Soil–water characteristic curves of extracellular polymeric substances-affected soils and sensitivity analyses of correlated parameters

Han Zhang, Jianmin Bian, Hanli Wan, Nan Wei and Yuxi Ma

ABSTRACT

Quantifying the ways in which biological activity may alter the hydraulic properties of soils (the soil–water characteristic curves; SWCCs) is vital for understanding and engineering water pollution and supply systems. The study used centrifugation and a sand funnel method to determine the SWCCs of pure sandy soils with different particle sizes and sandy soils mixed with different extracellular polymeric substance (EPS) analogs. The sensitivity of correlated parameters for SWCCs obtained using a van Genuchten (VG) model was analyzed by single-factor perturbation analysis. The results show the following. (1) Fine sand has the strongest water retention ability. (2) The more polysaccharide there is in the media, the stronger its water-holding capacity. Polysaccharide not only has its strong water-holding capacity, but also changes the structure of medium to increase water-holding capacity. The humic acid and protein components had little effect on the hydrodynamic properties of fine sandy soil. (3) Sensitivity analyses revealed that the saturated water content, θs, greatly affected the ability of solute transport to reach equilibrium concentrations. Therefore, it is essential to define the range of media particles and component content, and ensure the accuracy of VG model parameters in the practical application of soil media affected by biological activity.

Key words | EPS, parameter sensitivity analysis, soil–water curve, van Genuchten model

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HIGHLIGHTS

- Soil–water characteristics were explored using a van Genuchten model in Hydrus 1-D.
- Adding different extracellular polymeric analogs to soils had different impacts on water content and porosity.
- The addition of a polysaccharide had the greatest impact on hydraulic parameters.

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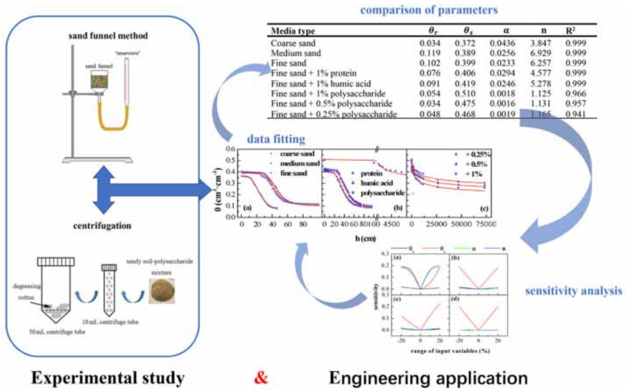
GRAPHICAL ABSTRACT



INTRODUCTION

An unsaturated zone is an intermediate zone between the subsurface and the atmosphere, and it plays a vital role in the hydrogeological cycle of groundwater (Bevington *et al.* 2016). Soil–water characteristic curves (SWCCs) represent the relationship between the saturation of unsaturated soils and matric suction and can indirectly describe the basic attributes of soil strength, deformation, and permeability. Additionally, SWCCs are of key importance in the study of unsaturated soil mechanics (Hu *et al.* 2013), which are important for studying unsaturated systems, the in-situ restoration of aquifers and irrigation clogging, and evaluating the economic benefit of engineering projects.

The nature of the soil itself and the composition of the medium are various factors affecting the water-holding capacity of soil. The influence of the presence of bacterial biofilms in its constituents should not be ignored. When surface sewage seeps underground, it will carry with it bacteria and other microorganisms into the soil. The same thing happens when reclaimed water is stored underground (Cui *et al.* 2019).

Biofilms are the main form in which bacteria are present in soil, and they are a complex aggregate of microorganisms attached to a solid surface and embedded within a matrix of extracellular polymeric substances (EPS) (Rosenzweig *et al.* 2012). The main components of the EPS matrix are polysaccharides, while it also contains proteins, humic acid, lipids, and extracellular DNA (Sutherland 2001; Or *et al.* 2007). Polysaccharides are secreted by bacteria and even small amounts can significantly affect the water-holding capacity of soil. For example, the addition of only 1 kg of EPS can increase the water-holding capacity of the soil by 15–20 kg (Chenu & Roberson 1996). Soil containing EPS can hold 5–10 times its weight in water at high pressure (Or *et al.* 2007). The presence of EPS separates the soil particles and opens the pore structure, so it not only has a strong water-holding capacity but also increases the water-holding capacity of the soil (Chenu & Roberson 1996). Different microbial species and environmental conditions result in different contents and properties of EPS; however, most bacteria have a high water-binding capacity for EPS (Flemming & Wingender 2010). It can not only bring favorable water retention, but also bring a certain plugging risk to the underground migration zone of water flow (Wang *et al.* 2018). By better understanding the interactions between biofilms, soils, and water, more efficient and economical technologies may developed for improving the water management of sandy soils.

The effects of bacterial EPS on the water-holding capacities of soils have been reported; however, to the best of our knowledge, most studies have focused on polysaccharides or substances capable of expansion, while other substances have been ignored, including: (1) the effects of humic acids and proteins, two other major components of extracellular polymers, on soil and water properties and (2) whether their presence will cause changes in the SWCCs.

Therefore, this study (1) completed the determination of the basic characteristic curves of sandy soil with different particle sizes using a sand funnel method, which served as the basis for comparison with other media with different substances added, (2) investigated the effects of three main components of extracellular polymers (xanthan, humic acid, and bovine serum albumin) on soil and water characteristic curves by centrifugation and (3) analyzed the sensitivity of the correlated parameters in the SWCCs obtained using a van Genuchten (VG) model via single-factor perturbation analysis.

This study is of great significance for engineering applications in the soil vadose zone as the findings give important information about the influence of microbial extracellular metabolites on the soil water-holding capacity. In the design and construction of geotechnical engineering, the water-holding characteristic of soil determines structure, safety and stability considerations (Ho *et al.* 2007). For the underground storage of reclaimed water and the in-situ remediation of groundwater, this study can provide an effective scientific basis for the benefits of recharging and storage and the risks of water quality remediation. In addition, the results provide a scientific basis and theoretical support for practical engineering applications in unsaturated areas with high biomass contents.

MATERIALS AND METHODS

Characteristics of soil media and the soil–water solution

Experiments were conducted using samples of a sandy soil taken from Jilin Province (northeastern China), which is a typical metropolis with a shortage of water resources. Three medium sizes were classified by sieving: coarse sand (0.5–2 mm); medium sand (0.25–0.5 mm); and fine sand (0.075–0.25 mm). The samples were soaked in 0.1 mol/L HCl^- solution overnight to remove carbonates and then rinsed with ultrapure water following the methods of Chenu (1993). All samples were sterilized before use by wet autoclaving (at 126 °C), followed by drying in an oven at 105 °C.

The experimental biofilm was a mixed microbiome containing cellular biomass and EPS. Previous studies have demonstrated that cellular biomass accounts for only a minute fraction of the organic matter in biofilms, where 70–90% of the total organic carbon exists outside of the cell.

Differences exist in the chemical composition of EPS formed under different environmental conditions. Polysaccharides, humic acids, and proteins are the main components of EPS, and hence, were the focus in this study. As analogs for the EPS component of the biofilm, the study used xanthan, commercial humic acid, and bovine serum albumin, all obtained from Xiya Reagent, China. Due to non-controllable phenomena occurring during experimental processes with live bacteria, EPS analogs were used instead, which function under static conditions while having the water-retaining property of a real biofilm. Throughout the experiments, to avoid bacterial contamination in the open system, we used ultrapure water with 0.1% bronopol and 0.1% NaN_3 (Sigma Aldrich, USA) as the simulated soil water solution (Rosenzweig *et al.* 2012).

Soil–water characteristic curves

The applicability of various SWCC test methods was evaluated and two methods were selected for use in this study: (1) the hanging column method (sand funnel method) (Dane & Hopmans 2002), for the low matric head range samples and (2) centrifugation, for the high matric head range samples. The experimental setup is shown in Figure 1. Three replicates were used for each experimental medium, while one additional sample was used to estimate evaporation.

For the part of the SWCC that can be measured with low matric suction, the hanging column method was used chosen.

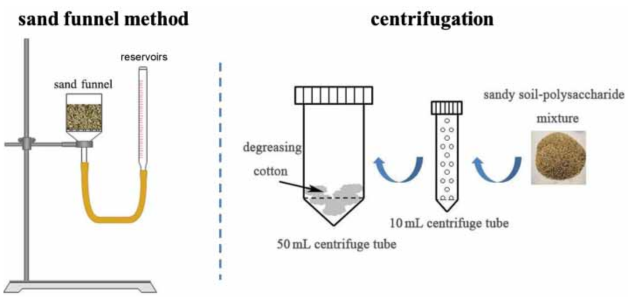


Figure 1 | Schematic of the experimental setup.

This method is based on the principle of connectivity method, where the matrix water head is changed by lifting the water column at one end of the sample tube and dehumidifying the sample at the other end to change the water content. First, the water is allowed to flow from the bottom to the top of sand funnel to remove the air from the sample and saturate it overnight. During the experiment, it is important that the hanging water column is covered with sealing films with holes in it, which reduces loss of water by evaporation while maintaining a constant atmospheric pressure. Nevertheless, some evaporation losses occur, which can affect long experiments and need to be considered when the water content is calculated from the water column. After saturation, the sample was placed higher than the free water surface by lowering the height of the water column, and the resulting matrix water head forces the saturated soil sample to drain and desorb water. The water content was calculated by measuring the drainage volume under equilibrium conditions, defined as no change in the water volume for 10 min. In contrast, the sorption curve was obtained by lowering the sample below the free water surface.

To measure the SWCC of the soil–EPS analog mixtures with high matric head, the study used the centrifugation method. The experiment loaded 10 mL of a soil analog mixture in a 10-mL centrifugal tube with holes to allow water flow. The small centrifugal tube and absorbent cotton were then placed into a 50-mL centrifugal tube for centrifugation. A high-speed cooling centrifuge with a six-sample rotor was used (TGL-20000-CR; Anting, Shanghai). Matric heads were generated by increasing the centrifugal force, while the water contents were calculated by measuring the weight of the absorbent cotton when the system reached equilibrium and water drainage ceased (i.e., unchanged weight of absorbent cotton over 10 min). Only the desorption part of the SWCCs was obtained using this method.

Analytical models of curve fitting and parameter sensitivity

Van Genuchten-fitted parameters

The VG model is widely used for fitting SWCCs. The model can represent SWCCs in the range of total negative pressure, and has a high fitting accuracy for different types of media, and is thus widely applicable. The expression for the VG model is as follows (van Genuchten 1980):

$$\theta = \theta_r + \frac{\theta_s - \theta_r}{[1 + (\alpha h)^n]^m} \tag{1}$$

where θ is the volumetric water content [L^3/L^3], θ_r and θ_s are the residual and saturated volumetric water contents [L^3/L^3], respectively, h is the soil matric head [L], α is the inverse of the air-entry value, and m and n are curve shape factors. The study applied a soft version of the VG equation (Equation (1)) to fit the parameters, which allowed us to quickly determine the optimal fitting values. The parameters of the polysaccharide–soil mixture SWCCs were adjusted manually owing to the initial centrifugal force being greater than the air-entry pressure.

In the sensitivity analysis using the uniform transport model Hydrus-1D, the transport equation needs to be modified; this is usually done by assuming a first-order dynamic process (Simunek et al. 2013):

$$\frac{\partial \theta c}{\partial t} + \rho \frac{\partial s^k}{\partial t} = \frac{\partial}{\partial z}\left(\theta D \frac{\partial c}{\partial z}\right) - \frac{\partial q c}{\partial z} - \varnothing \tag{2}$$

In Equation (2), c is the concentration in water [ML^{-3}], θ is the volumetric water content ($L^3\ L^{-3}$), t is time [T], ρ is the soil bulk density [$M\ L^{-3}$], z is the distance [L], s^k is the sorbed concentration of the kinetic sorption sites [$M\ M^{-1}$], D is the hydrodynamic dispersion coefficient [$L^2\ T^{-1}$], q is the volumetric flux density [$L\ T^{-1}$], and $\varnothing$ represents the sink/source term that accounts for various zero- and first-order or other reactions [$ML^{-3}\ T^{-1}$]. We studied the sensitivity of parameters affecting the variation in the SWCCs using the Hydrus-1D model. The water flow and solute transport values were used to build the conceptual model. According to the migration column test performed by Zhang et al. (2018), Cl^- was regarded as only having a leaching effect as a solute.

In this study, a one-dimensional soil column model with a height of 100 cm was constructed in Hydrus-1D. The upper boundary condition was assumed to be a constant pressure head of 2 cm, and the lower boundary was assumed to be free drainage. The initial condition was the pressure condition. The VG parameters chosen in the soil hydraulic model for water flow and transport during solute transport were adjusted by fitting values from the soft and the experimental values. According to the time ratio of the Cl^- concentration equilibrium from inflow to outflow, the study analyzed the sensitivity of the correlated parameters of SWCCs under these conditions. The flowchart (Figure 2) shows the research methodology.

RESULTS AND DISCUSSION

SWCCs of pure sandy soils and soil–EPS-analog mixtures

The SWCCs of the three types of sandy soils are shown in Figure 3. The fraction of saturated water in both medium and fine sand was approximately 0.4 and that of the coarse sand was slightly lower (0.37). Unsurprisingly, the residual water content of the coarse sandy soil was also slightly below that of the other soils. These findings indicate that the retention capacity of coarse sand was the lowest of all sandy media, and three stages were observed from the desorption curves. The first was the initial stationary stage, and its value always tended toward the saturation of sandy soils. The volumetric water content then declined with increasing matric head, and the inflection points between the two stages gradually increased with decreasing particle size. In the third stage, the volumetric water content remained nearly constant, and was equivalent to the residual water content. However, many previous experimental results have shown that there is an evident hysteresis effect on the SWCC (Pham *et al.* 2003; Lu *et al.* 2013).

The study found that the processes of desorption and sorption were inconsistent, and saturation did not correspond to matric suction. The factors that cause hysteresis in the SWCCs of unsaturated soils are very complex; however, the main factors are non-uniform pore sizes and channel sizes in unsaturated soils, which affect the transports paths of water and gas. Additionally, a bottleneck effect is caused by different constraints on water movement, which are in turn caused by differences in pore and channel sizes (Wei & Dewoolkar 2006). These characteristics can be

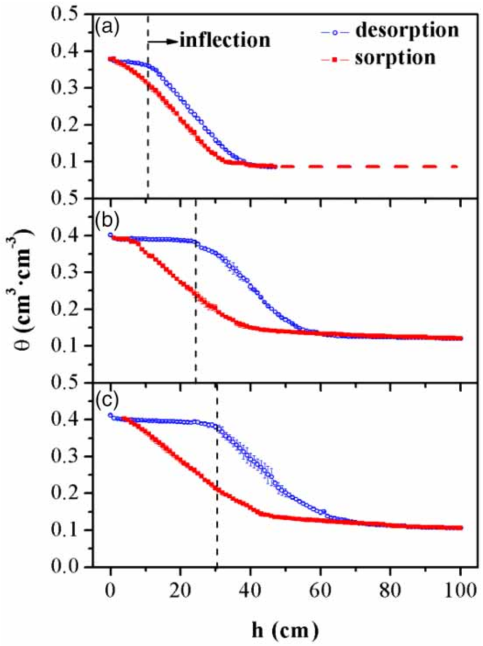


Figure 3 | Soil–water characteristic curves of sandy soils: (a) coarse sand, (b) medium sand, and (c) fine sand; θ is the volumetric water content and h is the matric head.

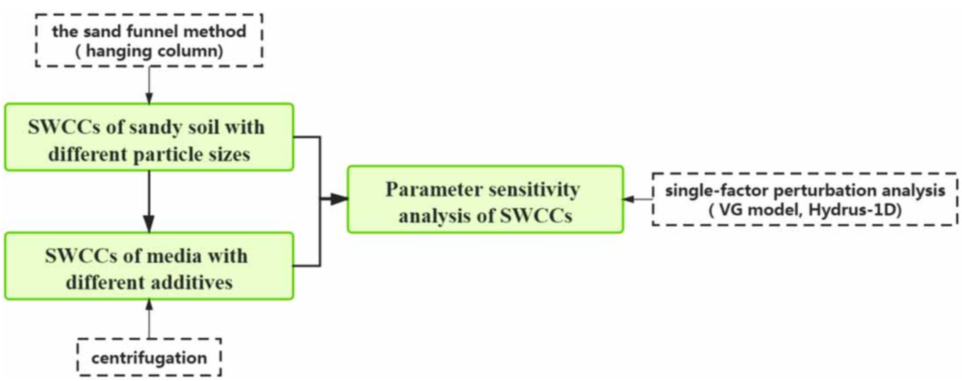


Figure 2 | Flowchart of the research methodology.

explained by various mechanisms, including the different length scales of the particle diameter (microscale) and interparticle spacing (macroscale). This results in various phenomena, including: (i) the geometric effect of the non-uniform distribution of soil pores (i.e., the bottleneck effect); (ii) capillary condensation, where the only hygroscopic processes are relevant for low water contents; (iii) residual gas in the closed pores that forms during the moisture sorption process; (iv) expansion and contraction, which alter the structure of fine-grained soils during moisture absorption and dehumidification; (v) hysteresis in the contact angle during moisture desorption and absorption, as contact angles on the interface between soil particles and pore water differ (Lu & Likos 2012). Smaller soil particles result in higher porosity. Our results showed that the hysteresis effect was more evident for smaller particle sizes, which is consistent with previous analyses (Rosenzweig *et al.* 2012).

The SWCCs of pure fine sandy soil and fine sand analog mixtures are presented in Figure 4 as a function of volumetric water content. Clearly, the SWCC of the sand–polysaccharide mixture was higher, and the inflection point occurred later than for the other mixtures during desorption. The study used xanthan as an analog for the polysaccharide component of EPS, which is a polysaccharide naturally produced by the soil bacterium *Xanthomonas campestris* and widely used as an analog (Rosenzweig *et al.* 2012).

Low-concentration xanthan solutions have a high viscosity and exhibit strong pseudoplasticity (Whitcomb & Macosko 1978), resulting in an ultra-high molecular weight and intermolecular interactions in aqueous solutions that produce a uniquely rigid bar conformation (i.e., a weak network structure; Figure 5). This network structure can readily control the flow of aqueous solutions, resulting in a high viscosity. At low shear rates, the weak network structure of xanthan solutions is not damaged and it maintains a high viscosity. As the shear rate increases, the weak network structure is destroyed, and shear thinning shows a strong pseudoplasticity. This network structure is not a real gel and is shear reversible (Wang 2015). Additionally, the viscosity of the xanthan solution decreases with increasing shear rate. The SWCCs of pure sand, sand–protein, and sand–humic-acid mixtures showed similar shapes and trends. At saturation, the addition of humic acid caused the saturated water content to be slightly higher than in the other mixtures.

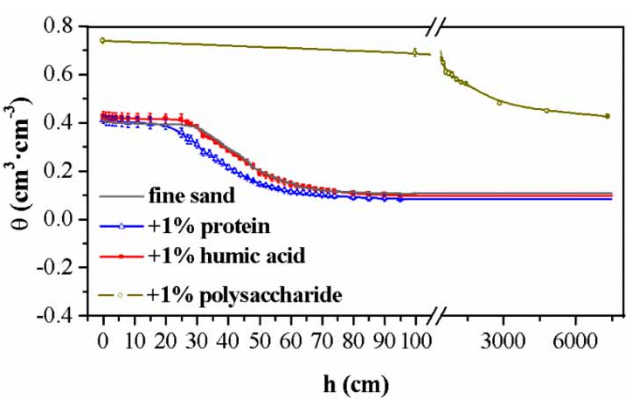


Figure 4 | Soil–water characteristic curves of fine sand with different media; θ is the volumetric water content and h is the matric head.

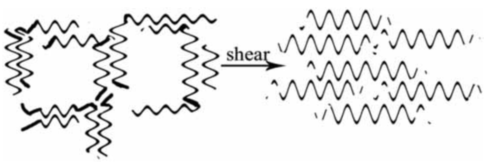


Figure 5 | Weak network of xanthan macromolecules in solution (from Urlacher & Noble 1997).

Humic acids are organic polymers found in nature; the study selected commercial humic acid as an analog of humic acid in EPS biofilms. Humic acid has both hydrophilic groups (e.g., phenolic hydroxyl and alcohol hydroxyl groups) and hydrophobic groups (e.g., carbonyl and quinone groups) in its molecular structure. It also has the characteristics of amphophilic molecules (Stempvoort & Lesage 2002; Tejeda-Agredano *et al.* 2014). Moreover, humic acid has favorable chemical and biological activities, such that the application of humic acid can improve soil aeration. However, the SWCCs of pure sand and the sand–humic acid mixture being similar led us to notice that the humic acid was discharged from the sand with the water during the desorption process. Over time, the reduced humic acid content resulted in the SWCCs of the two samples becoming increasingly similar. A previous study also found that humic acid was easily removed with the water and not trapped by the soil, while proteins behaved in the opposite manner, as shown in Figure 6 (Zhang *et al.* 2018). In other studies, the

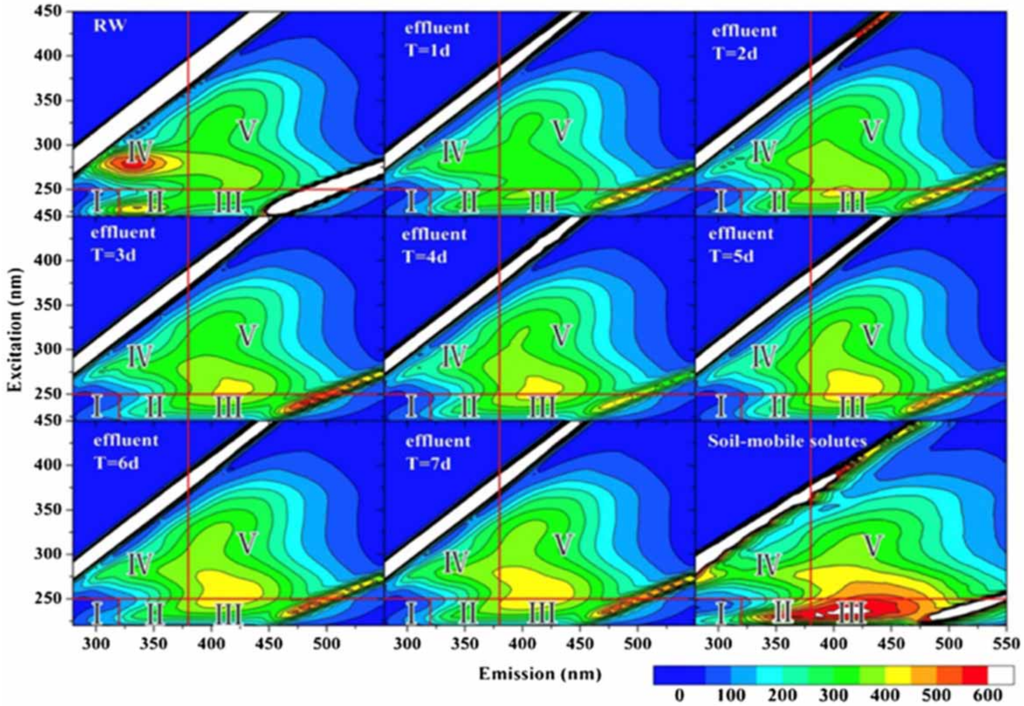


Figure 6 | Excitation–emission–matrix (EMM) spectra of experimental reclaimed water, soil-mobile solutes, and effluents (Zhang *et al.* 2018). Region II shows tyrosine/tryptophan proteins and region V shows humic acid-like organics.

effect of humic acid on the structural characteristics of sand over time was not clear (Cao 2007).

Surface hydrophobicity is an important characteristic of proteins and plays a decisive role in maintaining protein stability and functional activity (Haskard & Li-Chan 1998). The inflection value of the SWCC for the sand–protein mixture was less than those of other samples in the study, i.e., the θ values were lower than those of media at the same matric heads. The SWCC of the media with polysaccharide differed from those with the other EPS analogs (Figure 4); hence, the SWCCs of fine sand with three different polysaccharide concentrations were studied (Figure 7). The study found that the absence of the initial gentle phase (in which θ was near the saturated water content in the SWCCs) was caused by the inability to measure the low matric head range by centrifugation. This means that the air-entry pressure was lower than the matric head at the first measured point. With an increasing polysaccharide concentration, the water-holding capacity and equilibrium θ increased. These differences relative to the other analog additions were due to the structure and properties of the polysaccharide.

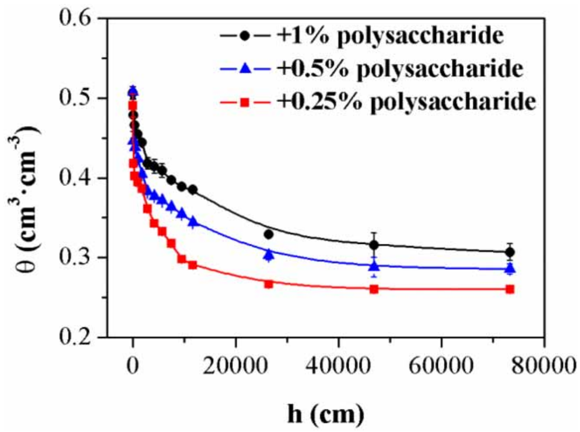


Figure 7 | Soil–water characteristic curves of fine sand with different polysaccharide concentrations; θ is the volumetric water content and h is the matric head.

The addition of the polysaccharide analog changed the pore size distribution of the sandy soil. Polysaccharides have a double effect on the morphology of the soil and SWCCs in the near-saturation state (Rosenzweig *et al.* 2012). When the matric water head pressure is in the range from zero to the air-entry pressure, the polysaccharides can resist the pressure drop and thus slow the decrease of water content. However, when the matric water head is lower than the air-entry pressure, the polysaccharides retain more water, which is the main mechanism for slowing the decrease in water content. When the matric water head decreases, the water content of the medium slowly decreases under the two-fold effect, and the soil–water characteristic curve becomes increasingly similar to that of the dense clay medium. With increasing mass concentration of xanthan, the solution viscosity also increases; the increase is slow for mass concentrations less than 4.0 g/L, but rapid for higher concentrations (Zhang & Huang 2014). The results showed that with increasing xanthan content, the volumetric water content, which tended toward equilibrium, also increased gradually.

Fitting SWCCs using the van Genuchten model

Figure 8 shows the curve fitting of experimental data points using the VG model. The fitting parameters (θ_r, θ_s, α, and n) and correlation coefficients (R^2) for the eight different samples obtained by fitting the experimental data with the VG model are listed in Table 1. When the polysaccharide content gradually increased from 0 to 1%, the parameter n gradually declined. The study of van Genuchten (1980) showed that n is related to the distribution of soil pore size, which directly affects the slope of the SWCC. Therefore, the pores in the coarse sand medium were small, as indicated by the high n value. On the contrary, the n value was generally lower for the medium with a higher fraction of fine grains. Hence, when the EPS analogs were mixed with the sandy soil medium, they filled the pores, resulting in a decrease in n, while their SWCCs showed a gradual slope and shapes similar to those of clay, which has fine and close pores.

Table 1 | Fitted parameters of the van Genuchten model for soil mixtures with 0–1% different analogs

Media type	θ_r	θ_s	α	n	R^2
Coarse sand	0.034	0.372	0.0436	3.847	0.999
Medium sand	0.119	0.389	0.0256	6.929	0.999
Fine sand	0.102	0.399	0.0233	6.257	0.999
Fine sand +1% protein	0.076	0.406	0.0294	4.577	0.999
Fine sand +1% humic acid	0.091	0.419	0.0246	5.278	0.999
Fine sand +1% polysaccharide	0.054	0.510	0.0018	1.125	0.966
Fine sand +0.5% polysaccharide	0.034	0.475	0.0016	1.131	0.957
Fine sand +0.25% polysaccharide	0.048	0.468	0.0019	1.165	0.941

The study expected the value of θ_r to increase with increasing content of EPS analog, similar to the phenomenon observed in the study of Rockhold et al. (2002) regarding sand that was incubated with bacteria for a week. However, inconsistent results were observed in this study, similar to the findings of Rosenzweig et al. (2012). In the pure sands, a general increase in θ_r was observed between coarse sand and medium/fine sand +1% polysaccharide, and both +0.5% and +0.25% polysaccharide mixtures. The exception, where medium sand +0.5% polysaccharide mixture had θ_r values lower than those of fine sand +0.25% polysaccharide, was attributed to the similar particle sizes and minor differences in concentrations. In the case of θ_s, a decrease in particle size and increase in polysaccharide content resulted in higher values, which became more regular. The values of parameter α behaved in exactly the opposite manner, where the polysaccharide

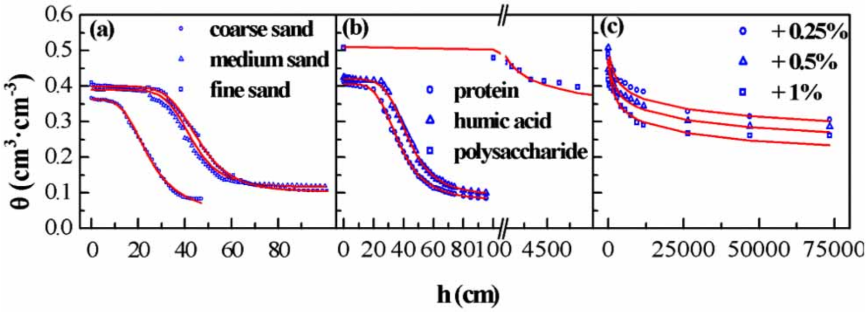


Figure 8 | Experimental SWCCs fitted using the van Genuchten model: (a) sandy soils of different sizes, (b) fine sands with different analogs added, (c) fine sands with different proportions of polysaccharides added.

concentration had no significant effect. For the complex case of polysaccharide addition, the value of R^2 determined by manual adjustment was not as high as that obtained by software fitting, though they both exceeded 0.9.

Sensitivity of parameters from the Hydrus-1D model

Figure 9 shows the four parameters, θ_r, θ_s, α, and n, of the VG model analyzed using the Hydrus-1D software with a step length of 10%, where the changes in the four media (pure fine sand, sand +1% protein, sand +1% humic acid, and sand +1% polysaccharide) were classified into five situations where their changes were ± 20%, ±10% and 0. The study found that the variability of the four parameters of pure sand was different from the others. For changes in the mixtures, θ_s was the significant parameter affecting the hydraulic characteristics of the media. The sensitivity of θ_s increased with increasing range of input variables. However, the sensitivities of parameters θ_r, α, and n always fluctuated around 0. The trends of α and n were similar, and were the main factors affecting the hydraulic behavior of the fine sand. Changes in the θ_s of fine sand were similar to those of α and n in the range from −20% to 0. Meanwhile, the sensitivity of θ_s increased slowly and then rapidly over the other range (0–20). That the sensitivity of θ_r was the lowest among the four parameters was also found.

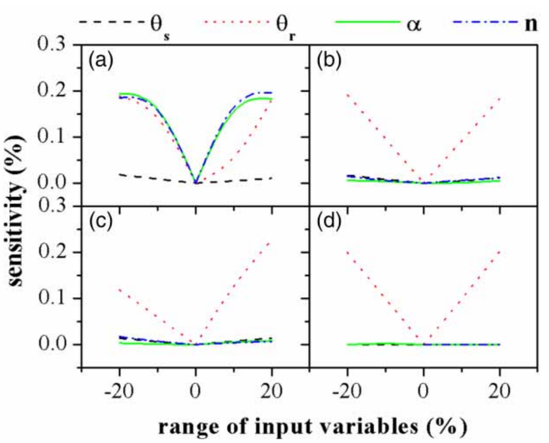


Figure 9 | Results of the sensitivity analysis of four media: (a) fine sandy soil, (b) sand +1% protein, (c) sand +1% humic acid, and (d) sand +1% polysaccharide mixture.

CONCLUSIONS

In order to better explore the characteristics and properties of soil and water based on unsaturated strata, the study used centrifugation and a sand funnel method to determine the SWCCs of pure sandy soils with different particle sizes and sandy soils mixed with different EPS analogs to simulate the biomass characteristics of soil, and a sensitivity analysis was carried out.

The inflection points of the matric head, which broke the sandy soil release barrier, increased with decreasing particle size. The degree of hysteresis observed between the desorption and sorption curves is related to the retention capacity. In the fine sandy soils with addition of different biofilm analog fractions, the hydraulic properties of the soil was dependent on the polysaccharide content, while the humic acid and proteinaceous materials had little effect. The SWCC for fine sandy soils with 1% polysaccharide clearly differed from those of the other mixtures due to the structural properties of the polysaccharide. However, the SWCCs of the mixtures of soil +1% humic acid and soil +1% protein were close to that of the fine sandy soil. The retention capacity increased with the increasing polysaccharide concentration. The polysaccharide not only has a strong water-holding capacity, but also changed the structure of medium to increase its water-holding capacity. Humic acid dissolved in the discharged water may be the reason why their curves finally coincided. Previous studies have focused on polysaccharides, an absorbent medium, often ignoring other unimportant factors, but humic acid also has an impact on groundwater pollution with the infiltration of flowing water. This indicates that polysaccharides cannot completely represent the fitting of EPS in biofilm.

Sensitivity analysis showed that θ_s significantly affected the ability of solute transport to reach an equilibrium concentration. Therefore, the accuracy of the VG model parameter θ_s should be ensured during practical application of soil media with biological activity.

These findings may prove useful for microbial ecological studies in which the amount of water available to soil bacteria is of interest, and for analyzing and designing bioremediation processes performed in the unsaturated zone, where high bacterial and EPS concentrations exist.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

Bevington, J., Piragnolo, D., Teatini, P., Vellidis, G. & Morari, F. 2016 On the spatial variability of soil hydraulic properties in a Holocene coastal farmland. *Geoderma* **262**, 294–305. https://doi.org/10.1016/j.geoderma.2015.08.025.

Cao, L. H. 2007 *Study of the Amendments on Soil Structure and Soil Water Characteristics in Different Soils on the Loess Plateau*. Dissertation for [master's] degree, Northwest A&F University, Xi'an.

Chenu, C. 1993 Clay– or sand–polysaccharide associations as models for the interface between micro-organisms and soil: Water related properties and microstructure. In: *Soil Structure/Soil Biota Interrelationships* (L. Brussaard & M. J. Kooistra, eds). Elsevier, pp. 143–156. https://doi.org/10.1016/B978-0-444-81490-6.50016-9.

Chenu, C. & Roberson, E. B. 1996 Diffusion of glucose in microbial extracellular polysaccharide as affected by water potential. *Soil Biology & Biochemistry* **28**, 877–884. https://doi.org/10.1016/0038-0717(96)00070-3.

Cui, X., Chen, C., Liu, Y., Zhou, D. & Liu, M. 2019 Exogenous refractory protein enhances biofilm formation by altering the quorum sensing system: a potential hazard of soluble microbial proteins from WWTP effluent. *Science of The Total Environment* **667**, 384–389. https://doi.org/10.1016/j.scitotenv.2019.02.370.

Dane, J. H. & Hopmans, J. W. 2002 Hanging water column. In: *Methods of Soil Analysis, Part 4, Physical Methods* (J. H. Dane & G. C. Topp, eds). Soil Science Society of America, Madison, pp. 680–683.

Flemming, H. C. & Wingender, J. 2010 The biofilm matrix. *Nature Reviews Microbiology* **8**, 623–633. https://doi.org/10.1038/nrmicro2415.

Haskard, C. A. & Li-Chan, E. C. Y. 1998 Hydrophobicity of bovine serum albumin and ovalbumin determined using uncharged (PRODAN) and anionic (ANS^-) fluorescent probes. *Journal of Agricultural and Food Chemistry* **46** (7), 2671–2677. https://doi.org/10.1021/jf970876y.

Ho, K. M. Y., Tse, J. M. K. & Ng, C. W. W. 2007 Influence of drying and wetting history and particle size on state-dependent soil-water characteristic curves (SDSWCCs). In: *Proc. 3rd Asian Conference on Unsaturated Soils*. Science Press, Nanjing, pp. 213–218.

Hu, R., Chen, Y. & Zhou, C. 2013 A water retention curve model for deformable soils based on pore size distribution. *Chinese Journal of Geotechnical Engineering* **35** (8), 1451–1462.

Lu, N., Kaya, M., Collins, B. D. & Godt, J. W. 2013 Hysteresis of unsaturated hydromechanical properties of a silty soil. *Journal of Geotechnical & Geoenvironmental Engineering* **139** (3), 507–510. https://doi.org/10.1061/(ASCE)GT.1943-5606.0000786.

Lu, N. & Likos, W. J. 2012 *Unsaturated Soil Mechanics*, Wei, C. F., Hou, L. & Jian. W. X. (translators). Higher Education Press, Beijing.

Or, D., Phutane, S. & Dechesne, D. 2007 Extracellular polymeric substances affecting pore-scale hydrologic conditions for bacterial activity in unsaturated soils. *Vadose Zone Journal* **6**, 298–305. https://doi.org/10.2136/vzj2006.0080.

Pham, H. Q., Fredlund, D. G. & Barbour, S. L. 2003 A practical hysteresis model for the soil–water characteristic curve for soils with negligible volume change. *Géotechnique* **53** (2), 293–298. https://doi.org/10.1680/geot.2003.53.2.293.

Rockhold, M. L., Yarwood, R. R., Niemet, M. R., Bottomley, P. J. & Selker, J. S. 2002 Considerations for modeling bacterial-induced changes in hydraulic properties of variably saturated porous media. *Advances in Water Resources* **25**, 477–495. https://doi.org/10.1016/S0309-1708(02)00023-4.

Rosenzweig, R., Shvit, U. & Furman, A. 2012 Water retention curves of biofilm-affected soils using xanthan as an analogue. *Soil Physics* **76** (1), 61–69. doi:10.2136/sssaj2011.0155.

Simunek, J. J., Sakai, M., Saito, H. & Van Genuchten, M. T. 2013 The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably saturated media, version 4.17[R]. Department of Environmental Sciences, University of California Riverside, Riverside, California. 15–18.

Stempvoort, D. R. V. & Lesage, S. 2002 Binding of methylated naphthalenes to concentrated aqueous humic acid. *Advances in Environmental Research* **6**, 495–504. https://doi.org/10.1016/S1093-0191(01)00076-4.

Sutherland, I. W. 2001 Biofilm exopolysaccharides: a strong and sticky framework. *Microbiology* **147** (1), 3–9. https://doi.org/10.1099/00221287-147-1-3.

Tejeda-Agredano, M. C., Mayer, P. & Ortega-Calvo, J. J. 2014 The effect of humic acids on biodegradation of polycyclic aromatic hydrocarbons depends on the exposure regime. *Environmental Pollution* **184**, 435–442. https://doi.org/10.1016/j.envpol.2013.09.031.

Urlacher, B. & Noble, O. 1997 Xanthan gum. In: *Thickening and Gelling Agents for Food* (A. P. Imeson, ed.). Springer, Boston, pp. 284–311, https://doi.org/10.1007/978-1-4615-2197-6_13.

Van Genuchten, M. T. 1980 A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal.* **44**, 892–898. https://doi.org/10.2136/sssaj1980.03615995004400050002x.

Wang, X. 2015 *Synthesis and Properties of Modified Xanthan gum*. Dissertation for [doctoral] degree, Shandong University, Shandong.

Wang, Y., Huo, M., Li, Q., Fan, W., Yang, J. & Cui, X. 2018 Comparison of clogging induced by organic and inorganic suspended particles in a porous medium: implications for choosing physical clogging indicators. *Journal of Soils and Sediments* **18** (9), 1–15. https://doi.org/10.1007/s11368-018-1967-6.

Wei, C. & Dewoolkar, M. M. 2006 Formulation of capillary hysteresis with internal state variables. *Water Resources Research* **420** (7), 260–273. https://doi.org/10.1029/2005WR004594.

Whitcomb, P. J. & Macosko, C. W. 1978 Rheology of xanthan gum. *Journal of Rheology* **22** (5), 493–505. https://doi.org/10.1122/1.549485.

Zhang, J. & Huang, X. 2014 Properties of xanthan from *Xanthomonas campestris*. *Food Science* **35** (23), 29–32. https://doi.org/10.7506/spkx1002-6630-201423006.

Zhang, H., Huo, M. X., Fan, W., Zhu, S. Y., Lu, Y., Xiong, H. F., Geng, W. Z. & Dong, L. L. 2018 Water quality variation and hydrogeochemical evolution during artificial groundwater recharge with reclaimed water: laboratory experimental and numerical simulation study. *Arabian Journal of Geosciences* **11**, 340. https://doi.org/10.1007/s12517-018-3704-2.

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