Wetting Angle and Water Sorptivity in Mineral Soils

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Abstract: Two simple models of a non-cylindrical (wavy) capillary have been applied to show the impact of pore shape and of wetting angle on water sorptivity in soils. Wetting angle derived from the Washburn approach gives an overestimated value because of pores are modelled as round capillary tubes, whereas in reality they are tortuous, wavy and interconnected. In wavy capillaries, the impact of wetting angle on water sorptivity and capillarity driven water transport can be much more pronounced in relation to Washburn approach. An observed wetting front movement can be seen as a superposition of micro jumps and rests. Experiments carried out with glass powder and two soils confirm the above predictions.

Keywords: sub-critical repellency; Washburn theory; wavy capillary

Wettability is one of the most important features of soils as it directly influences their physical, mechanical, chemical, biological and fertility properties. A majority of soils, especially cultivated ones, are wettable, with rain-water appearing to infiltrate readily. However, for the past 30–40 years it has been evident, especially in dry and hot climates, that soils water immbibition is restricted considerably or temporarily very limited (DeBano 2000). A drop of water placed on the surface of these soils can take seconds to hours to infiltrate, depending on the degree of soil water repellency (SWR). SWR is though to result from organic matter components coating the surface of mineral soil grains (Tschapek 1984; Ma'shum *et al.* 1988; Poulenard *et al.* 2004). The WDPT (Letey 1969) and the Molarity of an Ethanol Droplet (MED) tests (King 1981; Doerr 1998) are the most frequently applied measurement methods of SWR. A more quantitative measure is the contact angle. This surface property is influenced by the energy balance between water, vapour and solid. Although most soil physics research assumes the contact angle to be zero, a condition allowing perfect wetting, in reality the contact angle is much greater in most soils (Bachmann *et al.* 2000). Values greater than 30° are commonly found (Hajnos *et al.* 2003), with values greater than 90° representing highly water repellent soils (Grelewicz & Plichta 1985).

The phenomenon of soil water repellency occurs not only in dry and hot climate conditions. Recently one can find evidence in research papers that so called sub-critical repellency is rather the rule than an exception. The above term refers to a soil which is not perfectly wettable, even though it readily imbibes water (Clothier *et al.* 2000; Hallett *et al.* 2001, 2004; Eynard *et al.* 2006). These are the soils that will have contact angles greater than zero but less than 90°. Such a soil state is frequently called a sub-repellent one.

Application of indirect indices (WDPT, MED) of soil repellency is closely related to the lack of

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wetting angle measurement method in real porous media at all. In next chapters a short summary of present state of art in this respect will be presented together with a proposed modification concerning the impact of pore shape on measured wetting angle value.

From previous studies (CZACHOR 2006) one can expect that the water sorptivity S (PHILIP 1957; TILLMAN *et al.* 1989) of soils should be a strongly decreasing function of wetting angle θ. The aim of the paper is verification of the above hypothesis for real porous media (glass powder and two soils).

Meniscus movement in cylindrical capillary

The most frequently applied method of indirect soil-water wetting angle measurement is based on the Washburn theory (WASHBURN 1921), which

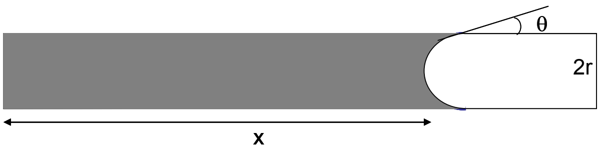

Figure 1. Meniscus in a cylindrical capillary of radius *r*

can be treated as a generalization of the so-called capillary bundle model where soil pores are modelled by straight, cylindrical capillaries as presented at Figure 1.

This theory defines the velocity of meniscus movement in a cylindrical, horizontal capillary $v(t)$ as

$$v(t) = \sigma r \cos\theta/(4\eta x) \quad (1)$$

and the kinetics of meniscus $x(t)$ can be presented in the form:

$$x(t) = \sqrt{\sigma r t \cos\theta/(2\eta)} \quad (2)$$

where

r – capillary radius (m)

σ – liquid surface tension

η – liquid viscosity

θ – wetting angle

t – time

Eq. (2) shows that the extent of water infiltration is proportional to $\sqrt{t}$. PHILIP (1957) recognised this relation in developing the first simple theories describing water absorption by soils. He showed that the cumulative infiltration in soil, $Q(t)$ changes with $\sqrt{t}$ depending on the sorptivity, S, of the soil:

$$Q(t) = S\sqrt{t} \quad (3)$$

For a perfect capillary, sorptivity is related to the applied liquid and solid phase properties

$$S = \sqrt{\sigma r \cos\theta/(2\eta)} \quad (4)$$

By analogy, the soil sorptivity S is a parameter which depends on pore size distribution, wetting angle θ and the properties of the applied liquid: surface tension σ and viscosity η. In this approach, wettability of a soil is determined by its wetting angle θ. If it is smaller than 90°, the soil is classified as wettable, or as water repellent when θ > 90° (LETEY 1969; WATSON & LETEY 1970). According to HARTMAN and VERPLANCK (1975), the wetting angle of water in soil θ_w can be calculated from the following equation:

$$\cos\theta_w = (S_w/S_a)^2\ \eta_w/\eta_a \times \sigma_a/\sigma_w \quad (5)$$

where subscripts w and a concern water and a perfectly wetting liquid like methyl or ethyl alcohol, respectively. In other words, the wetting angle of water in the investigated soil is determined from two experiments where water sorptivity and methanol sorptivity are measured. It is assumed here that an alcohol, as an apolar low-surface-tension liquid, perfectly wets the soil, e.g. θ_a = 0°.

Capillarity in wavy pores

However, the basic assumption of the above method seems to be unjustified. It is rather difficult to imagine cylindrical micropores between more or less rounded solid soil particles. In reality soil pores are tortuous and their cross section is variable. Moreover, all pores are interconnected, creating a soil pore network.

Let us analyse a simple case of axis periodic, symmetrical capillary where its geometrical radius is changing according to the equations

$$r_g(x) = r_1 + ax;\ -h/2 \le x \le h/2 \quad (6)$$

and

$$r_g(x) = r_1 - ax;\ h/2 \le x \le 3/2h \quad (7)$$

as it is presented in Figure 2. Meniscus movement in such a capillary is quite different in relation to the cylindrical one where wetting perimeter displacement equals the meniscus displacement. Let us imagine a liquid movement inside of it, driven by capillary pressure P_k, which is described by Laplace equation:

$$P_k = 2\sigma/r_\mathrm{m} \quad (8)$$

where:

r_m – meniscus curvature radius related to the geometrical radius r_g via equation

$$r_m = r_g/\cos(\alpha + \theta) \quad (9)$$

where:

α – wall slope angle in relation the axis

θ – wetting angle

If the wetting angle equals zero, the meniscus curvature radius r_m is perpendicular to the wall at the wetting point. The grey bold line in the left of Figure 2 corresponds to the radius r_m where point A shows a wetting point and point A1 – a meniscus position (observable meniscus bottom). This coordinate represents a critical meniscus state – if the wetting point would move right to a point A' a corresponding meniscus would cross a pore wall, which is a physical nonsense (see the grey dotted line in Figure 2). The next wetting point position where the meniscus fits in the capillary is shown in the middle of Figure 2 where points B and B1 are the wetting point and meniscus bottom positions, respectively (for the reason of readability the meniscus B was drawn in the middle of Figure 2). Analysing the positions of points A1 and B1 one can notice that in a certain part of the wavy capillary the meniscus bottom moved back, even if the wetting perimeter went forward (from A to B). Moreover, one cannot imagine a stable meniscus for wetting perimeter situated between these two points. In other words, in wavy capillaries there

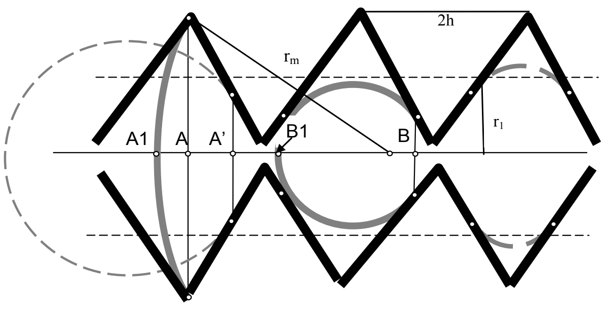

Figure 2. Menisci inside of periodic, axis-symmetrical wavy capillary (meniscus movement from left to right)

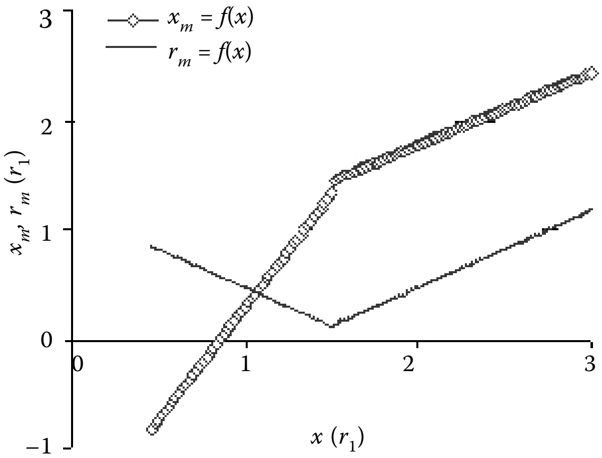

Figure 3. Meniscus position x_m and meniscus curvature radius r_m vs. wetting perimeter position x in the axis-symmetrical capillary described by $r_g(x) = r_1 \pm ax$, ($r_g(x)$ – geometrical radius, r_1 – mean radius, wall slope a = 0.6)

exists a range of wetting perimeter positions where the meniscus has to be unstable.

Figure 3 presents the relationships between meniscus radius and meniscus position vs. wetting perimeter position, e.g. $r_m = f(x)$ and $x_m = f(x)$ for a capillary from Figure 2 (Eqs. 6 and 7). There are no x_m and r_m values for wetting perimeter coordinates $0 < x < 0.4$ for the reason of meniscus instability. One can notice that in the left part of the capillary domain the displacement velocity is large in relation to the right one. Moreover, a meniscus jump occurs in the middle of the domain (for $x = 1.5$). The left part of the curve has no points for the wetting perimeter position $0 < x < 0.4$. As shown earlier, this range corresponds to the unstable meniscus range. One can speculate that such instability should slow down the meniscus movement.

A similar model concerning a different geometry of wavy pores has been presented in (Czachor 2007), where the pore shape has been approximated by

$$r_g(x) = r_1 + r_2 \sin\pi x/h;\ r_1 > r_2 \quad (10)$$

An example of meniscus kinetics in such type of capillaries is shown in Figure 4, which illustrates the meniscus vs. wetting perimeter position relationship. The meniscus velocity ($\mathrm{d}x/\mathrm{d}t$) varies quickly and its movement can be regarded as a succession of jumps and rests. It was shown in (Czachor 2007), that the wetting angle derived from experimental data for two liquids and from the Washburn theory is related to the Young wetting angle θ and to the pore shape parameter r_2/h.

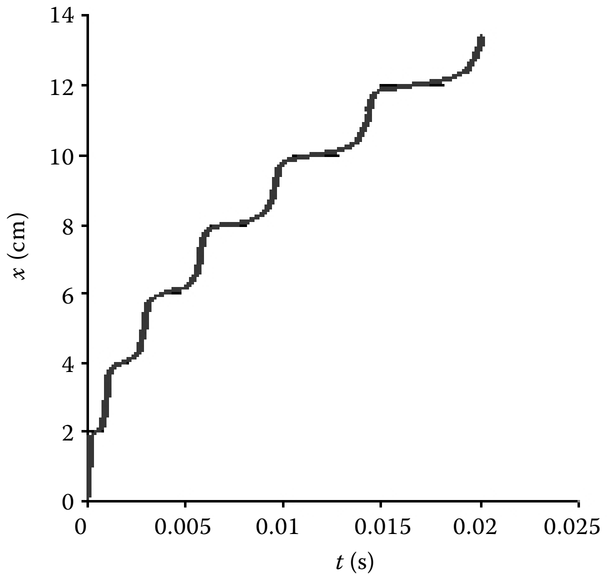

Figure 4. Kinetics of meniscus displacement in a sinusoidal capillary

In the case of capillary shape described by Eq. (10), an analytical formula for a wetting angle derived from Washburn theory θ^{Wash} was presented

$$\cos\theta^{\mathrm{Wash}} = \langle \cos\theta - \pi r_2/h \sin\theta \sin\pi x/h \rangle \qquad (11)$$

where:

θ – Young wetting angle

The ‹› brackets in Eq. (11) denote a mean harmonic value of the enclosed expression. Analysis of Eq. (11) shows that the wetting angle θ^{Wash} depends on the pore shape parameter r_2/h and it has to be larger in relation to θ *e.g.* $\theta^{\mathrm{Wash}} > \theta$. The difference $(\theta^{\mathrm{Wash}} - \theta)$ *vs.* θ for 4 different shaped capillaries is shown in Figure 5. It is always positive and increases when both the Young wetting angle θ and the parameter d_2

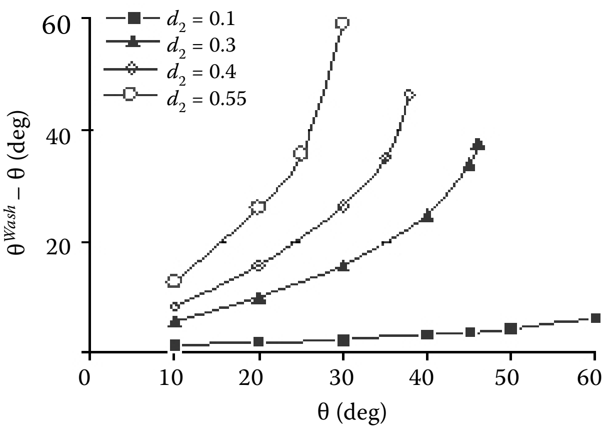

Figure 5. $\theta^{Wash} - \theta$ vs. θ for some capillaries of different shapes ($d_2 = r_2/h$)

increase. It is worth mentioning that Eq. (11) does not take into account the meniscus instability effect and that the Washburn theory derived wetting angle equals the Young wetting angle, $\theta^{\mathrm{Wash}} = \theta$, when $r_2/h = 0$ in a cylindrical pore only.

So in the case of a wavy capillary, Eq. (4) should be written as

$$S_w = \sqrt{\sigma r \cos\theta^{\mathrm{Wash}}/(2\eta)} \qquad (12)$$

where:

S_w – sorptivity of wavy capillary

θ^{Wash} – defined by Eq. (11)

From the analysis of Figure 5 and of Eq. (12) one can expect that the water sorptivity S should be a strongly decreasing function of wetting angle θ.

The goal of the paper is verification of the above hypothesis concerning $\theta^{\mathrm{Wash}} = f(\theta)$ relationship for real porous media (glass powder and two soils).

Experimental procedure

The observed smooth movement of a wetting front in soils can be treated now as an averaging effect of a huge number of micro menisci jumps and near-repose positions occurring in between single pores created by soil grains. Beside liquid properties, water sorptivity of a soil depends on pore sizes and wetting angle. Soil water sorptivity S is a parameter that quantifies the above process. If the approach proposed in this paper is valid, one can predict that the water sorptivity of soil should not be proportional to cosθ but to $\cos\theta^{\mathrm{Wash}}$ expressed by Eq. (11). However, in the case of soil the wetting angle θ is always unknown. To overcome the above difficulties the authors decided to verify the above theory by means of experiments with an artificial grain medium where θ can be directly measured. Small pieces of window glass were ground and sieved to obtain 100 g of 50–200 micrometers fraction powder. Glass powder was treated by means of hydrochloric acid, distilled water and dried. Thereafter, 20 g of glass powder were packed in 10 mm ID glass column for liquid kinetics measurements (Czachor 2007). The same procedure was applied for two soils sampled from 0–30 cm layer of silty loam (Haplic Luvisol) and loose sand (Cambic renosol) sampled in Lublin region (south-east Poland), which contained 9.8 and 10.9 g/kg of organic carbon, respectively. The soils were dried and sieved through a 1mm sieve. Before experiments the soil samples and glass powder were kept for at

Table 1. Young wetting angle θ and Washburn theory wetting angle θ^{Wash} for two soils and glass beads

Medium	θ (°)	θ^{Wash} (°)
Flat glass	< 0.2 methanol 27.4 water	
Glass beads (diameter 90–150 µm)		72.6
Silty loam (Orthic Luvisol)		79.1
Loose sand (Cambic renosol)		76.4

least 5 days in a desiccator under stable relative humidity conditions of RH = 40%.

Simultaneously a flat piece of the same glass (~10 cm^2) was carefully cleaned and then 5 small drops of distilled water/methyl alcohol were placed on its surface. Their images were analysed by the Aphelion Image Analyze package to determine the drop geometry, and then the wetting angle of liquid related to investigated glass was calculated.

Experimental verification of the model

Measurement of water and methyl alcohol sorptivities was done by means of a simple device composed of glass column, Mariotte bottle and electronic balance. The column was filled with glass powder or soil and thereafter the powder/soil was gently compacted by micro vibrations to a prescribed volume. The end of the horizontal column was connected to the Mariotte bottle and thereafter the time t and the mass of absorbed liquid were recorded. Three replications were made for each medium examined and for both applied liquids: distilled water and methyl alcohol. An example of the measurement in a glass bead composed of 90–150 micrometers particles is shown in Figure 6. Experiments with the glass beads were fundamental for the reason of direct wetting angle measurement done on a flat piece of glass. The resulting wetting angle equals 27.4° for water and < 0.2° for methyl alcohol.

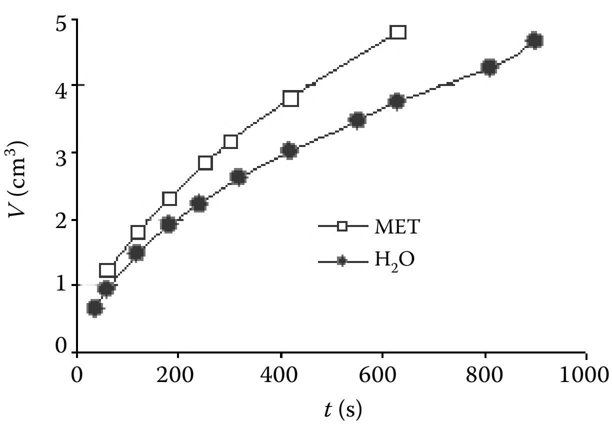

Figure 6. Water (H_20) and methanol (MET) kinetics in a 90–150 micrometers glass bead

The data from horizontal infiltration concerning water and methyl alcohol allowed calculation of a second wetting angle θ^{Wash}=72.6°. The difference $\theta^{Wash} - \theta = 45.2°$ is a result of applied cylindrical model of pore which describes its shape incorrectly.

As both wetting angles θ^{Wash} and θ from Eq. (11) are known, one can determine the r_2/h value which was found to be equal 0.556. The above parameter concerns a relatively mono-size grain distribution. Generally one can speculate that it should be a grain size distribution and soil bulk density dependent value.

One can expect that similar relationships should occur in the case of all soils and other porous media. The results concerning both wetting angles θ^{Wash} and θ for glass and two soils are presented in Table 1.

One of the most interesting observations, which can be easily made, is the three-fold difference between θ and θ^{Wash}. Another interesting observation is that θ^{Wash} values for the glass beads is similar to natural soils that also contain carbon and greater distribution of particle sizes. Even if soil organic matter should change the wetting angle, all obtained values are close to each other. Understanding the above results can be done by means of the nearly 30° + 60° = 90°. In the measured case θ = 27.4° and the determined value of θ^{Wash} = 72.6° (see Table 1). The ratio of cosines corresponding both values, e.g. $\cos\theta/\cos\theta^{Wash} = \cos(27.4)/\cos(72.6) = 2.97$. If one assume the same values of θ and r_2/h for a silty loam (Orthic Luvisol) the ratio $\cos\theta/\cos\theta^{Wash}$ = 4.70 means two times larger in relation to the previous case. It is clear that this ratio will go to infinity when θ^{Wash} approaches 90°.

In other words it seems that both θ^{Wash} and the water sorptivity of soils are strongly dependent on Young wetting angle θ value and soil pore shape and size.

CONCLUSIONS

The capillary bundle model does not take into account an important feature of all porous media concerning variable cross section of real pores. As a consequence the Washburn theory applied to real porous body has to give an overestimated value of wetting angle, which frequently is called an apparent or effective contact angle (Philip 1971). The impact of non cylindrical shape of pores on a calculated apparent wetting angle θ^{Wash} can be much larger than the Young wetting angle θ. The above opinion explains the relatively small difference between wetting angles of very different porous media like glass beads and soils from humus layers. In consequence, the water sorptivity of soils depends not only on pore size but on pore shape as well. Moreover, its dependence on the Young wetting angle θ is/can be much stronger in relation to the earlier model. This has serious implications to the interpretation of wetting angle data obtained from infiltration tests using water and wettable liquids.

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