



Water repellency as conditioned by particle size and drying in hydrophobized sand

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ABSTRACT

The effects of particle size and soil moisture on water repellency (WR) from hydrophobized sand are studied in this research. Quartz sand samples were separated into three sieve fractions: 0.5–2 mm (coarse sand, CS), 0.25–0.5 mm (medium sand, MS), and 0.05–0.25 mm (fine sand, FS). WR of sand was induced using different concentrations of stearic acid (SA; 0.5, 1, 5, 10, 20 and 30 g kg⁻¹). Moist samples have been exposed to two types of drying: air-drying at standard laboratory conditions and oven-drying at 50 °C. Change in moisture content, and water repellency has been monitored every 24 h for 10 days. After 1 day of drying, SA concentrations ≥ 10 g kg⁻¹ caused extreme WR in oven-dry samples, independently of sieve fraction. In air-dried samples, time of drying and decreasing soil moisture content increased WR, but an erratic behaviour was observed in MS and FS samples. All air- and oven-dried samples became extremely water repellent after 7 days of treatment. At all SA concentrations and drying temperatures, WR was extreme in the CS fraction after one day. Superhydrophobicity of CS samples is suggested as a possible explanation of this response. In MS and FS samples, water repellency showed an erratic behaviour at lower SA contents, which may be due to contact of water droplets with a high proportion of areas not covered by hydrophobic coatings. The higher severity of WR observed in CS is in agreement with the idea of hydrophobicity associated with coarser particles. Coarse-textured soils have a lower specific surface than fine-textured soils, and a limited amount of organic matter may cause higher WR than in finely textured soils.

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1. Introduction

Water repellency (WR) is a property of soils that reduces water infiltration capacity. Soil WR also affects evaporation, erosion, structure and the hydrological behaviour of soils (Feng et al., 2001; Mataix-Solera et al., 2011; Wallis and Horne, 1992; Wallis et al., 1991). This property is a very common soil phenomenon occurring in different climatic regions, soil types and land use types, which has a very important hydrological implications in soil erosion, overland flow and runoff/infiltration rates. It has been reported from different regions, climates, soil types and land uses by many researchers (DeBano, 2000; Doerr et al., 2000).

Under natural conditions, wettable soil mineral surfaces are often coated by hydrophobic organic compounds (Doerr et al., 2000; Goebel

et al., 2004), causing soil WR. However, many other factors are involved, and the presence of hydrophobic coatings does not always induce soil WR, as it has been reported by Doerr et al. (2005), Leelamanie and Karube (2007), and Mataix-Solera et al. (2008). Soil WR is associated with content and chemical nature of soil organic matter (Doerr and Thomas, 2000), vegetation (Dekker and Ritsema, 1996a; Doerr et al., 1998), microorganisms (Jex et al., 1985; Savage et al., 1969), soil mineralogy and soil type (Mataix-Solera et al., 2008; Zavala et al., 2009a), texture (Bachmann et al., 2006; Woche et al., 2005) and high temperatures occurring during wildfires (Doerr et al., 2006; Granged et al., 2011; Jordán et al., 2010; Jordán et al., 2011; Zavala et al., 2009b; Zavala et al., 2010a).

It has long been argued that soil WR is associated with coarse soil textural fractions (Roberts and Carbon, 1972; McGhie and Posner, 1980; DeBano, 1991). If a certain amount of hydrophobic substances is coating soil particles, larger particles are more susceptible to develop WR because of its lower specific surface (Giovannini and Lucchesi, 1983; Blackwell, 1993). In soils under eucalyptus, Crockford et al.

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(1991) observed that WR increased with particle size. Furthermore, DeBano (1991) concluded that WR is most likely to occur in soils with less than 10% clay content. It is now well established that the addition of clays can be very effective in reducing the soil WR in sandy (Ma'shum et al. 1988; Cann and Lewis, 1994; Carter and Hetherington, 1994; Harper and Gilkes, 1994; McKissock et al., 2000; Dlapa et al., 2004). Besides increasing the surface/volume ratio, clay helps to decrease soil WR by coating hydrophobic surfaces (Ward and Oades, 1993). In contrast, it has been observed that soils containing 25–40% clay showed extreme WR (Chan, 1992; Crockford et al., 1991; Dekker and Ritsema, 1996b). It has been suggested that aggregation induced by clays reduces the surface necessary to produce WR by coating with hydrophobic substances (Bisdorf et al., 1993; Wallis et al., 1991). It may also happen that the size of the particles of hydrophobic organic material is sufficiently small to enhance the degree of repellency on the fine fractions compared to the thick ones (de Jonge et al., 1999).

Some authors have wondered whether specific surface or the size of sand or aggregates is more important (Harper et al., 2000), since the interaction between hydrophobic compounds and soil can occur between organic particles and aggregates, rather than single crystals (Franco et al., 1995). For example, the exposed surface in pores of size about 0.1 nm between silicate layers of smectite and illite could not contribute to soil WR, as hydrophobic molecules cannot enter them. In other cases, it has been shown that a certain amount of organic matter in the soil may be sufficient to cover fine particles, in addition to the mineral particles and coarse aggregates (Doerr et al., 1996). If this occurs, a fine textured soil could also show appreciable WR. Several authors (Chan, 1992; Crockford et al., 1991; Doerr et al., 1996) have confirmed this fact, as observed levels of WR in fine-textured soils as high as in other soil types.

Several studies have reported that soil WR decreases linearly with water content, with soils becoming wettable above a critical water content (Dekker et al., 2001; Lichner et al., 2006; Poulencard et al., 2004; Regalado and Ritter, 2005). But other authors have reported contradictory results, showing that soil WR may vary nonlinearly with moisture content. King (1981), for example, observed a rapid increase in soil WR with increasing moisture content between air-dry and wilting point, peaking around wilting point, and decreasing again rapidly when moisture content approached field capacity. In addition, de Jonge et al. (1999, 2007) observed complex responses to soil moisture content. According to their conclusions, some soils are completely wettable independently of water content or temperature. Some soils show a one-peak behaviour, with WR increasing with water content and decreasing after a certain threshold. Finally, some soils show a two-peak behaviour. In this case, soils show some degree of repellency when water content is very low (after oven drying), but WR declines and increases again reaching a second peak, after which soil becomes wettable. Goebel et al. (2004) observed that small variations in water potential may have significant impacts on the wettability of subcritical water-repellent soils, and concluded that maximum WR does not necessarily occur in oven-dry soil, but at certain specific soil water potentials. So, oven-dry soil samples may become increasingly wettable and significant differences may exist between wettability from oven-dry soil samples and soils under natural conditions with less negative water potential.

Severity of soil WR may change over time affecting geomorphological and hydrological soil processes (Dekker et al., 2001; Feng et al., 2001; Jordán et al., 2009; Leelamanie and Karube, 2007; Leighton-Boyce et al., 2005; Wallis and Horne, 1992; Wallis et al., 1991). According to Doerr et al. (2000), this variation depends on soil moisture content, and is related with the wetting/drying cycles caused by seasonal variations of soil moisture (de Jonge et al., 1999; Doerr and Thomas, 2000; Leelamanie and Karube, 2007; Zavala et al., 2009a). Recently, the influence of soil management on soil WR in the medium and long term has been highlighted. Although conservative practices and

mulching contribute to reduced soil erosion risk and considerably improve soil quality, some authors have found that high mulching rates enhance soil WR, increasing runoff generation rates (García-Moreno et al., 2013; González-Peñaloza et al., 2012).

However, although soil WR and its causes and consequences are well known phenomena, there are still gaps in research and some contradictions in the results reported by different investigators. In the case of sandy non-structured soils, the relationship between soil WR and texture, hydrophobic organic matter content, soil moisture content or drying temperature must be studied to better understand the involved mechanisms and processes. The objectives of this research are to study the effect of soil moisture content, drying temperature and the amount of hydrophobic organic matter in the severity and evolution of WR from different sand sieve fractions hydrophobized with stearic acid during air- and oven-drying.

2. Methods

2.1. Preparation of samples and experimental design

Quartz sand samples were collected from the top 15 cm of homogeneous sand horizons from the coast of Cádiz (SW Spain). When present, macroscopic organic residues were removed first by hand, then dry sieving (2 mm) and later by immersion of sand samples in distilled water, carefully removing any floating residues from the water surface. In order to guarantee the complete removal of the original organic matter from the sand material, soil samples were treated with H₂O₂ (6%) until effervescence disappeared. Sand samples were oven-dried (80 °C, 24 h) and carefully homogenised and separated into different sieve fractions: 0.5–2 mm (coarse sand, CS), 0.25–0.5 mm (medium sand, MS), and 0.05–0.25 mm (fine sand, FS). Organic C content was determined in triplicate samples from each sieve fraction by the Walkley–Black method (Walkley and Black, 1934). Extraction solutions were gently boiled (150 °C, 30 min) for complete digestion of organic C (Mebius, 1960), and organic C was measured by UV–vis spectrophotometry (600 nm). In all cases the result was 0.0000 g kg^{−1}. At this stage, complete wettability of all samples was checked using the WDPT test (see description below), with water drops infiltrating instantaneously in all cases.

Sieve fractions were each divided into various subsamples and a selection covered with solutions of stearic acid (SA) in diethyl ether. SA is a long-chain hydrophobic acid (molecular weight 284.5) which is considered to be a common organic acid in natural soils (Braids and Miller, 1975; Piccolo et al., 1996) able to increase the hydrophobic character of soil particles (Leelamanie and Karube, 2007; Leelamanie et al., 2008; Piccolo and Mbagwu, 1999). Using atomic force microscopy, Cheng et al. (2010) observed that SA is able to increase strong WR in comparison with other organic compounds due to its chemical structure and interactions with mineral surfaces. SA and sieve fractions were mixed using a magnetic stirrer in glass beakers during 2 h. Subsamples were kept in the fume hood overnight until all the diethyl ether had evaporated. In this way, precipitation of excess SA on the wall of glass beakers or as a layer above the sand was avoided. A range of sand subsamples containing 0.5, 1, 5, 10, 20 and 30 g kg^{−1} SA was obtained (Fig. 1 shows detailed views of CS sieve fractions coated with SA).

Individual sand subsamples from each sieve fraction and SA content (30 g, no replication) were placed in Petri dishes (approximately 10 mm depth for each sample), moistened with distilled water until 10% water content in weight, and homogenised. After a period of 30 min, persistence of WR was determined (see method below) and all samples were found wettable. To study differences between slow and fast drying cycles (e.g., between soil drying under cool conditions or under extreme hot dry weather), a set of subsamples (3 sieve fractions × 6 SA contents) was left air-drying at standard laboratory conditions in a controlled chamber (approx. 50% relative humidity, 25 °C), and a similar set was placed in an oven (50 °C) during the

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