A MOLECULAR BASIS FOR, AND THE ALLEVIATION OF WATER-REPELLENCY IN SOILS

by

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SUMMARY

A literature survey of the extent and nature of water-repellency in soils showed that the phenomenon occurs world-wide and is a particular agricultural problem across southern Australia. A number of soils from areas notorious for non-wetting sands (South East of South Australia and coastal areas of South West of Western Australia) were obtained for examination of the water-repellent phenomenon.

In chronological order, this thesis covers the following aspects :

1. Effects of wetting, drying and salt treatments on water-repellent soils.

It was observed, that water-repellent soils were rendered wettable after freeze drying of moist soils, however, air and oven drying of the moistened soils only marginally reduced water-repellency. These effects have been attributed to a re-orientation of organic molecules. The orientation of hydrophobic and hydrophilic groups of organic matter is controlled by the presence of water-molecules. The hydrophilic groups tend to hydrogen bond to water molecules in wet situations and as the water is lost, polar groups hydrogen bond with each other causing the exposure of hydrophobic chains and a water-repellent surface. However, during the lower temperatures of the freeze drying process the water molecules are apparently lost without significant molecular rearrangements leaving a hydrophilic surface with exposed polar groups.

There were considerable changes observed in water-repellency as affected by treatments with some aqueous solutions and chloride salts. The type of cations present on water-repellent surfaces was noted to be important because cations also affect orientation of hydrophobic organic matter in soils.

Water-repellency in soils is known to be reduced by agitation due to the abrasive removal of organic matter from sand surfaces. However, floatable organic particles in soils are also hydrophobic. In soils such particles are intermixed with sand particles.

2. *Extraction of causal agents from water-repellent soils.*

Soxhlet extraction was chosen to minimize abrasion during the extraction of water-repellent materials from soils. The decrease in water-repellency of residual soil in the thimble was monitored as a function of time and provided clear data on the relative efficacy of various solvent mixtures.

Refluxing with an amphiphilic mixture of *iso*-propanol/15.7 M ammonia (7:3, by volume) completely extracted water-repellent materials from all soils examined. The residual soil in the thimble was readily wettable after 8 h extraction. By contrast, relatively non-polar lipid solvents, such as chloroform, ether and tetrachloroethylene, only marginally reduced water-repellency of soils. Thus the importance of polarity of solvent was established.

All of the extracted materials created water-repellency when they were coated upon acid washed sand. However, the degree of water-repellency induced at an arbitrary constant concentration of 400 mg kg^{-1}, as measured by the MED values, varied with the type of extractant. This variation may be ascribed to the presence of differing ratios of hydrophobic to hydrophilic components in the crude extracts.

3. *Characterization of water-repellent materials.*

Spectroscopic and chromatographic data established that water-repellent materials extracted by the mixture of *iso*-propanol/ammonia from sandy soils collected from Tintinara in the South East of South Australia were a mixture of long chain polymethylene waxes consisting of acids, alcohols and their compound esters. Major constituents of the extracted materials were long chain (16-32 carbon) fatty acids and long chain (14-28 carbon) alcohols. The most prominent acids were palmitic acid (C_{16}) and behenic acid (C_{22}), whereas up to 44 % of the alcohol content in the unsaponifiable fraction was cetyl alcohol (C_{16}).

Cetyl alcohol was observed to create highly water-repellent sands and has provided a useful model system for studies of water-repellency. It was necessary for the sand to be coated with an amount of cetyl alcohol equivalent to one uniform monolayer before it exhibited any measurable water-repellency; but to reach the plateau of maximum hydrophobicity (MED value 7), an amount of cetyl alcohol equivalent to 16 monolayers was required. A scanning electron micrograph of the sand coated with cetyl alcohol at a concentration of 400 mg kg^{-1} showed a papillate appearance of coalescent globules (diameter ~ 150-300 nm) covering all the sand grains.

4. Development of practical procedures for alleviation of water-repellency.

The degree of water-repellency produced by both natural and reference organic compounds on sand surfaces was found to be positively correlated with their concentration up until the maximum plateau level was reached and is also a function of the surface area of the sand. These data suggested, that the water-repellent problems of light textured soils might be nullified by simply increasing their surface area.

Laboratory experiments established that the application of fine particle materials such as oxides, lime, aerosil (a finely divided commercial silica) and clays to either Tintinara soils or acid washed sand coated with cetyl alcohol reduced the severity of their water-repellency. Incorporation of clays appears to be a useful approach to combat the problem, because clay would provide additional benefits, such as increased cation exchange capacity, to the soils. In laboratory studies the application of clay at a concentration of 10 g kg^{-1} (which is equivalent to 10 tonnes ha^{-1}) rendered a water-repellent Tintinara soil (MED value 3.5) wettable (MED value 0).

The dispersibility of clays, which determines their ability to mix with sands, was found to be an important feature in their effectiveness for minimizing water-repellency. This applies to both the natural sandy soils as well as the model cetyl alcohol-sand mixture. It is therefore important to consider factors influencing the dispersibility, such as sodicity and mineralogy, when selecting a particular clay to ameliorate the water-repellency of soils.

The initial field trial was commenced before the significance of dispersible clays was recognised. Nevertheless, the application of a flocculated clay to a sandy soil (MED value 3.1) near Keith in the South East of South Australia in a field experiment measurably reduced water-repellency of the soil. Clay spread on the surface at a rate of 20 tonnes ha^{-1} produced a continuous decrease in MED values from 3.1 to 0.8 over a period of 46 weeks. The incorporation of clay also improved the water regime of the sandy soil. However, there were no significant differences observed in lucerne establishment. With hindsight it is to be anticipated that better results will be obtained in the future with more dispersive clays.