into soil by burning organic litter." Soil Sci. Soc. Amer. Proc. **34** 130-133.

DeBano, L. F. and Rice, R. M. (1973)."Water repellent soils: their implications in forestry." J. For. **71** 220-223.

DeBano, L. F., Savage, S. M. and Hamilton, D. A. (1976)."The transfer of heat and hydrophobic substances during burning." Soil Sci. Soc. Amer. J. **40** 779-782.

Derjaguin, B. V., Altoiz, B. A. and Popovsky, Y. M. (1992)."Orientationally ordered layers of saturated hydrocarbons and their derivatives on quartz surfaces." J. Coll. Interface Sci. **148** 56-62.

Dinel, H., Schnitzer, M. and Mehuys, G. R. (1990) "Soil lipids: origin, nature, content, decomposition, and effect on soil physical properties." *in:* Soil Biochemistry Vol. 6. Ed. Bollag, J.-M., and Stotsky, G. Marcel Dekker, New York pp 397-429.

Dinel, H., Lévesque, M. and Mehuys, G. R. (1991)."Effects of long chain aliphatic compounds on the aggregate stability of a Lacustrine silty clay." Soil Sci. **151** 228-239.

Dinel, H., Lévesque, M. and Jambu, P. (1992)."Effects of long chain aliphatic compounds on the germination and initial growth of corn, radish and spinach seedlings, and on hydrological properties of a sand growth medium." Can. J. Soil Sci. **72** 107-112.

Diouf, B., Skidmore, E. L., Layton, J. B. and Hagen, L. J. (1990)."Stabilising fine sand by adding clay: Laboratory wind tunnel study." Soil Tech. **3** 21-31.

Dommergues, Y. R., Belser, L. W. and Schmidt, E. L. (1978)."Limiting factors for microbial growth and activity in soil." Adv. Microb. Ecol. **2** 49-104.

Emerson, W. W. and Bond, R. D. (1963)."The rate of water entry into dry sand and calculation of the advancing contact angle." Aust. J. Soil Res. **1** 9-16.

Endo, R. M., Letey, J., Valoras, N. and Osborn, J. F. (1969)."Effects of nonionic surfactants on monocots." Agron. J. **61** 850-854.

Farmer, V. C. and Pisaniello, D. L. (1985)."Against an aromatic structure for soil fulvic acid." Nature **313** 474-475.

Fehl, A. J. and Lange, W. (1965)."Soil stabilization induced by growth of microorganisms on high-calorie mold nutrients." Soil Sci. **100** 368-374.

Fink, D. H. (1970)."Water repellency and infiltration resistance of organic film-coated soils." Soil Sci. Soc. Amer. Proc. **34** 189-194.

Fink, D. H. and Myers, L. E. (1969) "Synthetic hydrophobic soils for harvesting precipitation." *in:* Water Repellent Soils. Ed. DeBano, L. F. and Letey, J. University of California pp 221-239.

Fraps, G.S. (1915)."The effect of organic compounds in pot experiments." Texas Agr. Exp. Sta. Bull. No. 174

French, R. J. and Schultz, J. E. (1977)."Variation in temperature input, water use, growth rate and yield of wheat due to time of sowing." Aust. Cereal Agronomy Conf., Perth **1** 20-22.

Fridland, Y. V. (1976)."Lipid (alcohol-benzene) fraction of organic matter in different soil groups." Sov. Soil Sci. **8** 548-557.

Fridland, Y. V. (1982)."Some characteristics of soil lipids as a function of ecological conditions." Sov. Soil Sci. **14** 80-88.

German, W. L. and Harding, D. A. (1969)."The adsorption of aliphatic alcohols by montmorillonite and kaolinite." Clay Mins. **8** 213-227.

Giles, C. H., MacEwan, T. H., Nakhwa, S. N. and Smith, D. (1960)."Studies in Adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface area of solids." Chem. Soc. J. (Lond.) 3973-3993.

Giovannini, G. and Lucchesi, S. (1983)."Effect of fire on hydrophobic and cementing substances of soil aggregates." Soil Sci. **136** 231-236.

Giovannini, G. and Lucchesi, S. (1984)."Differential thermal analysis and infrared investigations on soil hydrophobic substances." Soil Sci. **137** 457-463.

Giovannini, G., Lucchesi, S. and Cervelli, S. (1983)."Water repellent substances and aggregate stability in hydrophobic soil." Soil Sci. **135** 110-113.

Greenland, D. J. (1963)."Adsorption of polyvinyl alcohols by montmorillonite." J. Colloid. Sci. **18** 647-664.

Greig-Smith, R. (1910)."Contributions to our knowledge of soil fertility. I. The action of wax-solvents and the presence of thermolabile bacteriotoxins in soil." Proc. Linn. Soc. N.S.W. **35** 808-822.

Greig-Smith, R. (1911)."Contributions to our knowledge of soil fertility. IV. The agricere and bacteriotoxins of soil." Proc. Linn. Soc. N.S.W. **36** 679-699.

Grimalt, J. O., Hermosin, B., Yruela, I. and Saiz-Jimenez, C. (1989)."Lipids of soil humic acids. II. Residual components after hymatomelanic acid extraction." The Sci. Total Env. **81/82** 421-428.

Grimalt, J. O. and Saiz-Jimenez, C. (1989)."Lipids of soil humic acids. I. The hymatomelanic acid fraction." The Sci. Total Env. **81/82** 409-420.

Hammond, L. C. and Yuan, T. L. (1969) "Methods of measuring water repellence of soils." *in:* Water Repellent Soils. Ed. DeBano, L. F. and Letey, J. University of California pp 49-59.

Hatcher, P. G., Maciel, G. E. and Dennis, L. W. (1981)."Aliphatic structure of humic acids: a clue to their origin." Org. Geochem. **3** 43-48.

Hedges, J. I. (1977)."The association of organic molecules with clay minerals in aqueous solutions." Geochim. Cosmochim. Acta. **41** 1119-1123.

Hedrick, R. M. and Mowry, D. T. (1952)."Effect of synthetic polyelectrolytes on aggregation, aeration, and water relationships in soils." Soil Sci. **73** 427-441.

Heijnen, C. E., Hok-A-Hin, C. H. and Van Elsas, J. D. (1993)."Root colonization by *Pseudomonas fluorescens* introduced into soil amended with bentonite." Soil Biol. Biochem **25** 239-246.

Heijnen, C. E., Hok-A-Hin, C. H. and van Veen, J. A. (1992)."Improvements to the use of bentonite clay as a protective agent, increasing survival levels of bacteria introduced into soil." Soil Biol. Biochem. **24** 533-538.

Heijnen, C. E. and van Veen, J. A. (1991)."A determination of protective microhabitats for bacteria introduced into soil." FEMS Microbiol. Ecol. **85** 73-80.

Hempfling, R. and Schulten, H.-R. (1991)."Pyrolysis-(gas chromatography/)mass spectrometry of agricultural soils and their humic fractions." Z. Pflanzenernähr. Bodenk **154** 425-430.

Hillel, D. (1980) "Fundamentals of soil physics." Academic Press, New York

Hoffmann, R. W. and Brindley, G. W. (1960)."Adsorption of non-ionic aliphatic molecules from aqueous solutions on montmorillonite. Clay-organic studies – II." Geochim. Cosmochim. Acta **20** 15-29.

Hofmann, V. U. and Klemen, R. (1950)."Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung." Z. Anorg. Allg. Chem. **262** 95-99.

Holzhey, C. S. (1969) "Water repellent soils in southern California." *in:* Water Repellent Soils. Ed. DeBano, L. F. and Letey, J. University of California pp 31-41.

Ivanek, O. and Schmidt, P. (1991)."Hydrophilicity and surface molecular structure of sandy podzol E with high content of quartz." Z. Pflanzenernäehr. Bodenk. **154** 127-130.

Jambu, P., Amblès, A., Dinel, H. and Secouet, B. (1991)."Incorporation of natural hydrocarbons from plant residues into an hydromorphic humic podzol following afforestation and fertilization." J. Soil Sci. **42** 629-636.

Jamison, V. C. (1942)."The slow reversible drying of sandy surface soils beneath citrus trees in central Florida." Soil Sci. Soc. Amer. Proc. **7** 36-41.

Jamison, V. C. (1945)."The penetration of irrigation and rain water into sandy soils of central Florida." Soil Sci. Soc. Amer. Proc. **10** 25-29.

Jamison, V. C. (1946)."Resistance to wetting in the surface of sandy soils under citrus trees in central Florida and its effect upon penetration and the efficiency of irrigation." Soil Sci. Soc. Amer. Proc. **11** 103-109.

Janczuk, B., Bialopiotrowicz, T. and Wojcik, W. (1989)."The surface tension components of aqueous alcohol solutions." Coll. and Surfaces **36** 391-403.

Jaynes, W. F. and Bigham, J. M. (1987)."Charge reduction, octahedral charge, and Lithium retention in heated, Li-saturated smectites." Clays & Clay Mins. **35** 440-448.

Jex, G. W., Bleakley, B. H., Hubbell, D. H. and Munro, L. L. (1985)."High humidity-induced increase in water repellency in some sandy soils." Soil Sci. Soc. Amer. J. **49** 1177-1182.

Kaiser, E.-A., Mueller, T., Joergensen, R. G., Insam, H. and Heinemeyer, O. (1992)."Evaluation of methods to estimate the soil microbial biomass and the relationship with soil texture and OM." Soil Biol. Biochem **24** 675-683.

Kemper, W. D., Evans, D. D. and Hough, H. W. (1974) "Crust strength and cracking: Part 1. Strength." *in:* Soil Crusts. Ed. Cary, J. W. and Evans, D. D. Ariz. Agr. Res. Sta. Tech. Bull. No. 214 pp 31-38.

Kieft, T. L. (1991)."Soil microbiology in reclamation of arid and semi-arid lands." *in* Semi-arid Lands and Deserts: soil resource and reclamation. Ed. Skujiņš, J. Marcel Dekker, New York.

King, P. M. (1974) "Alleviation of water repellence in sandy soils of the USA" Sagric Internal Publ. S.26 14p

King, P. M. (1981)."Comparison of methods for measuring severity of water repellence of sandy soils and assessment of some factors that affect its measurement." Aust. J. Soil Res. **19** 275-285.

Krosshaven, M., Bjørgum, J. O., Krane, J. and Steinnes, E. (1990)."Chemical structure of terrestrial humus materials formed from different vegetation characterized by solid state 13-C NMR with CP-MAS techniques." J. Soil Sci. **41** 371-377.

Kunc, F. and Stotsky, G. (1974)."Effect of clay minerals on heterotrophic microbial activity in soils." Soil Sci. **118** 186-195.

Letey, J. (1969) "Measurement of contact angle, water drop penetration time, and critical surface tension." *in:* Water Repellent Soils. Ed. DeBano, L. F. and Letey, J. University of California pp 43-47.

Letey, J., Osborn, J. and Pelishek, R. E. (1962a)."Measurement of liquid-solid contact angles in soil and sand." Soil Sci. **93** 149-153.

Letey, J., Pelishek, R. E. and Osborn, J. (1961)."Wetting agents." Calif. Agric. **15** 8-9.

Letey, J., Welch, N., Pelishek, R. E. and Osborn, J. (1962b)."Effect of wetting agents on irrigation of water repellent soils." Calif. Agric. **16** 12-13.

Lunt, O. R., Sciaroni, R. H. and Enomoto, W. (1963)."Organic matter and wettability for greenhouse soils." Calif. Agric. **17** 6.

Ma'shum, M. (1988) "A molecular basis for, and the alleviation of water repellency in soils." PhD. Thesis. University of Adelaide pp 148.

Ma'shum, M. and Farmer, V. C. (1985)."Origin and assessment of water repellency of a sandy South Australian soil." Aust. J. Soil Res. **23** 623-626.

Ma'shum, M., Oades, J. M. and Tate, M. E. (1989)."The use of dispersible clays to reduce water repellency of sandy soils." Aust. J. Soil Res. **27** 797-806.

Ma'shum, M., Tate, M. E., Jones, G. P. and Oades, J. M. (1988)."Extraction and characterization of water repellent materials from Australian soils." J. Soil Sci. **39** 99-110.

Mackintosh, E. E. (1969) "The displacement of potassium from micaceous minerals." Ph.D. Thesis. University of Adelaide

Mallik, A. U. and Rahman, A. A. (1985)."Soil water repellency in regularly burned Calluna heathlands: comparison of three measuring techniques." J. Env. Mgt. **20** 207-218.

Marshall, K.C. and Roberts, F.J. (1963). "Influence of fine particle materials on survival of *Rhizobium trifolii* in sandy soil." Nature **198** 410-411.

Martin, J. P. and Haider, K. (1986)."Influence of mineral colloids on turnover rates of soil organic carbon." ***in*** Interactions of soil minerals with natural organics and microbes. Ed. Huang, P M, and Schnitzer, M. Soil Sci. Soc. of Amer. Special Publication No. 17.

McFarlane, D. J., Howell, M. R., Ryder, A. T. and Orr, G. J. (1992)."The effect of agricultural development on the physical and hydraulic properties of four Western Australian soils." Aust. J. Soil Res. **30** 517-532.

McGhie, D. A. (1979)."Managing water repellent soils." J. Agric. (W.A. Dept. Agric.) **20** 78-81.

McGhie, D. A. (1980)."The contribution of the mallet hill surface to runoff and erosion in the Narrogin region of Western Australia." Aust. J. Soil Res. **18** 299-307.

McGhie, D. A. and Posner, A. M. (1980)."Water repellence of a heavy textured Western Australian surface soil." Aust. J. Soil Res. **18** 309-323.

McGhie, D. A. and Posner, A. M. (1981)."The effect of plant top material on the water repellence of fired sands and water repellent sands." Aust. J. Agric. Res. **32** 609-620.

McGhie, D. A. and Tipping, P. I. (1983)."Beating the non-wetting soil problem." J. Agric. (W.A. Dept. Agric.) **24** 84-86.

Meyers, P. A. and Quinn, J. G. (1971)."Fatty acid-clay mineral association in artificial and natural sea water solutions." Geochim. Cosmochim. Acta. **35** 628-632.

Meyers, P. A. and Quinn, J. G. (1973)."Factors affecting the association of fatty acids with mineral particles in sea water." Geochim. Cosmochim. Acta. **37** 1745-1759.

Miller, R. H. and Wilkinson, J. F. (1977)."Nature of the organic coating on sand grains of nonwettable sand greens." Soil Sci. Soc. Amer. J. **41** 1203-1204.

Miyamoto, S. (1985)."Effects of wetting agents on water infiltration into poorly wettable sand, dry sod and wettable soils." Irrig. Sci. **6** 271-279.

Moucawi, J., Fustec, E. and Jambu, P. (1981)."Biooxidation of added and natural hydrocarbons in soils: effect of iron." Soil Biol. Biochem. **13** 335-342.

Muljadi, D., Posner, A.M. and Quirk, J.P. (1966). "The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite. Part 1. The isotherms and effect of pH on adsorption." J. Soil Sci. **17** 212-229.

Mustafa, M. A. and Letey, J. (1969)."The effect of two nonionic surfactants on aggregate stability of soils." Soil Sci. **107** 343-347.

Mustafa, M. A. and Letey, J. (1971)."Effect of two nonionic surfactants on penetrability and diffusivity of soils." Soil Sci. **111** 95-100.

Nakaya, N., Motomura, S. and Yokoi, H. (1977)."Some aspects on water repellency of soils." Soil Sci. Plant Nutr. **23** 409-415.

Nayak, D. C., Varadachari, C. and Ghosh, K. (1990)."Influence of organic acidic functional groups of humic substances in complexation with clay minerals." Soil Sci. **149** 268-271.

Oades, J. M. (1984)."Interactions of polycations of aluminium and iron with clays." Clays Clay Mins. **32** 49-57.

Oades, J. M. (1986)."Associations of colloidal materials in soils." Trans. XIII Congr. Int. Soc. Soil Sci. Hamburg **6** 660-674.

Oades, J. M., Vassallo, A. M., Waters, A. G. and Wilson, M. A. (1987). "Characterization of organic matter in particle size and density fractions from a Red-brown Earth by solid state 13C N.M.R." Aust. J. Soil Res. **25** 71-82.

Oades, J.M., Waters, A.G., Vassallo, A.M., Wilson, M.A., and Jones, G.P. (1988)."Influence of management on the composition of organic matter in a red-brown Earth as shown by ^{13}C nuclear magnetic resonance." Aust. J. Soil Res. **26** 289-299.

Olsen, S. R., Watanabe, F. S., Clark, F. E. and Kemper, W. D. (1964)."Effect of hexadecanol on evaporation of water from soil." Soil Sci. **97** 13-18.

Osborn, J., Letey, J., DeBano, L. F. and Terry, E. (1967)."Seed germination and establishment as affected by non-wettable soils and wetting agents." Ecology **48** 494-497.

Osborn, J. F., Pelishek, R. E., Krammes, J. S. and Letey, J. (1964)."Soil wettability as a factor in erodibility." Soil Sci. Soc. Amer. Proc. **28** 294-295.

Parfitt, R. L. and Greenland, J. D. (1970)."Adsorption of polysaccharides by montmorillonite." Soil Sci. Soc. Amer. J. **34** 862-866.

Parr, J. F. and Norman, A. G. (1964)."Effects of nonionic surfactants on root growth and cation uptake." Plant Physiol. **39** 502-507.

Pelishek, R. E., Osborn, J. and Letey, J. (1962)."The effect of wetting agents on infiltration." Soil Sci. Soc. Amer. Proc. **26** 595-598.

Pennell, K. D., Rhue, R. D. and Harris, W. G. (1991)."The effect of heat treatments on the total charge and exchangeable cations of Ca-, Na-, and Li-saturated kaolinite." Clays & Clay Mins. **39** 306-315.

Peterson, J. B. (1944)."The effect of montmorillonitic and kaolinitic clays on the formation of platy structures." Soil Sci. Soc. Amer. Proc. **9** 37-48.

Philip, J. R. (1971)."Limitations on scaling by contact angle." Soil Sci. Soc. Amer. Proc. **35** 507-509.

Prescott, J. A. and Piper, C. S. (1932)."The soils of the South Australian mallee." R. Soc. S. Aust. Trans. **56** 118-147.

Prusinkiewicz, Z. and Kosakowski, A. (1986)."Zwilzalnosc prochnicy jako czynnik ksztaltujacy gospodarke wodna gleb lesnych." Rocz. Glebozn. **37** 3-23.

Rao, H. K., Cases, J. M. and Forssberg, K. S. E. (1991)."Mechanism of oleate interaction on salt-type minerals. V. Adsorption and precipitation reactions in relation to the solid/liquid ratio in the synthetic flourite-sodium oleate system." J. Coll. Interface Sci. **145** 330-348.

Rawitz, E. and Hazan, A. (1978)."The effect of stabilized, hydrophobic aggregate layer properties on soil water regime and seedling emergrnce." Soil Sci. Soc. Amer. J. **42** 787-793.

Roberts, E. C. and Lage, D. P. (1965)."Effects of an evaporation retardant, a surfactant, and an osmotic agent on foliar and root development of Kentucky Bluegrass." Agron. J. **57** 71-74.

Roberts, F. J. (1966)."The effects of sand type and fine particle amendments on the emergence and growth of Subterranean Clover (Trifolium subterranean L.) with particular reference to water relations." Aust. J. Agric. Res. **17** 657-672.

Roberts, F. J. and Carbon, B. A. (1972)."Water repellence in sandy soils of south-western Australia. II. Some chemical characteristics of the hydrophobic skins." Aust. J. Soil. Res. **10** 35-42.

Rybina, V.V. (1973)."Effect of surface wettability on the capillary movement of water in the soil." Sov. Soil Sci. **5** 623-627.

Sansone, F. J., Andrews, C. C. and Okamoto, M. Y. (1987)."Adsorption of short chain organic acids onto nearshore marine sediments." Geochim. Cosmochim. Acta. **51** 1889-1896.

Savage, S. M. (1974)."Mechanism of fire induced water repellency in soil." Soil Sci. Soc. Amer. Proc. **38** 652-657.

Savage, S. M., Martin, J. P. and Letey, J. (1969a)."Contribution of humic acid and a polysaccharide to water repellency in sand and soil." Soil Sci. Soc. Amer. Proc. **33** 149-151.

Savage, S. M., Martin, J. P. and Letey, J. (1969b)."Contribution of some soil fungi to natural and heat induced water repellency in sand." Soil Sci. Soc. Amer. Proc. **33** 405-409.

Savage, S. M., Osborn, J., Letey, J. and Heaton, C. (1972)."Substances contributing to fire-induced water repellency in soils." Soil Sci. Soc. Amer. Proc. **36** 674-678.

Sawada, Y., Aylmore, L. A. G. and Hainsworth, J. M. (1989)."Development of a soil water dispersion index (SOWADIN) for testing the effectiveness of soil wetting agents." Aust. J. Soil Res. **27** 17-26.

Schnitzer, M. and Neyroud, J.A. (1975) "Alkanes and fatty acids in humic substances." Fuel **54** 17-19.

Scholl, D. G. (1971)."Soil wettability in Utah juniper stands." Soil Sci. Soc. Amer. Proc. **35** 344-345.

Scholl, D. G. (1975)."Soil wettability and fire in Arizona chaparral." Soil Sci. Soc. Amer. Proc. **39** 356-361.

Schreiner, O. and Shorey, E. C. (1910)."Chemical nature of soil organic matter." U.S. Dept. Agr. Bureau Soils Bull. **74** 1-48.

Schulten, H.-R., Hempfling, R., Haider, K., Gröblinghoff, F. F., Lüdemann, H.-D. and Fründ, R. (1990)."Characterization of cultivation effects on soil organic matter." Z. Pflanzenernäehr. Bodenk. **153** 97-105.

Schulten, H.-R. and Schnitzer, M. (1992)."Structural studies on soil humic acids by Curie-point pyrolysis-gas chromatography/mass spectrometry." Soil Sci. **153** 205-224.

Scott, D. F. and Van Wyk, D. B. (1990)."The effects of wildfire on soil wettability and hydrological behaviour of an afforested catchment." J. Hydrol.(Amst.) **121** 239-256.

Sevink, J., Imeson, A. C. and Verstraten, J. M. (1989)."Humus form development and hillslope runoff, and the effects of fire and management, under Mediterranean forest in NE-Spain." Catena **16** 461-475.

Sharma, P. K. (1990)."Use of urea formaldehyde as a soil conditioner in improving hydrophysical properties of sand." Ind. Soc. Soil Sci. J. **38** 528-530.

Sidheswaran, P., Bhat, A. N. and Ganguli, P. (1990)."Intercalation of salts of fatty acids into kaolinite." Clays and Clay Mins. **38** 29-32.

Solinas, V., Melis, P., Premoli, A. and Gessa, C. (1988)."On the lipidic fraction of some typical Mediterranean soils from micaschists." Z. Pflanzenernäehr. Bodenk. **151** 357-362.

Stevenson, F. J. (1966)."Lipids in soils." Amer. Oil. Chem. Soc. J. **43** 203-210.

Tegelaar, E. W., de Leeuw, J. W. and Saiz-Jimenez, C. (1989)."Possible origin of aliphatic moieties in humic substances." The Sci. Total Env. **81/82** 1-17.

Theng, B. K. G. (1974) "The chemistry of clay-organic reactions." Adam Hilger Ltd., London pp 343.

Theng, B. K. G., Churchman, G. J. and Newman, R. H. (1986)."The occurrence of interlayer clay-organic complexes in two New Zealand soils." Soil Sci. **142** 262-266.

Tillman, R. W., Scotter, D. R., Wallis, M. G. and Clothier, B. E. (1989)."Water repellency and its measurement by using intrinsic sorptivity." Aust. J. Soil Res. **27** 637-644.

Tschapek, M., Ardizzi, G. P. and de Bussetti, S. G. (1973)."Wettability of humic acid and its salts." Z. Pflanzenernäehr. Bodenk. **135** 16-30.

Tucker, K. A., Karnok, K. J., Radcliffe, D. E., Landry, G. J., Roncadori, R. W. and Tan, K. H. (1990)."Localised dry spots as caused by hydrophobic sands on bentgrass greens." Agron. J. **82** 549-555.

Valat, B., Jouany, C. and Riviere, L. M. (1991)."Characterisation of the wetting properties of air-dried peats and composts." Soil Sci. **152** 100-107.

Valoras, N., Letey, J. and Osborn, J. F. (1974)."Uptake and translocation of a nonionic surfactant by barley." Agron. J. **66** 436-438.

Van Dam, J. C., Hendrickx, J. M. H., Van Ommen, H. C., Bannink, M. H., Van Genuchten, M. T. and Dekker, L. W. (1990)."Water and solute movement in a coarse-textured water repellent field soil." J. Hydrol. (Amst.) **120** 359-379.

van't Woudt, B. D. (1954)."On factors governing subsurface storm flow in volcanic ash soils, New Zealand." Amer. Geophys. Un. Trans. **35** 136-144.

van't Woudt, B. D. (1959)."Particle coatings affecting the wettability of soils." J. Geophys. Res. **64** 263-267.

Varadachari, C., Mondal, A. H. and Ghosh, K. (1991)."Some aspects of clay-humus complexation: Effect of exchangeable cations and lattice charge." Soil Sci. **151** 220-227.

Vecchioli, G. I., Del Panno, M. T. and Painceira, M. T. (1990)."Use of selected autochthonous soil bacteria to enhance degradation of hydrocarbons in soil." Environ. Poll. **67** 249-258.

Velasco-Molina, H. A., Swoboda, A. R. and Godfrey, C. L. (1971)."Dispersion of soils of different mineralogy in relation to sodium adsorption ratio and electrolyte concentration." Soil Sci. **111** 282-287.

Vityn', Ya. V. (1961)."Sandy soils of the Latvian SSR." Tr. Inst. Lesokhozyaystvennykh Problem, Riga, No. 3.

Wallis, M. G. and Horne, D. J. (1992)."Soil water repellency." Advances in Soil Science Volume 20, pp 91-146.

Wallis, M. G., Scotter, D. R. and Horne, D. J. (1991)."An evaluation of the intrinsic sorptivity water repellency index on a range of New Zealand soils." Aust. J. Soil Res. **29** 353-362.

Wander, I. W. (1949)."An interpretation of the cause of water repellent sandy soils found in citrus groves of central Florida." Science **110** 299-300.

Ward, S. C. (1984) "Increasing the productivity of sandy soils by amendment with the fine residue from bauxite mining." *in:* Proc. Aust. Soil Sci. Soc. Nat. Soils Conf., Brisbane pp 348.

Watson, C. L. and Letey, J. (1970)."Indices for characterising soil-water repellency based upon contact angle-surface tension relationships." Soil Sci. Soc. Amer. Proc. **34** 841-844.

Weiss, A. (1963)."Mica-type layer silicates with alkylammonium ions." Clays and Clay Mins. **10** 191-224.

Wessel, A. T. (1988)."On using the effective contact angle and the water drop penetration time for classification of water repellency in dune soils." Earth Surf. Processes and Landforms **13** 555-561.

Wetherby, K. G. (1984)."The extent and significance of water repellent sands on Eyre Peninsula." Dept. Agric. South Aust. Technical Report No. 47.

Wetherby, K. G., Davies, W. J. and Matheson, W. E. (1983)."Wind erosion on Eyre Peninsula 1975-1979." Dept. Agric. South Aust. Technical Report No. 31.

Wilkinson, J. F. and Miller, R. H. (1978)."Investigation and treatment of localised dry spots on sand golf greens." Agron. J. **70** 299-304.

Yariv, S. and Shoval, S. (1982)."The effects of thermal treatments on the associations between fatty acids and montmorillonite." Israel J. Chem. **22** 259-265.