

Effect of kaolinite and Ca-montmorillonite on the alleviation of soil water repellency

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ABSTRACT

The effects of adding 1–3% (weight) kaolinite or Ca-montmorillonite on the wettability of silica sand, made highly water repellent with stearic acid, was studied during wetting and prolonged drying phases at 50°C. The persistence of water repellency was estimated with the water drop penetration time (WDPT) test. After wetting water repellency disappeared in all the samples. During the drying phase, water repellency re-appeared in all samples (untreated and clay-treated) as the water content decreased below 1%. Repellency did, however, not reach pre-wetting levels. The effect of clay additions on water repellency differed strongly between the two clay types. Kaolinite reduced *WDPT*, while Ca-montmorillonite caused an increase in *WDPT* in the already highly repellent sand. Potential mechanisms for the alleviation effectiveness of kaolinite are proposed, with key factors being the high adhesion forces between water and clay mineral surfaces, and the ability kaolinite to disperse. In the case of Ca-montmorillonite, its lower affinity for water may lead to a displacement of water molecules at mineral surfaces by amphiphilic organic compounds, which may result in increased repellency. This phenomenon clearly requires further investigation.

Keywords: water repellency; kaolinite; Ca-montmorillonite; stearic acid

The occurrence of water repellency in many soils worldwide has been well established (e.g. Mašum et al. 1989, Ritsema and Dekker 1996, Dekker and Ritsema 1997, Doerr et al. 2000, Jaramillo et al. 2000, Gerke et al. 2001, Guerrero et al. 2001, Hallett et al. 2001, Buczko et al. 2002). During a soil survey of the Slovak soils we found that Eutric Fluvisol (site Demänovská dolina Valley, *WDPT* = 2000 s in A horizon), Cambic Arenosol (Borská nížina Lowland, *WDPT* = 145 s and 11 700 s in A₀ and B_{vs} horizons, respectively), and Histi-Haplic Podzol (Malá Fatra Mts., *WDPT* = 11 130 s and 672 s in Ot and Bsh horizons, respectively) are susceptible to water repellency (WRB 1994, Dlapa et al. 2003).

Soil water repellency (hydrophobicity) can reduce agricultural production and contribute to land degradation caused by increasing run-off and erosion (Shakesby et al. 2000). For example it can cause delayed germination of pastures and crops leaving soil bare for a longer time and prone

to wind erosion. Yields are reduced by the patchy growth and the delay in germination reduces the effective growing seasons (McKissock et al. 2000). The water repellency of the topsoil reduces the infiltration capacity of the soil matrix, which can lead to enhanced overland flow and associated soil erosion (Shakesby et al. 2000) and nutrient washout (Lennartz et al. 1997). This may be particularly the case where heavy rainstorms follow prolonged dry periods, a combination of events that is increasing in frequency and intensity as a consequence of climate change (Cebulak et al. 2000). Soil water repellency generally increases during dry weather, while it is reduced or completely eliminated after prolonged and/or heavy precipitation (Doerr et al. 2000). Water repellency is, however, not restricted to seasonal climates as, for example, a very humid conditions are particularly favourable for the production of organic matter and thus of also the organic compounds causing repellency (Jaramillo et al. 2000).

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An effective method to prevent soil water repellency, which is often used in sport turfs to prevent dry patches, or localised dry spotting, is to irrigate frequently, thus maintaining high soil moisture levels (Cisar et al. 2000). Other methods to mitigate this include the use of surfactants as commonly applied to golf greens (Cisar et al. 2000, Kostka 2000) and the addition of clay to the top soil (claying) either by deep ploughing into a clayey subsoil, or by a top dressing with clay, as used successfully in some regions in Australia (Carter et al. 1998).

Laboratory investigations have shown that the efficiency of clay additions may depend on clay mineralogy. During repeated wetting and drying phases, the clays dominated by kaolinite were much more effective in reducing water repellency than their montmorillonite-rich counterparts (McKissock et al. 2000, 2002). But in sand in which repellency was artificially induced by cetyl alcohol, montmorillonite was more effective than kaolinite (Ward and Oades 1993).

The objective of this study was to evaluate the ability of kaolinite and Ca-montmorillonite to alleviate water repellency in sand made highly water repellent by stearic acid. The sands were subjected to a wetting phase and a prolonged drying phase at 50°C to simulate the effects of wet as well as hot dry spells on water repellency.

MATERIAL AND METHODS

The effectiveness of kaolinitic and Ca-montmorillonitic clays to alleviate soil water repellency was studied on silica sand with a particle size distribution showed in Table 1. Water repellency of the silica sand was induced by the addition of stearic acid (Aldrich, purity 95%, molecular weight 284.5), resulting in a homogenous and highly repellent model soil. Stearic acid dissolved in diethylether (Riedel-de Haën, p.a.) was added to the silica sand and mixed until total volatilisation of diethylether. In this way, samples of stearic acid sand containing 10 and 30 g/kg stearic acid were prepared.

The clay mineral material (well-ordered kaolinite KGa-1b and Ca-montmorillonite) were purchased from the Source Clay Minerals Repository (University of Missouri, Columbia, USA). The

physical, chemical, and mineralogical characteristics of the clay minerals used in this study are described in Olphen and Fripiat (1979).

Air-dried silica sand was placed in a glass vial, and the relevant clay mineral was added to obtain samples (without duplicates) with the mass of 5 g and the clay contents of 0, 1, 2, and 3% (mass). The vial was gently shaken end-over-end for 2 min at 30 rpm to mix the clay with the sand. The samples were then placed in the Petri dishes, and the persistence of water repellency was estimated with the widely used water drop penetration time (WDPT) test in all of the samples. The persistence of water repellency determines how long water repellency persists on a porous surface. This measure is thought to be highly relevant to the hydrological effects of water repellency in soils as it relates to the time required for raindrops to infiltrate (Doerr 1998).

A wetting phase was imposed through adding 2 g of distilled water on the surface of each sample, and allowing it to penetrate for three days. Then the samples were gently mixed to obtain the constant moisture ($w = 40\%$) in the whole volume. It should be mentioned that water remained on the surface of the mixtures of the repellent sands containing 30 g/kg stearic acid and treated with Ca-montmorillonite even after three days. A drying phase was subsequently induced by drying samples at 50°C. During the drying phase, water repellency was measured repeatedly by WDPT test in all the samples. After approaching $w = 0$, the heating of the samples was continued to simulate a prolonged hot dry spell. Control samples (treated only with stearic acid) and samples with kaolinite additions were heated for 1245 h, the mixture of sand with Ca-montmorillonite for 576 h. A temperature of 50°C was chosen as the temperature that may commonly be reached at the surface of a bare soil during a hot summer (Doerr and Thomas 2000).

For the WDPT test one to three drops of distilled water from a medicinal dropper were placed onto the soil surface and the actual time required for infiltration was recorded. The volume of water in a droplet was $58 \pm 5 \mu\text{l}$. A standard droplet release height of approximately 10 mm above the soil surface was used to minimise the cratering effect on the soil surface (Wylie et al. 2001). Evaporation of water from the drop is considered to be negligible during the relatively short exposure times of the water drops (Gerke et al. 2001). The following classes of the persistence of water repellency were distinguished: wettable or non-water-repellent soil (the water drop penetration time $WDPT < 5$ s); slightly ($WDPT = 5-60$ s), strongly ($WDPT = 60-600$ s), severely ($WDPT = 600-3600$ s), and extremely ($WDPT > 3600$ s) water repellent soil (Dekker and Ritsema 1995).

Table 1. Particle size distribution of the silica sand used in this study

| Particle size (μm) | 315-400 | 400-800 | > 800 |
|---------------------------------|---------|---------|-------|
| Sand particles (% weight) | 0.3 | 86.3 | 13.4 |

RESULTS AND DISCUSSION

The silica sand, kaolinite and Ca-montmorillonite used in the experiments were originally wettable with *WDPT* < 1 s. Results of the *WDPT* test for the sample mixtures before wetting or drying are listed in Table 2. After treatment with stearic acid the sand was extremely water repellent for both treatments with 10 and 30 g/kg stearic acid, with *WDPT*s of 6540 and 10 860 s, respectively. The effect of added clay minerals on the *WDPT* of the stearic acid sand was somewhat inconsistent at the beginning of experiments (i.e. before the wetting and drying phases). When mixed with the sand containing 10 g/kg of stearic acid, the kaolinite reduced *WDPT* by an order of magnitude. However, it was less effective if mixed with the sand containing 30 g/kg of stearic acid. In this case, the *WDPT* decreased by 37–48%. For the Ca-montmorillonite treatments, an increase in *WDPT* was observed for the sand containing 10 g/kg of stearic acid, and a decrease in *WDPT* for the sand containing 30 g/kg of stearic acid.

After the wetting phase, the water repellency disappeared in all the samples, although, as outlined above, for the samples with the sand containing 30 g/kg of stearic acid treated with Ca-montmorillonite, complete wetting was only achieved by physical mixing. During the drying phase, water repellency of the stearic acid sand did not re-appear until the water content decreased below the critical moisture content of 1%. This finding is in accordance with the relative low moisture contents, required for repellency to occur from field observations from a seasonally repellent or sandy soil in the Netherlands (Dekker et al. 2001).

The rate of the *WDPT* increase associated with the prolonged heating can be seen in Figures 1–3. It was found that heating at 50°C for more than 48 h did not result in further *WDPT* rise for the mixtures of the sand with kaolinite, and for the

Table 2. The results of the *WDPT* test on the samples before wetting

| Sample | <i>WDPT</i> (s) | |
|---|----------------------|----------------------|
| | 10 g/kg stearic acid | 30 g/kg stearic acid |
| Stearic acid sand | 6 540 | 10 860 |
| Stearic acid sand + 1% kaolinite | 263 | 6 400 |
| Stearic acid sand + 2% kaolinite | 283 | 5 660 |
| Stearic acid sand + 3% kaolinite | 880 | 6 800 |
| Stearic acid sand + 1% Ca-montmorillonite | 8 280 | 7 300 |
| Stearic acid sand + 2% Ca-montmorillonite | 8 660 | 6 920 |
| Stearic acid sand + 3% Ca-montmorillonite | 6 900 | 8 000 |

mixtures of the sand containing 30 g/kg of stearic acid with Ca-montmorillonite. That heating for more than 80 h did not result in further *WDPT* rise for the mixtures of the sand containing 10 g/kg of stearic acid with Ca-montmorillonite. In contrast, the *WDPT* rise stopped only after 810-h heating in the sand containing 30 g/kg of stearic acid, but did not stop even after 1240-h heating in the sand containing 10 g/kg of stearic acid. The initial *WDPT* value measured before the wetting and drying cycle, however, was not reached in any sample even after 1240-h heating at 50°C.

It is notable that the water repellency re-appeared during a drying phase at a water content between 10–20% in a previous study (Lichner et al. 2002). Water repellency in the same sand ma-

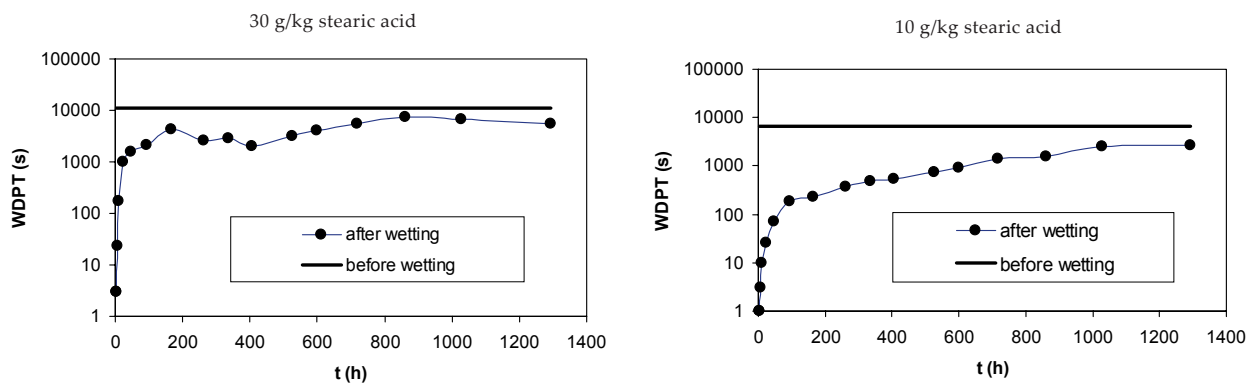


Figure 1. Relationship between the water drop penetration time *WDPT* and duration *t* of drying and heating at 50°C for the samples of stearic acid sand; note that the line representing the before wetting status is only given to facilitate a comparison; a prolonged heating of samples before wetting was actually not carried out

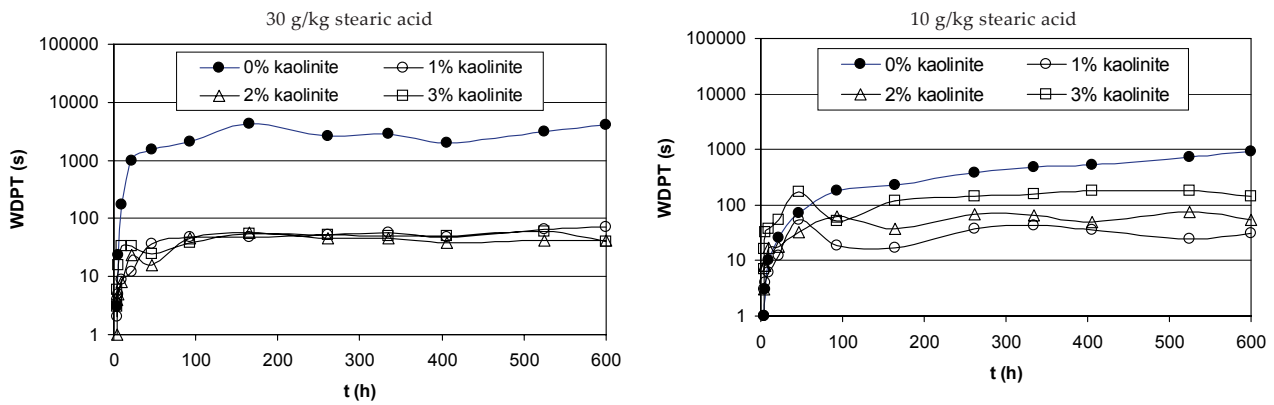


Figure 2. Effect of kaolinite addition on the relationship between the water drop penetration time *WDPT* and duration *t* of drying and heating at 50°C

material had been induced by an addition of humic acids, and was alleviated with kaolinite. The critical moisture content depended on the percentage of kaolinite (5 and 10%) and drying temperature (30 and 60°C).

The results demonstrate that kaolinite is effective in alleviating the water repellency induced with stearic acid (Figure 2). In all cases the *WDPT* of mixtures with kaolinite is lower than the initial *WDPT* of the stearic acid sand. In contrast, Ca-montmorillonite is not effective in alleviation of the water repellency induced with stearic acid (Figure 3). In all cases the *WDPT* of mixtures with Ca-montmorillonite is higher than initial *WDPT* of the stearic acid sand.

The results obtained in this study are in agreement with those by Ma'shum and Farmer (1985) that oven-drying can re-establish water repellency to some extent, although not to its initial level. After repeated wetting and drying phases, McKissock et al. (2002) observed decrease in water repellency for untreated soils and for soils with added Georgia kaolinite, but an increase in water repellency after addition of Wyoming bentonite to studied soils. It has been suggested by Doerr and Thomas (2000)

that a new input of hydrophobic substances may be required to fully restore water repellency after its cessation during wetting. During the heating, the polar (hydrophilic) groups of organic substances are oriented towards the mineral surfaces, and the non-polar (hydrophobic) parts of organic molecules are oriented towards the free space (air). The rate of transition depends on the height of activation energy, which represents an energy barrier that must be overcome by supplied energy.

It was found that *WDPT* was higher for higher clay contents in the majority of measurements, as it is presented in Figures 2 and 3. This phenomenon was surprising, and the authors do not have a satisfactory explanation for this phenomenon at this stage.

The results presented above suggest that clay mineralogy is the most important factor, which determine the range of changes in *WDPT*. A high effectiveness of clay minerals from kaolinite group was suggested already by Ma'shum et al. (1989) and McKissock et al. (2002). This is the case despite the comparatively small surface area and large particle size of kaolinite. An important factor de-

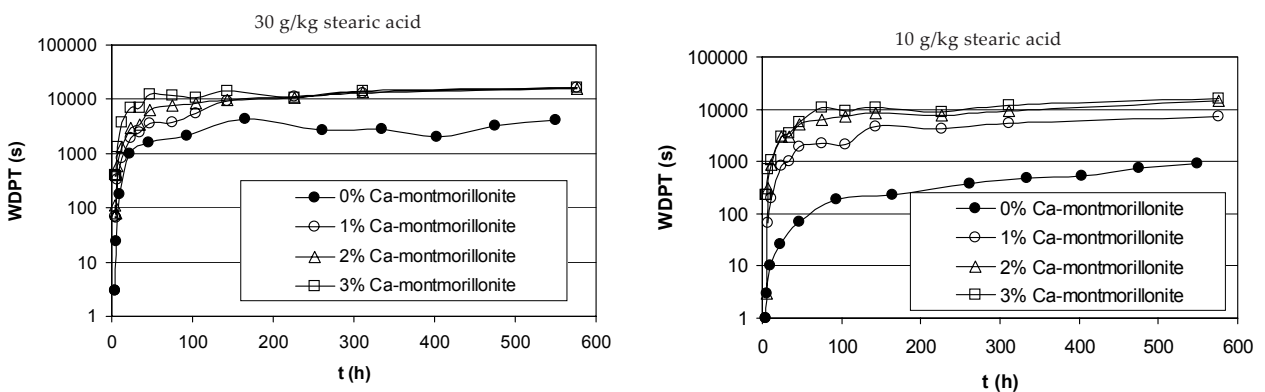


Figure 3. Effect of Ca-montmorillonite addition on the relationship between the water drop penetration time *WDPT* and duration *t* of drying and heating at 50°C

termining clay effectiveness can be the difference in the ability of clay minerals to mask hydrophobic surfaces and to facilitate water penetration. In this sense, kaolinite could be more effective than Ca-montmorillonite after the wetting and drying because Ca-montmorillonite tends to aggregate, whereas kaolinite remains dispersed, allowing to retain an effective covering of hydrophobic surfaces (McKissock et al. 2002).

Montmorillonite in the mixture with sand tends to aggregate even when it is initially dispersed (McKissock et al. 2000). Flocculation and dispersion depend on the crystal structure and crystal chemistry of clay minerals. Clay minerals with high surface charge tend to flocculate whilst clay minerals with low charge remain dispersed on sand surface. Flocculation and dispersion is also strongly affected by exchangeable cations present. Tendency to flocculation will increase with increasing cationic charge and with decreasing concentration of soil solution. For these reasons chemical properties of soil can markedly affect the behaviour of clay minerals added for the purpose of mitigation of water repellency. This may be a reason why the results of this present study, in which stearic acid was used are in part contrasting to the results in the study by Ward and Oades (1993) outlined in the introduction, in which cetyl alcohol was used to impart water repellency.

In addition the differences in dispersion behaviour of the clays, we propose an additional mechanism to explain the clay mineral effect on the persistence of water repellency, which is related to the water adhesion forces. Hydrophobic or hydrophilic properties result from the balance between cohesion and adhesion forces. Cohesion originates from hydrogen bonding between water molecules. Adhesion is attraction of water by solid surfaces. Strong adhesion comes from the hydrogen bonding of water molecules to mineral surfaces. Slight adhesion occurs between water and the hydrophobic organic surfaces, where the Lifshitz-van der Waals forces predominate (Michel et al. 2001). The hydrophilicity of minerals increases with the density of their charges and polar groups, mainly $-OH^-$, on the surface (Bachmann and van der Ploeg 2002). Mineral structure of kaolinite with hydroxyl groups on the basal plane, resulting in the higher density of hydroxyl groups on the kaolinite surface probably makes kaolinite more hydrophilic than Ca-montmorillonite, irrespective of the water binding capacity. In our opinion, the difference in the ability to attract water (hydrophilicity) is also a key factor affecting the ability of clay minerals to reduce the *WDPT* in water repellent soils. Thus, the more hydrophilic kaolinite is more effective in alleviation of water repellency than the less hydrophilic Ca-montmorillonite. Low affinity for

water of Ca-montmorillonite probably can lead to a displacement of water molecules at mineral surface by amphiphilic organic compounds, which in turn resulted in the increase in *WDPT* in treated water repellent soil.

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ABSTRAKT

Účinek kaolinitu a Ca-montmorillonitu na zmírňování vodoodpudivosti půd

Účinek kyseliny stearové, kaolinitu a Ca-montmorillonitu na vodoodpudivost křemenného písku jsme studovali v průběhu cyklu navlhčení a vysušení a též prodlouženého ohřevu na 50 °C, kterým jsme simulovali důsledky klimatické změny. Teplotu 50 °C dosahuje v létě povrch půdy bez vegetace. Stálost vodoodpudivosti jsme určovali měřením doby vniku kapky vody do půdy – tzv. WDPT (water drop penetration time) testem. Po skončení cyklu navlhčení byly všechny vzorky smáčivé (hydrofilní). Během cyklu vysušení se vodoodpudivost v žádném vzorku písku neobjevila dříve, dokud nepoklesla vlhkost pod 1 %. Působení jílu na vodoodpudivost záviselo na jejich mineralogickém složení. Přidání kaolinitu k písku mělo za následek zkrácení doby vniku kapky vody do půdy (WDPT), zatímco přidání Ca-montmorillonitu vedlo k prodloužení této doby v porovnání s variantou s pískem pokrytým kyselinou stearovou bez přidání jílu. Vysvětlení tohoto jevu je založené na novém mechanismu, odvozeném z rozdílu adhezních sil mezi vodou a povrchy jílových minerálů. V důsledku toho je hydrofilnější kaolinit efektivnější ve zmírňování vodoodpudivosti půd než méně hydrofilní montmorillonit.

Klíčová slova: vodoodpudivost; kaolinit; Ca-montmorillonit; kyselina stearová

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