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Links between nanoscale and macroscale surface properties of natural root mucilage studied by atomic force microscopy and contact angle

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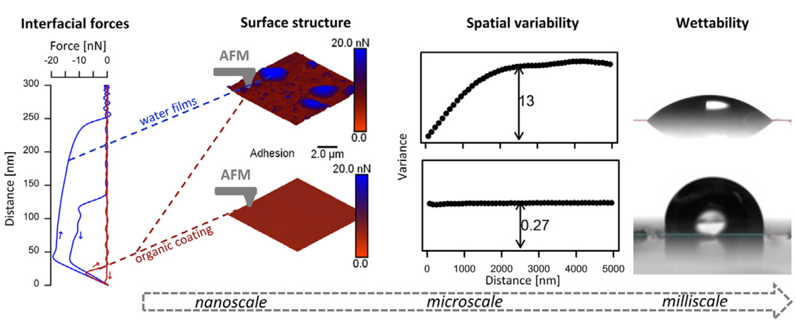
GRAPHICAL ABSTRACT



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ABSTRACT

Soil water repellency originating from organic coatings plays a crucial role for soil hydraulics and plant water uptake. Focussing on hydrophobicity in the rhizosphere induced by root-mucilage, this study aims to explore the link between macroscopic wettability and nano-microscopic surface properties. The existing knowledge of the nanostructures of organic soil compounds and its effect on wettability is limited by the lack of a method capable to assess the natural spatial heterogeneity of physical and chemical properties.

In this contribution, this task is tackled by a geostatistical approach via variogram analysis of topography and adhesion force data acquired by atomic force microscopy and macroscopic sessile drop measurements on dried films of mucilage. The results are discussed following the wetting models given by Wenzel and Cassie-Baxter.

Undiluted mucilage formed homogeneous films on the substrate with contact angles >90°. For diluted samples contact angles were smaller and incomplete mucilage surface coverage with hole-like structures frequently exhibited increased adhesion forces. Break-free distances of force curves indicated enhanced capillary forces due to adsorbed water films at atmospheric RH (35 ± 2%) that promote wettability. Variogram analysis enabled a description of complex surface structures exceeding the capability of comparative visual inspection.

Abbreviations: AFM, atomic force microscope; θ, contact angle; EDX, energy dispersive X-ray spectroscopy; ESEM, environmental scanning electron microscope; PFQNM, peak force quantitative nanomechanical mapping; R_f, roughness factor; ROI, region of interest; r_{rms}, root-mean-square roughness; SOM, soil organic matter; SWR, soil water repellency.

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1. Introduction

1.1. Structure of organic coatings and soil water repellency

Soil water repellency (SWR) influences plant growth, surface and subsurface hydrology and soil erosion [1]. SWR is attributed to coatings of soil organic matter (SOM) with an abundance of various organic substances derived from living or decomposing plants or microorganisms [1]. The organic molecules may form accumulations of hydrophobic sites during drying events [2]. Consequently, wetting properties are heterogeneously distributed in the range of individual soil grains, as suggested by Bachmann et al. [3] using small scale contact angle mapping and variograms.

Mechanistic wetting models have been developed in order to link physical and chemical surface properties with the water contact angle [4–6]. Young's law [7] considers the contact angle θ_e as the equilibrium of the interfacial energies between the three phases in a solid-liquid-vapour system with an ideally smooth solid surface. Wenzel's relation [8] scales the cosine of θ_e with a roughness factor R_f (Eq. (2)) to express the observed contact angle θ_o on real rough surfaces. Cassie-Baxter systems of heterogeneously composed interfaces arise on rough surfaces where air is entrapped in pores or between bumps, increasing the macroscopic θ_o [9]. Contrariwise, gaps filled with water increase θ_o, so that the effect of gaps on a rough surface, which enhance water repellence or wetting, depends on the entrapment of air or water [5].

However, it is difficult to apply those concepts to organic coatings in soil, owing to the limited knowledge of surface structures. Still, there are no mechanistic investigations detailing the physical and chemical relationships within these biogeochemical interfaces that dictate wetting behaviour [10]. To fill this gap of knowledge, we need to establish a spatially resolved view of the interfacial properties at the scale of nano- and micrometres [11–13].

1.2. AFM studies of hydrophobicity – from model to natural surfaces

Atomic Force Microscopy (AFM) seems a promising tool for the exploration of biogeochemical interfaces [13,14] and their properties related to wetting behaviour [10,15–19]. The controlled subnanometre movement of the AFM probe relative to the sample and the detection of probe-sample forces by measuring force-distance curves [20,21] allows mapping of both, topography and interaction forces in the nano- and piconewton range at high spatial resolution [22–24].

Truong et al. [10] found the nano- and microtopologies of coatings of various SOM model substances imaged by AFM to influence soil wettability, attested by nano- and micro-air trapping leading to a Cassie-Baxter wetting state. These model systems do not approach the complexity of natural SOM. For soil particles coated by variable amounts of unspecified natural organic matter and model systems, Cheng et al. [19] found a correlation between the nanoscale hydrophobicity and macroscopic water contact angles. However, the study does not account for space relation of surface heterogeneity when evaluating root-mean-square roughness (r_{rms}) and adhesion force distributions from AFM data. Though demonstrating the importance of nanoscale surface properties for bulk soil hydrophobicity, SWR could not really be attributed to a specific property of the organic coatings. Thus far, a mechanistic explanation for the wetting properties by the nanostructures of organic substances in soil is still missing.

1.3. Objectives and hypotheses of the study

In this work we focus on root-derived mucilage, to exemplify an organic soil compound with natural complexity but known origin and references for its chemical composition [25–28]. Gelling properties and the ability to hold large volumes of water [29] characterize the biohydrogel [30]. Mucilage released by nodal roots [31] is surrounding the cell wall and extending into the root environment [32] where it impregnates and clings together soil particles [33], stabilizes aggregates [34] and influences the hydraulic properties of the soil [35,36], turning the rhizosphere hydrophobic when drying [37,38].

The objective of this study was to link nanoscale surface properties with macroscale wettability of dried root mucilage films on wettable reference glass surfaces. We hypothesize that:

Dry mucilage induces water repellency by coverage of the surface and by modification of the surface topography: (a) The higher the mucilage concentrations on a wettable surface, the higher is the contact angle of macroscopic water drops. (b) With increasing concentration of dried mucilage, variations in topography increase and lead to a Cassie-Baxter wetting state with entrapped air, while variations in adhesion forces decrease with increasing mucilage concentration due to a more complete organic coverage.

Differences in topography and the spatial distribution of adhesion forces can be quantitatively described by geostatistical parameters (variograms) which may reflect the macroscopic wettability better than averaged values of surface roughness or adhesion forces.

Therefore, dried films of natural root-mucilage were studied by AFM nanomechanical mapping, Environmental Scanning Electron Microscopy (ESEM) and optical contact angle measurements. Using the obtained data and derived variograms we aimed to find indications for the wetting mechanisms mentioned above. Further, the experimental set-up and spatial analysis will be discussed with regard to comparative and representative characterization of complex surfaces by AFM within a feasible range of replicates and regions of interest (ROI).

2. Materials and methods

2.1. Sample preparation

Mucilage of sorghum (*Sorghum* sp., moench) collected from living roots with the procedure described in Ahmed et al. [38], was provided by the Division of Soil Hydrology, Georg-August University of Göttingen. The sample material was delivered and stored in frozen state in order to prevent microbial degradation. An undiluted mucilage sample (ND) and three differently diluted samples (D1-3), prepared by mixing mucilage with deionized water, were spread on borosilicate glass cover slides covering an area of 4 cm^2. A blank control sample (BL) was prepared by pipetting deionized water on a glass slide. The samples were air dried for at least 24 h in a laminar flow box to prevent dust deposition on the surface. For the determination of the sample concentration in terms of weight of dry mucilage per surface area, the glass slides were weighed empty and reweighed after air-drying of the mucilage films.

2.2. AFM imaging

AFM imaging was performed prior to contact angle measurements to eliminate alterations of surfaces through the contact with the water drops. Topography and adhesion forces were studied with an Atomic Force Microscope (Dimension Icon, Bruker) in PeakForce Tapping mode (software: Nanoscope, Bruker) using silicon nitride probes with v-shaped cantilevers (SNL10-A probes with a nominal spring constant of 0.58 N m^{-1} and a nominal tip radius of 5 nm, Bruker) at a scan rate of 0.5 Hz and a modulation frequency (PeakForce frequency) of 2 kHz. Measurements were per-