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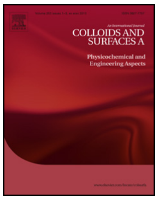

Soil water repellency: Dynamics of heterogeneous surfaces

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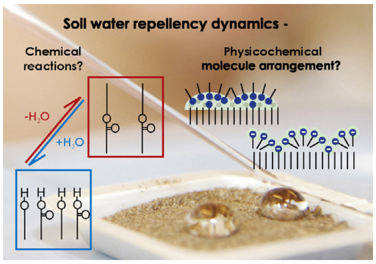
HIGHLIGHTS

- Suggested mechanisms of soil water repellency dynamics at two anthropogenic sites.
- Chemical nature of repellency: hydrolysis–condensation reaction.
- Physico-chemical nature of repellency: micelle-like aggregation of humic substances.

GRAPHICAL ABSTRACT



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ABSTRACT

Processes controlling the dynamics of the soil–water interfacial properties have a high impact on habitat, filter, buffer, storage, and transformation functions of a soil. Besides surface roughness and chemical heterogeneity, also the dynamics of surfaces properties in soils limit the application of well established methods of wettability determination for solid materials. Numerous studies investigated the influence of changing environmental conditions, like water content, pH and drying and wetting temperature on the repellency of soils. The present paper presents an integral approach linking some of the individual results of several studies. Two hypothetical models are suggested in order to explain differences in the nature of repellency between two types of sites and between wettable and repellent samples within each type of site. The chemical nature dominating the soil water repellency at the one type of sites can be best explained by hydrolysis–condensation reactions. The physico-chemical nature dominating the repellency on the other type of site is probably controlled by micelles- or reverse-micelles-like arrangement of amphiphilic molecules during drying. Wetting properties of the surface layers of organic coating on the soil particles then depend on number and size of amphiphilic molecules, pH and ionic strength in the soil solution. It is concluded that local site properties, e.g., soil-type, climate, or land-use, determine which mechanism controls the dynamics of repellency. Future research has to verify the suggested mechanisms before critical environmental conditions can be identified in order to prevent the negative impacts of soil water repellency.

1. Introduction

1.1. *Environmental relevance of soil water repellency*

Soil water repellency (SWR) is a surface property of soil which reduces or prevents water infiltration into the soil [1] with high impact on soil hydrology [2] and thereby on processes like mobilisation, transport and immobilisation of substances within a soil. Reduced infiltration capacity may lead to increased surface run off, increased erosion of top soil components [3–5], and thus an increased risk of surface waters pollution. By the development of uneven wetting patterns [6], the filter function of soil may be significantly reduced in repellent soils whereby the risk of groundwater contamination increases [7–9]. Repercussions of SWR on crops are reduced seed emergence and plant growth caused by water deficiency in the root zone [10,11]. In contrast, positive effects of SWR

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have been reported with regard to the stability of soil aggregates [12–16] and sequestering organic carbon [17–20]. Furthermore, SWR leads to a reduced loss of soil water by evaporation [21–23].

The appearance of SWR is found for a wide range of climatic conditions, parent soil material, and under various land use. The high complexity and chemical heterogeneity of soil makes it difficult to investigate its surface properties. Therefore, some methods of surface properties and their applicability in soil science are presented. Furthermore, wetting characteristics of soils are subjected to continuous changes under the influence of environmental conditions such as water content (WC), pH, temperature, and time. Therefore, the present review aims at a better understanding of the mechanisms which lead to changes in SWR. Results of studies investigating different influencing factors for SWR as well as process oriented investigations are presented. Finally, these results are linked to each other and under the consideration of site specific influences, two hypothetical models are suggested which may explain some of the presented results.

1.2. Determination of SWR

Numerous well established methods exist for the determination of wetting characteristics of solid material, e.g., Wilhelmy plate method, capillary rise method or sessile drop method (for details see textbooks, e.g., [24]). However, the chemical heterogeneity and macroscopic and microscopic surface roughness of soil material makes the application of most of these methods for determination of SWR difficult. Furthermore, soil surface properties are not static but may change with liquid contact time. In the following, some of the most common SWR methods and their limits of significance are presented.

The Water drop penetration time (WDPT) test is a very simple and rapid method. A drop of water is placed on a flattened soil surface and the time needed for the drop to penetrate into the soil is recorded [25]. For a better reproducibility, soil samples are calibrated to a defined ambient relative humidity [26], sieved, placed on a dish and smoothed [27,28] because surface roughness and pore geometry have an effect on the penetration process [29], and measured at defined temperature, e.g., at 18–23 °C [30]. The applied drop volume varies, e.g., between 35 μL [31] and 200 μL [32]. Drops of high volumes underlie the influence of gravity. At the same time, they are larger than the largest pores in the soil sample [33] and better in considering the heterogeneity of soil material. However, WDPT of different drop sizes cannot be compared with each other. The interpretation of WDPT is controversially discussed. Letey [25] considers instantaneous penetration to indicate an initial contact angle (Θ) smaller 90°. Longer penetration times would indicate that the soil–water contact angle decreases and penetration occurs when $\Theta = 90^\circ$ is reached. Therefore, WDPT is considered to be a measure of persistence of repellency rather than of actual wettability. Since WDPT related to 90° are ranging between <1 s and several minutes, the distinction between wettable and repellent soils using WDPT can be only arbitrary. A widely accepted practise is the interpretation of WDPT using repellency classes [27].

Molarity of an ethanol droplet (MED) test, also known as alcohol percentage test, determines the ethanol molarity of an aqueous mixture which is necessary for instant drop penetration into a soil sample [34]. Drops with decreasing ethanol molarity (increasing surface tension) are applied to the soil until one drop resists instant infiltration. In contrast to the WDPT test, MED test assesses the actual repellency, i.e., the surface energy of the tested soil.

For the Sessile drop contact angle (Θ_{sess}) determination on soil samples, a modified method [35] is applied in soil science. The soil samples are fixed by double sided adhesive tape on a glass slide and drops of deionized water placed on the so formed one grain layer. In contrast to Bachmann et al. [36], who applied drop volumes of 2–10 μL and used a microscope and goniometer for the determination of sessile drop contact angle, other studies [37,38] applied drops of 50–100 μL and use digital pictures for geometrical analysis of drop shape and calculation of the respective contact angles. The larger area covered by one drop better considers the high heterogeneity of the investigated samples but also requires additionally to the influence of roughness and chemical heterogeneity, the consideration of the gravity effect on the exact drop shape [38]. The consideration of hydrostatic pressure in the Young–Laplace equation requires a numerical solution for the drop shape [39–42]. Diehl and Schaumann [38] used a simplifying approximation for the drop shape, assuming an axis symmetric ellipsoidal cap as a gravity-influenced drop shape model which was suggested by McHale et al. [43]. Thereby, the apparent contact angle (Θ_{app}) is underestimated especially in the range greater than 90° and can only be compared with Θ_{app} obtained with the same drop size [38]. McHale et al. [44] described the influence of surface roughness using Cassie-Baxter equation and of chemical heterogeneity using the Wenzels equation on Θ_{app} measured on granular samples. In a further model, influence of surface roughness on Θ_{sess} was approximated by considering soil particles as ideally smooth spheres with a uniform radius r and a constant distance $2\varepsilon r$ between each other [45]. This model was tested with spherical glass beads and irregular soil particles, treated with dichlorodimethylsilane (DCDMS) and compared with Young contact angles, obtained from smooth DCDMS treated glass surfaces. The model produced reasonably accurate predictions of the Θ_{sess} for a range of liquid surface tensions with ε between 0.26 and 0.31 [45]. However, to adapt and establish the efficacy of these methods for naturally hydrophobic soils, further work has to be done [46].

The capillary rise method (CRM) is a common method to determine wettability of porous material [e.g., 47–49] which is at least partially wettable, i.e., with $\Theta < 90^\circ$. The measurement principle is based on the Washburn equation for rising flow in a vertical thin cylindrical capillary [50]. At least two measurements have to be carried out for each sample: one with an optimally wetting liquid, e.g., n-hexane, in order to determine the geometrical factor C reflecting porosity and tortuosity of the pores and substituting the pore radius in the Washburn equation and another measurement with a fresh sample with the wetting liquid of interest (in soil science normally water). The factor C depends on particle size and packing density of the measured medium. Therefore both samples should be prepared in a comparable way. Marmur [51] and Siebold et al. [52] reported that Θ_{adv} measured by CRM is often overestimated in comparison with corresponding equilibrium contact angles. Furthermore, contact time of the sample with the testing liquid depends on Θ_{adv} and may lead to systematic errors, e.g., due to sorption kinetics of the vapour on the solid surface (Bachmann et al., 2006), or even due to chemical modification with contact time.

Also the adaption of Wilhelmy plate method (WPM) [53] to soil science requires some simplification. Samples are fixed on a rectangular glass slide completely covered by double-sided adhesive tape and immersed and emerged from a water body. Also the so obtained advancing (Θ_{adv}) and the receding contact angle (Θ_{rec}) are influenced by surface roughness. The wetted length (L_W), i.e., the three phase line at which the measured forces are acting is increased by surface roughness. For ideal smooth plates, L_w is equal to the perimeter of the plate (l_s) and Θ_{adv} and Θ_{rec} are equal. The suggestion of approximating L_w by l_s [45] led to $\cos\Theta_{\text{adv}} < 1$ or to $\cos\Theta_{\text{rec}} > 1$ for several sandy samples (not published) which can be only explained by an underestimation of L_w. Thus, L_w has to be estimated. As a very rough estimation, the soil covered plate can be assumed as formed by close-packed solid hemispheres in Wenzel's state (no entrapped air between the particles from the first moment of immersion). Then L_w is the sum of the arc lengths of semicircles (U_i) in the intersecting planes of