Mechanisms controlling dynamics at the soil-water interface

Dörte Diehl and Gabriele E. Schaumann

Department of Environmental and Soil Chemistry, Institute for Environmental Sciences, University Koblenz-Landau, Landau, Germany, Email diehl@uni-landau.de

Abstract

Since the characteristics of the soil-water interface are not static but continuously changing, the relevant processes and mechanisms have a high impact on habitat, filter, buffer, storage and transformation functions. Linking the individual results and conclusions of recent studies regarding the dynamics of wetting characteristics under changing environmental conditions as water content (WC), pH and drying and wetting temperature of two contrasting anthropogenic sites in Berlin (Germany), lead to two hypothetical models explaining differences in the nature of repellency between the sites and between wettable and repellent samples within each site. The chemical nature of repellency found at the one site can be best explained by hydrolysis-condensation reactions. The physicochemical nature of repellency on the other site seems to be controlled by the arrangement of amphiphilic molecules as micelles or reverse micelles during the drying process. The surface characteristics of the so formed layers on the soil particle surfaces depend on number and size of amphiphilic molecules, pH and ionic strength in the soil solution. Probably, specific local soil characteristics determine which mechanism dominates and controls the nature of repellency. Thus, critical conditions which may favour SWR may be identified. A challenge for the further research is the development of methods which may verify the suggested mechanisms with model substances as well as with complex natural soil samples and to verify the relevance of the suggested mechanisms for soils of differing soil-type, climate, and land-use.

Key Words

Soil water repellency, pH, wetting, drying, activation energy, amphiphile

Introduction

Surface characteristics of soils are one of the main factors controlling processes at the soil-water interface like wetting, sorption or dissolution processes and, thereby, have a high impact on natural soil functions like habitat, filter, buffer, storage and transformation functions. Since surface characteristics are not static soil properties but continuously changing, the relevant processes and mechanisms are in the focus of the presented study. These mechanisms help to gain further insight into the behaviour of soil and its dynamics under changing environmental conditions. In recent studies, the wetting and surface characteristics of soils from two contrasting anthropogenic sites, the former sewage disposal field Berlin-Buch and the inner-city park Berlin-Tiergarten were investigated with regard to their dependence on environmental parameters such as water content (WC), pH and drying and wetting temperature of wettable and repellent soils (Hurraß and Schaumann 2006; Bayer and Schaumann 2007; Diehl and Schaumann 2007; Diehl *et al.* 2009; Diehl *et al.* submitted). The aim of the present discussion is to link the individual results and conclusions of these studies with each other and to find a more general explanation for dynamics at the soil-water interface.

Results

The overview of main results obtained at the two sites Buch and Tiergarten (Table 1) not only shows a correlation of repellency with environmental conditions but also highlights principal differences in responses of repellency to changes in environmental conditions between the respective sites:

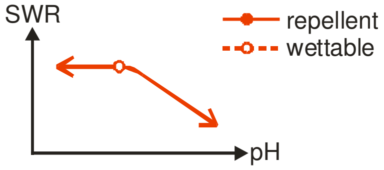
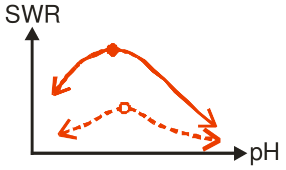
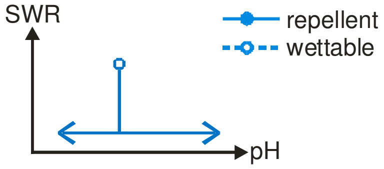
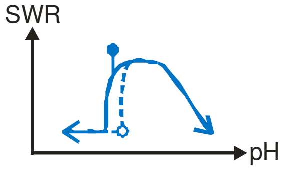
In Buch samples, drying resulted in an approach of SWR of initially wettable and repellent samples. Higher drying temperatures lead to an increased degree of surface hydrophobicity. Since wetting, the reverse process, requires high activation energy, the surface hydrophobization is probably controlled by chemical processes which are strongly linked with changes in water content. The effect of pH on repellency is only observable when moisture status of samples remained unchanged during artificial pH alteration. In Tiergarten samples, repellency differences between initially wettable and repellent samples remain following drying under various conditions as well as following artificially induced pH changes via gas phase. These differences disappear only after addition of liquid NaOH. In contrast to Buch samples, repellent Tiergarten samples have a lower pH and a higher EC in its aqueous extracts than wettable samples and the wetting process requires activation energy in the range of physicochemical processes.

Discussion

Chemical nature of repellency in Buch samples

To our current knowledge, hydrolysis-condensation reactions can be best explaining the nature of repellency of Buch samples (Table 1). Ester hydrolysis has already been suggested as a possible chemical reaction in the course of wetting of water repellent samples (Todoruk *et al.* 2003). Bound by ester groups, aliphatic dicarboxylic acids may act as bridges between alkyl chains and fatty acids, alcohols and aromatic acids and may be disrupted by base catalysed hydrolysis (Grasset and Amblès 1998) leading to an increasing number of carboxylate groups, i.e., an increasing number of charged sites at the SOM surface and thus an increased wettability.

Table 1. Overview of the main observations of differences in soil characteristics and in responses on changes in environmental conditions between wettable and repellent samples from Buch and Tiergarten.

	Buch	Tiergarten
Drying (Diehl *et al.* 2009)	Increases repellency; differences between wettable and repellent samples decrease.	Increases repellency; differences between wettable and repellent samples remain.
High drying temperature (Diehl *et al.* 2009)	Increases surface hydrophobicity (DRIFT-CH_N).	Does not significantly affect surface hydrophobicity (DRIFT-CH_N).
Activation energy of wetting (Diehl and Schaumann, 2007)	65-94 kJ/mol Chemical reactions.	8-42 kJ/mol Physicochemical processes.
pH alteration via gas phase: - exposition to NH_3 or gaseous HCl enriched atmosphere (Diehl *et al.* submitted)	 Wettable = repellent samples.	 Wettable < repellent samples.
pH alteration via liquid phase: - addition of liquid NaOH or HNO_3 solution (Bayer and Schaumann, 2007)	 Wettable = repellent samples.	 Wettable = repellent samples.
Field pH (Hurraß and Schaumann, 2006)	No significant relation with SWR.	Repellency only with pH < 4.6.
Electrical conductivity (Hurraß and Schaumann, 2006)	No significant relation with SWR.	Higher conductivity for repellent samples.
Surface tension of aqueous extracts (Hurraß and Schaumann, 2006)	Lower surface tension for repellent samples.	Lower surface tension for repellent samples.

The base catalysed hydrolysis (Equation 1) is an irreversible process (Schmeer *et al.* 1990) and follows two competing reaction pathways in its second step. The one is characterised by a direct proton transfer, and the other by a water-assisted proton transfer through which the energy barrier for the decomposition is significantly lower than through the direct proton transfer (Zhan *et al.* 2000). Thus, under dry conditions, these reactions are slow and accelerated only by increasing OH- concentration, i.e. with increasing pH. This may explain why the dry Buch samples develop increasing wettability with increasing pH after treatment with gaseous NH_3 (Table 1, Buch, red curve). The presence of water accelerates alkaline hydrolysis reactions (Zhan *et al.* 2000). This could explain why Buch samples are completely wettable after addition of liquid NaOH and subsequent incubation for 1 week at 20°C in closed containers (Bayer and Schaumann 2007); (Table 1, Buch, blue curve). Since alkaline hydrolysis is a non-reversible reaction, no recombination of esters is possible under alkaline conditions:

$$R_1\text{-}C(=O)\text{-}O\text{-}R_2 + OH^- \longrightarrow R_1\text{-}C(=O)\text{-}O^- + R_2\text{-}OH^- \qquad (1)$$

In contrast, long-term drying and drying at elevated temperatures under the original acidic pH conditions led to enhanced esterification and to an establishment of cross-linking, e.g. between carboxylic and hydroxyl functional groups. This has been observed in solid state reactions between carboxylic acids and hydroxyl-groups of cellulosic material (Pantze *et al.* 2008) and could explain why samples from Buch which reveal significant differences in wettability in field moist state reached a comparable degree of repellency after long-term drying or after drying at elevated temperatures.

A reduction in pH favours acidic catalysed hydrolysis (Equation 2) which is a reversible process driven by excess or deficiency of water. The ester concentration at the equilibrium point is independent from the pH but highly depends on the amount of available water. The pH solely determines the rate at which the equilibrium is reached. This can explain why the repellency of dry Buch samples remains constant with decreasing pH (Table 1, Buch, red curve). Only the addition of liquid acid solution (Bayer and Schaumann 2007) provides the excess of water necessary for shifting the equilibrium towards a significantly higher number of hydroxyl and carboxyl groups and leading to a complete wettability (Table 1, Buch, blue curve).

$$R_1\text{-}C(=O)\text{-}O\text{-}R_2 + H_2O \xrightleftharpoons{[H^+]} R_1\text{-}C(=O)\text{-}OH + R_2\text{-}OH^- \qquad (2)$$

The suggested mechanism is not restricted to esterification but generally includes hydrolysis-condensation reactions which in SOM can occur between a variety of substances, e.g., carbohydrates, proteins, lipids etc.

Physicochemical nature of repellency in Tiergarten

The physicochemical nature of repellency in Tiergarten linked with differences in pH, electrical conductivity (EC) and surface tension in aqueous extracts between wettable and repellent samples may be best explained by changes in the spatial orientation of amphiphilic molecules on the soil particle surface during wetting and subsequent drying:

At high ionic strength, repulsion forces between charged functional groups are effectively shielded by the counter ions (Fleer *et al.* 1993). This allows charged groups to stay closer to each other and leads to more compact structures at the water-air interface. Upon drying, water evaporates slowly from the outside to the inside of the hydrated SOM surface layer. Hydrophilic groups orientate towards the inwards receding water front whereas hydrophobic chains orientate towards the air (Swift 1999; Horne and McIntosh 2000). Smaller, water-soluble amphiphilic molecules may form a hydrophobic layer by micelle-like intermolecular aggregations at the surface (Terashima *et al.* 2004); (Figure 1, top).

At low ionic strength, a smaller amount of amphiphilic molecules may enrich at the water-air interface resulting in a higher concentration in the solution. This leads to the formation of micelles when critical micelle concentration is reached. Upon drying, hydrophilic groups tend to stay as long as possible in contact with water avoiding approaching each other, and form an outward directed hydrophilic layer (Figure 1, bottom).

These mechanisms may also explain how the addition of liquid NaOH solution may transform wettable into repellent samples. Thereby not only pH but also ionic strength increases and may therefore induce a change in conformational arrangement of amphiphilic molecules at the SOM surface. Despite increasing pH and an increasing number of negatively charged groups, repellency persists within a certain pH range because the ionic strength also increases. At a higher pH, deprotonation overbalances the effects of ionic strength. Thus, in a pH range above 7, repulsion forces cannot be effectively weakened leading to an aggregation of hydrophobic groups and surface exposition of hydrophilic groups (Table 1, Tiergarten, blue curve).

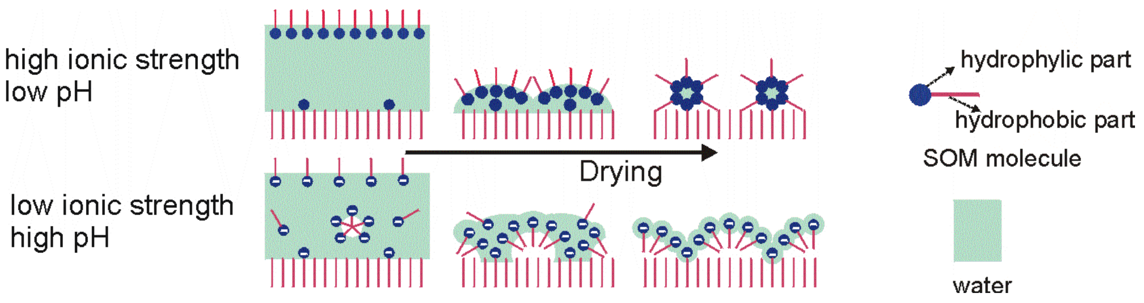


Figure 1. Suggested model of orientation of amphiphilic organic molecules at the SOM surface during drying in dependence of pH and ionic strength of the soil solution.

Conclusion

The differences in the nature of repellency between the sites and between wettable and repellent samples within each site help to draw some conclusions on the appearance of SWR and on the factors which determine the degree and nature of SWR. The two suggested mechanisms of chemical and physicochemical control of repellency are probably not restricted to one of the two sites but occur in some degree on both sites. Furthermore, it cannot be excluded that additional mechanisms play an important role for repellency at other sites. Specific local soil characteristics determine which mechanism dominates and controls the nature of repellency. However, the two suggested mechanisms together with the previous history of the sites allow identifying critical conditions which may favour SWR: Long hot and dry periods may enhance soil water repellency especially in soils with low pH and high organic accumulation. In these soils chemically bonded water can be released from organic matter by condensation reactions. Rewetting requires high activation energy, i.e. it is slow at ambient temperatures but can be accelerated by elevated temperature as long as the water does not evaporate. Special care is also needed in soils with a relatively high salt concentration, a low pH, and a SOM containing a relatively high amount of water soluble amphiphilic molecules. The combination of high ionic strength and low pH in the soil solution can favour the appearance of SWR after drying. In order to verify the suggested mechanisms, further investigations are needed. On the one hand, smaller-scaled methods are required to investigate the respective processes in molecular range, starting with model substances and extending these methods to complex natural soil samples. On the other hand, the relevance of the identified processes for a wide ranges of climates, soil types and land-use has to be tested and, eventually, additional relevant processes to be identified.

References

Bayer JV, Schaumann GE (2007) Development of soil water repellency in the course of isothermal drying and upon pH changes in two urban soils. *Hydrological Processes* **21,** 2266 - 2275.

Diehl D, Bayer JV, Woche SK, Bryant R, Doerr SH, Schaumann GE (submitted) Reaction of soil water repellency on artificially induced changes in soil pH. *Geoderma*

Diehl D, Ellerbrock RH, Schaumann GE (2009) DRIFT-Spectroscopy of untreated and dried soil samples of different wettability. *European Journal of Soil Science* **60,** 557-566.

Diehl D, Schaumann GE (2007) Wetting mechanism assessed from time dependent sessile drop shape. *Hydrological Processes* **21,** 2255 - 2265.

Fleer GJ, Stuart MAC, Scheutjens MHM, Cosgrove T, Vincent B (1993) ‘Polymers at Interfaces’. (Chapmann and Hall: London).

Grasset L, Amblès A (1998) Structure of humin and humic acid from an acid soil as revealed by phase transfer catalyzed hydrolysis. *Organic Geochemistry* **29,** 881-891.

Horne DJ, McIntosh JC (2000) Hydrophobic compounds in sands in New Zealand-extraction, characterisation and proposed mechanisms for repellency expression. *Journal of Hydrology* **231-232,** 35-46.

Hurraß J, Schaumann GE (2006) Properties of soil organic matter and aqueous extracts of actually water repellent and wettable soil samples. *Geoderma* **132,** 222-239.

Pantze A, Karlsson O, Westermark U (2008) Esterification of carboxylic acids on cellulosic material: Solidstate reactions. *Holzforschung* **62,** 136–141.

Schmeer G, Riembauer S, Barthel J (1990) The influence of hydrophobic solvation on the alkaline hydrolysis of ethyl esters of polar substituted 2-methylpropionic acids in water. *Journal of Solution Chemistry* **19,** 1175-1189.

Swift RS (1999) Macromolecular properties of soil humic substances: fact, fiction, and opinion. *Soil Science* **164,** 790-802.

Terashima M, Fukushima M, Tanaka S (2004) Influence of pH on the surface activity of humic acid. Micelle-like aggregate formation and interfacial adsorption. *Colloids and Surfaces, A: Physicochemical and Engineering Aspects* **247,** 77-83.

Todoruk TR, Litvina M, Kantzas A, Langford CH (2003) Low-Field NMR Relaxometry: A Study of Interactions of Water with Water-Repellant Soils. *Environmental Science and Technology* **37,** 2878-2882.

Zhan CG, Landry DW, Ornstein RL (2000) Reaction Pathways and Energy Barriers for Alkaline Hydrolysis of Carboxylic Acid Esters in Water Studied by a Hybrid Supermolecule-Polarizable *Continuum Approach. Journal of American Chemical Society* **122,** 2621-2627.