Soil Water Repellency a Global Phenomenon: Impact, Measurement and Mechanisms

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Abstract

Food security and production is a major global issue. It has become essential to work the land efficiently, through better soil management and agronomy, whilst protecting the environment from air and water pollution. The reduced ability of some soils to become wetted and absorb water - soil water repellency - is a major environmental problem in many parts of the world. It can have serious environmental implications such as increased overland flow and soil erosion, poor uptake of agricultural chemicals, and increased risk of groundwater pollution due to the rapid transfer of contaminants and nutrient leaching through uneven wetting and preferential flow pathways. The initial degree of water repellence of the soil surface is usually assessed by measurement of the soil-water contact angle, whilst the time-dependent wettability is most commonly assessed by measuring the time taken for water drops to eventually penetrate the soil completely. Both chemical and physical factors play a role in determining soil water repellency. Organic compounds deposited on soil mineral or aggregate surfaces have long been recognised as a major factor, and the surface structure of the soil has also been implicated particularly in influencing soil-water contact angle. Here we discuss the environmental impact of soil water repellency, the factors and mechanisms which are thought to be important in causing repellency, the way repellency is measured and classified, and our current work on the significance of surface structure in influencing solid-water contact angles for non-planar surfaces such as soils.

Keywords: soil, water-repellency, contact-angle, surface-structure, environment

Introduction

Soil water repellency is the reduced ability of some soils to be wetted and absorb water. It is a global phenomenon that can lead to major environmental problems. It can have serious environmental implications such as increased overland flow and soil erosion, poor uptake of agricultural chemicals, and increased risk of groundwater pollution due to the rapid transfer of contaminants and nutrient leaching through uneven wetting and preferential flow pathways.

When a drop of liquid is brought into contact with a flat solid surface, the final shape taken up by the drop, and the solid-liquid contact angle, Θ, depend on the relative magnitudes of the molecular forces that exist within the liquid (cohesive) and between the liquid and solid (adhesive) (Jaycock and Parfitt, 1981). The term wetting is often used loosely, for practical purposes it is usually said if $\Theta>90^{o}$ the liquid does not wet the solid and if $\Theta<90^{o}$ the liquid does wet the solid, although strictly wetting only occurs if $\Theta=0$.

Soil water repellency has been researched extensively, particularly over the last few decades, and researchers continue to investigate the chemical and physical factors behind this phenomenon in an attempt to understand how and why it occurs, and how it may be reduced and managed.

Here we briefly discuss the environmental impact of soil water repellency, the factors and mechanisms which are thought to be important in causing repellency, the way repellency is measured and classified, and our current work on the significance of surface structure in influencing contact angles on non-planar surfaces such as soils.

We also note that the study and understanding of liquid/surface contact angles is important in other disciplines and in a number of industries, such as flotation, painting and weather-proofing (Pashley and Karamen, 2004).

Impact – Environmental Implications

Soil water repellency can have serious environmental implications. If water cannot infiltrate and be absorbed into the soil, there is risk of overland flow. This can lead to flooding and enhanced soil erosion. Overland flow, in particular, has been linked to fire-induced or fire-enhanced water repellency by wildfires (Mainwaring, 2004). Water repellency also indirectly contributes to soil erosion by wind as soils can become more susceptible to erosion when left bare and dry, which is more likely to occur in soils that are water repellent (Carter, 1990).

Soil water repellency can also lead to the poor uptake of agricultural chemicals which is particularly important for food security. If agrochemicals, fertilisers and water cannot penetrate into the soil profile where required, it is likely to lead to decreased soil fertility, patchy crops and increased disease levels, leading to reduced overall yields and production. There is already an increased pressure on food production due to a growing global population and managing soil water repellency is likely to become increasingly important to ensure global food production.

Another environmental issue linked to soil water repellency is the increased risk of groundwater pollution by the rapid transfer of contaminants and nutrient leaching due to uneven wetting and preferential flow pathways. Valuable nutrients can not only be leached out rapidly through flow pathways within the soil profile but also, as a result of these, fail to reach other parts of the soil, which can lead to crop and soil nutrient deficiencies. Preferential flow paths can also lead to the depletion of plant available water (Dekker and Ritsema, 1996). Groundwater pollution through the leaching of nutrients and agrochemicals too rapidly through the soil profile can also be a serious issue resulting in pollution of water sources which in turn may affect aquatic habitats and water quality.

Whilst many of the environmental implications of soil water repellency are detrimental, there are also some beneficial effects. Water repellent soils have been used to direct the flow and collect runoff in drought-prone areas (Blackwell, 2000); they can also be used to prevent water loss through evaporation by creating an upper layer of soil that acts as an effective mulch which reduces the capillary rise of water (Wallis and Horne, 1992); and many plants have also now adapted to survive in severely water repellent conditions (Mainwaring, 2004).

Mechanisms

Both chemical and physical factors play a role in determining the occurrence and severity of soil water repellency.

Chemical factors

Organic compounds deposited on soil mineral or aggregate surfaces have long been recognized as a major factor for causing/inducing soil water repellency. The main groups of organic compounds involved are long chain acids, alkanes, amides, aldehydes/ketones and sterols (Mainwaring *et al*, 2004; Morley *et al*, 2005). Aliphatic hydrocarbons and polar substances with amphiphilic structures are considered the two chemical compounds regarded as most important in causing soil hydrophobicity (McIntosh and Horne, 1994). Mainwaring *et al* (2013) found that a combination of long chain acid and alkane to be most effective at inducing water repellency, but the extent of water repellency induced on acid washed sand varied considerably with compound type.

Organic compounds with hydrophobic properties are present as a coating on soil mineral and aggregate surfaces and also as interstitial matter. Within a soil, a mixture of wax-containing globules, clean soil particles, completely or partly coated soil particles and hydrophobic remnants such as roots, leaves and stems may be present. Possible sources of these compounds include: plant roots which can provide lipid-rich organic matter; surface waxes that can be mechanically eroded from plant leaves; fungal hyphae which can contain hydrophobic compounds; and lipids from the decomposition of ‘litter’. Wildfires can vaporize and alter organic matter, some of which condenses back into the soil (DeBano, 2000).

Physical factors

As well as chemical factors, the surface structure of the soil influences water repellency.

Physical factors such as particle size can influence the occurrence and severity of soil water repellency. It has been reported that for soil samples obtained from grass and forest areas the finer sieve fraction shows the most severe water repellency (Doerr *et al*, 1996; Rodriguez-Alleres *et al*, 2007). Sandy soils have the lowest specific surface areas, so a given amount of hydrophobic material will affect a greater proportion of particles in a sandy soil than in a loamy or clayey soil (Woche *et al*, 2005). Surface roughness affects interfacial energies and therefore individual particles can amplify the contact angle of the soil water repellency (Ahn, 2014).

Measurement Techniques

The initial degree of soil water repellency is usually assessed by measurement of the soil water contact angle, whilst the time-dependent wettability is most commonly assessed by measuring the time taken for water drops to eventually penetrate the soil completely.

Water Drop Penetration Time (WDPT) Test

The time-dependent wettability is most commonly assessed by measuring the time taken for water drops to eventually penetrate the soil completely, the Water Drop Penetration Time (WDPT). The methodology of WDPT tests is discussed in greater detail in Doerr (1998) and more recently by Hallin *et al* (2013). Dekker *et al* (2009) classified soil water repellency in six classes from 0 to 6 going from wettable to extremely water repellent as WDPT increases. It is a crude measurement of the severity of water repellency but can be a useful and straightforward method for use in both the laboratory and in the field.

Contact Angle

The initial degree of soil water repellency can be assessed by measurement of the soil-water contact angle and this is often done using the sessile drop method (Bachmann *et al*, 2000). Liquid water has a high surface energy, or surface tension. Solids with low surface energies (or low surface tensions), such as hydrocarbons are not wetted by water and have water repellent surfaces, whereas solids with high surface energies such as silica are wetted and have wettable surfaces. The contact angle between a liquid and a solid surface is determined by the balance of interfacial tensions of the three phases present (solid, liquid and vapour) (Jaycock and Parfitt, 1981). A liquid drop with high surface tension resting on a low energy solid forms a spherical shape with a high contact angle. As the solid surface energy increases, the drop forms a flatter, lower profile shape and gives a lower contact angle (Llewellyn, 2005). Hence, a large contact angle indicates high water repellency, and a low contact angle indicates a hydrophilic surface.

In general, the measured contact angles of irregular surfaces are higher than those of a flat surface of the same material. Understanding the amplification of contact angle by surface structure has for many years been based on the theoretical models of Cassie and Baxter (1944), for bridge-like wetting over the top of protrusions, and Wenzel (1936) for complete wetting of a jagged surface. Both models are based on the thermodynamics of surface energies, i.e. the contact angle is calculated from the energy required to expand the surface. In the Cassie-Baxter model this energy is great that for a flat solid surface because the water drop hangs in the air between the protrusions, and thus expansion of the 'surface' requires expansion of both the water-air and water-solid interfaces. The surface has an apparent surface energy lower than that for the flat solid surface because it is a mix of solid material and air. The decrease in surface energy can be calculated from the geometry of the surface, e.g. Cassie and Baxter gave an analysis of a 'surface' made of equally space thin round wires. In the Wenzel model the energy is greater for the irregular surface because the 'true' liquid-solid contact area is greater than the 'apparent' surface area because of the surface roughness; Wenzel introduced a roughness factor into the surface energy equations to account for this.

In order to apply the Cassie-Baxter model to soils, McHale *et al* (2005) developed a geometric model of the soil surface in which soil particles were approximated as smooth spheres in a hexagonally packed arrangement. The Cassie and Baxter model (1944) was then applied to their model which includes, as a parameter, the inter-particulate distance which allows for the effect of imperfect packing. The inter-particulate distance is zero for perfect close packing and as the inter-particulate distance increases, the solid-liquid interface fraction decreases while the liquid air interface fraction increases and consequently the contact angle increases according to the Cassie-Baxter equation (Ahn, 2014). However there were some limitations to the model as it failed to include the effect of particle surface texture (Ahn, 2014).

Even though still widely used, there is currently much debate in the literature about the validity of these models and their applicability to soil science and soil water repellency. In 2007 Gao and McCarthy challenged the validity of the Wenzel (1936) and Cassie and Baxter equations (1944). They argue that it is contact lines and not contact areas which are key to determining contact angles. Gao and McCarthy (2007) argue that the interactions that take place between the liquid and solid at the 3-phase contact line is responsible for determining the contact angle and this is not linked to the interfacial area within the contact perimeter.

At the moment contact angles are used by soil scientists as an empirical measurement as they are widely used and relatively straight forward to carry out. It is important to remember that contact angles can be affected by many variables that include: temperature, relative humidity, surface roughness, droplet volume and sample preparation

Current Work – an experimental approach to evaluate the suitability of Cassie-Baxter for non-planar and irregular surfaces and application to soils

Both the Cassie and Baxter (1944) and Wenzel (1936) equations have adjustable parameters which can be used to fit data, and as a result these models can almost always give a fit for contact angle measurements. However, the required fitting parameter values are sometimes found to be physically unreasonable. For example, in the case of Cassie and Baxter the inter-particle distance (i.e. the length of the air gap between particles) is an adjustable parameter which, for the best fit to the experimental data, is often required to be bigger than physically sensible. A better approach to examining the suitability of the Cassie-Baxter equation for irregular surfaces would be to replace this adjustable parameter with a measured parameter. However, for soils there is the difficulty of inhomogeneous particle sizes, variable particle surface roughness, and essentially unknown particle packing arrangements. The literature to date has used soil and semi-homogenous glass spheres or semi-homogenous roughly close-packed spheres, so modelling of the data is complicated by particle inhomogeneity and variable packing efficiency. In answer to this we are taking a fundamental approach to this problem, and exploring contact angles on precisely controlled surfaces. In earlier work (Ahn, 2014) we used homogenous, water repellent silanised glass spheres, and recently we have used coated steel spheres and rods of very precise size which can be close packed and held in place using magnetic strips.

Methodology

In work by Ahn (2014) chemically hydrophobized glass beads were fixed using double adhesive tape on a flat microscope slide, or held on printed plastic templates by applying pressure and heat. For our current work, homogenous metal spheres were coated with paraffin wax using a rotary evaporator, and then fixed onto a magnetic strip attached to a microscope slide to achieve closely packed arrays (Fig.2).

Distilled water was placed onto surfaces using a syringe with a blunt tip needle (19 gauge Luer-Lock blunt ended needles, Sylmaster, UK). Approximately 5μl of water was expelled from the syringe to make a small hanging drop on the tip of the needle and the syringe was lowered until the drop contacted the surface. Then water was dispensed at the rate of 100μl min^{-1} to let the drop advance upon the surfaces (Ahn, 2014), until a final drop volume of 85μl was obtained. Contact angles were measured using videos (6.25fps) recorded using the EasyDrop FM40 KRAUSS goniometer. The left and right contact angles as viewed in the instrument at each advancing angle were averaged from the appropriate video stills using the Drop Shape Analysis (DSA) 100 software package (Ahn, 2014). At least 15 advancing angles per sample were taken at intervals through the video footage and averaged to give the overall result.

Preliminary Results

Measuring contact angles on smooth solid surfaces is relatively easy as the plane of the solid/liquid interface is easily recognizable. The placement of the horizontal baseline (see Figs 1 and 2) is key to obtaining an accurate contact angle for the surface being measured within the DSA software. Once placed in the appropriate place the droplet contour can be extracted using the DSA software and an average contact angle measurement from the left and right side angles can be obtained. For paraffin wax on a glass microscope slide we found a water-solid contact angle of $111.7^{o} \pm 0.6^{o}$ in reasonable agreement with the literature value 111^{o} (Jaycock and Parfitt, 1981).

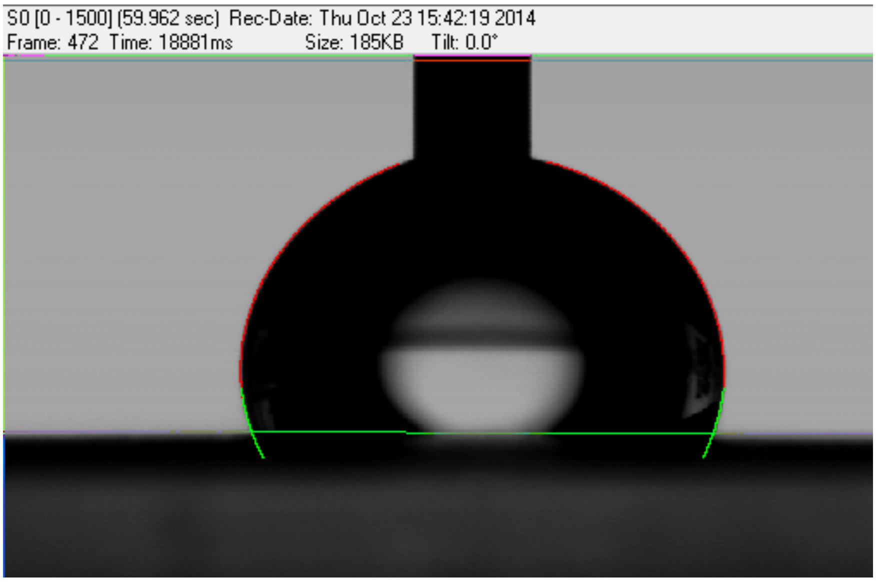

Figure 1 Video still of water droplet on a planar surface coated in paraffin wax with droplet contact angles extracted using DSA software

Figure 2 shows the video still for one of our precisely controlled homogenous close packed metal sphere surfaces. The 1mm diameter metal spheres are coated in paraffin wax and the advancing contact angle on this surface is 133.7^{o} $\pm 0.9^{o}$. This is considerably higher than the 111^{o} for a flat paraffin wax surface, and higher than the value of 129.8^{o} we have calculated using the modified Cassie-Baxter equation for close-packed spheres. Furthermore, we calculate fitting the data to Cassie-Baxter with a free fit inter-particulate distance would require an inter-particle air-gap of about 0.08 mm whereas these particles are perfectly close-packed without any inter-particle air-gap.

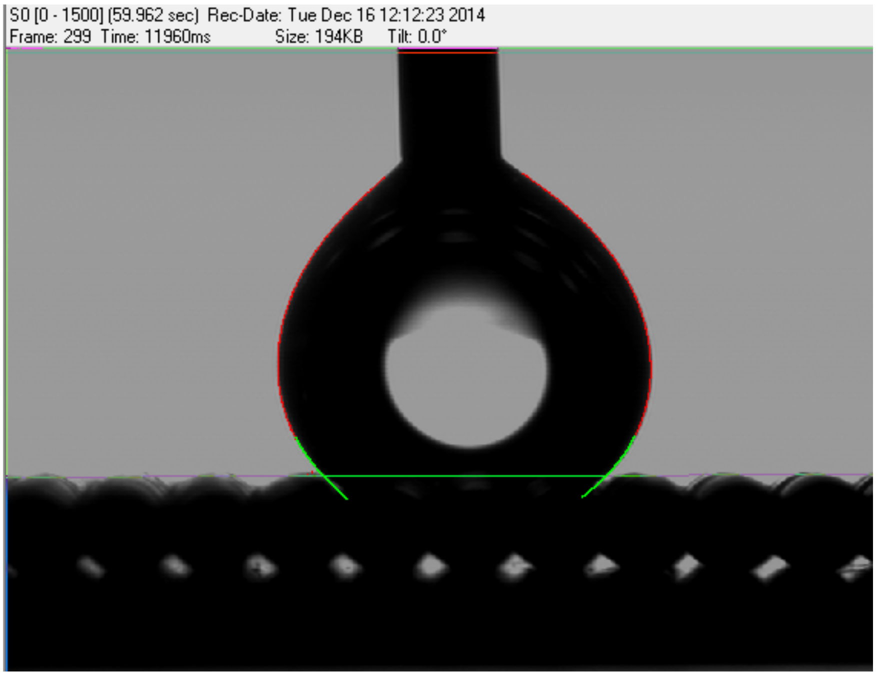

Figure 2 Video still of water droplet on a precisely controlled model surface of metal spheres coated in paraffin wax with droplet contact angles extracted using DSA software

All of our results to-date give contact angles that are larger than those calculated using the Cassie and Baxter equation. We are currently tentatively examining alternative interpretations of the origin of the apparent large contact angles on non-planar surfaces based on the way the droplet sits on the surface, in particular the geometry of the particle water drop interface and its relation with the choice of 'horizontal' reference line in the instrumental analysis.

Conclusions and Future Work

Based on our preliminary results with precisely controlled non-planar surfaces we find that the Cassie-Baxter (1944) model does not fit our experimental data; the experimental contact angles are bigger than those predicted by application of the Cassie-Baxter model.

We are currently examining alternative interpretations of the origin of the measured large contact angles on soils and other non-planar surfaces. Future work will include using model systems with different spheres sizes and different organic coating, as well as surfaces made with mixed spheres of various sizes and coatings along with different packing arrangements. Following this, application of knowledge gained from these studies of precisely controlled surfaces will be made to model soils, made up of sand grains with organic coatings, and then extended to natural soils.

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