Determination of soil-water contact angles in peatmoorsh soils by capillary rise experiments

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The liquid-soil contact angle indicates the wettability of a solid. This study was conducted to determine the apparent water-solid contact angle in peat-moorsh soils located in the Biebrza River Valley using two indirect methods. One of them was the height of the capillary rise at the equilibrium, and the other was a dynamic capillary rise approach. The measured values of the contact angle ranged from 64.2 to 83.1 degrees using the equilibrium height of capillary rise approach, whereas for the dynamic capillary rise method varied from 86.3 to 89.8 degrees. Comparison of the experimental results showed that the values of contact angles obtained using the dynamic capillary rise approach were about 12% higher than the values obtained from the capillary rise equation. The determined value of the apparent contact angle was affected by the gravimetric moisture content and bulk density. The contact angle values measured in peatmoorsh soils confirm that these soils exhibit some degree of hydrophobicity (water repellency) at all water contents and packed densities.

Key words: water repellency, apparent contact angle, capillary rise

INTRODUCTION

Water repellency has been reported to occur under a wide variety of soil and climatological conditions (Wallis & Horne 1992). Water repellency (wettability) depends on several factors, which are principally related to the characteristics of the organic matter of the soil. Ma'shum & Farmer (1985) produced evidence which indicated that the molecular orientation of organic matter determines the repellency of the soil. A value, which indicates the wettability of a solid, is the liquidsolid contact angle (Watson & Letey 1970). If a drop of water is placed on a hydrophobic or nonwettable surface, it balls up, so the liquid-solid contact angle will be large. A water drop that is placed on a wettable surface spreads and has a small contact angle. The contact angle for wettable soils is often assumed to be 0 degrees, but for water repellent soils the angle may be large, even larger than 90 degrees (Kutilek & Nielsen 1994).

The methods of determining the contact angle are divided into two groups: direct methods and indirect methods (Wallis & Horne 1992). Direct methods of measuring contact angles are the most common, and are obtained by placing a drop of water on the material surface and measuring the contact angle. The contact angle is then measured either directly from the profile of the volume of the droplet using an optical goniometer, or from the geometrical dimensions: volume, height and length. The technique is applicable to extremely

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hydrophobic soils, because in less water-repellent soils the drop will penetrate making geometric measurements impossible. However, even in externally repellent soils, surface roughness and pore size distribution will affect the measured values. Indirect methods are based on the rate of water movement or the height of capillary rise, which are influenced by the liquid-solid contact angles. Equations have been developed, which relate the height of the capillary rise (Letey et al. 1962) or rate of water flow through soil (Emerson & Bond 1963, Hammond & Yuan 1969) to the contact angle. If values for all the variables in the equations describing water flow or capillary rise are known, except for the liquid-solid contact angle, the liquid-solid contact angle can be calculated by measuring the rate of water flow or height of capillary rise. A contact angle measured by this means would therefore be an apparent contact angle.

The contact angle in organic soils was measured using direct methods (Valat et al. 1991, Lambert & Vanderdeelen 1996, Holden 1998). However, there is no evidence of values of the contact angle measured by indirect methods. The primary purpose of this paper is to apply indirect methods of measuring the water-solid contact angle in peatmoorsh soils. The secondary objectives are to compare two indirect methods. The first one was proposed by Letey et al. (1962) and assumes the measurement of the liquid-solid contact angle by the height of the capillary rise at equilibrium. The second method uses a dynamic capillary rise approach as developed by Malik et al. (1984).

MATERIALS AND METHODS

The soil-water contact angle was determined for 19 samples representing four different peatmoorsh soil profiles located in the Biebrza River Valley. These soils were formed as a result of drainage and intensive use of peatlands, which caused the moorshing process (Okruszko 1976). Moorshing of organic soils comprises biological, chemical and physical changes caused by a decrease in the water content and, consequently, by increased content of air in the soil. These processes lead to the formation in the top layers of a new material called moorsh. The basic feature differentiating the moorsh level from the parent layer is the structure of the soil formation: in the moorsh it is usually grainy; in the parent formation it ranges from fibrous to amorphous, depending on the degree of humification of plant remains. The soil-water contact angle values were determined from capillary rise experiments. Soils were air dried and passed through a 2 mm sieve. The capillary rise experiments were conducted in vertical glass tubes (2.5 cm in diameter and 30 cm long). The soils were packed to constant bulk density in the tubes, which were then placed on a ringstand and clamped into a vertical position in contact with either water or ethanol. Different bulk density and different values of initial moisture content of the peat soils in the columns were used in the experimental procedure. For such soil columns the height of the capillary rise was measured for a short period (1 hour) and a long period (more than 120 hours).

For long-term experiments the soil-water contact angle was determined using a method proposed by Letey et al. (1962). This method utilises the capillary rise equation:

$$h = \frac{2\sigma \cos\alpha}{\rho gr}$$
(1)

where h = height of liquid capillary rise (m), σ = surface tension of liquid (N m⁻¹), ρ = density of liquid (kg m⁻³), α = soil liquid contact angle(°), g = gravitational acceleration (m s⁻²), r = effective pore radius (m).

In this method, ethanol was used as a reference liquid (which is assumed to wet all soils readily at a 0° wetting angle) to calculate the effective pore radius (r). The process was than repeated with water to determine the apparent contact angle (α). This method assumes constant pore geometry in the soil-filled tubes and equilibrium of the capillary rise.

For short-term capillary rise experiments the contact angle was obtained by applying the equation proposed by Malik et al. (1984), which has the following form:

$$t = \frac{1}{K^2} \left[-KZ - A \ln \left(1 - \frac{K}{A} Z \right) \right]$$
(2)

where parameters K and A are calculated from



Fig. 1. Rate of capillary rise as a function of time for peatmoorsh soil (a) and values of contact angle (b) determined according to Letey et al. (1962) method.

the following formulae:

$$K = \frac{\rho g r^2}{G \eta}$$
(3)

$$A = \frac{2 \sigma r \cos \alpha}{G \eta} = \frac{\lambda^2}{2}$$
(4)

In the equations (2–4) the used symbols are defined as follows: t = time (s), Z = height of capillary rise (m), K = weighted mean hydraulic conductivity of the transmission zone (m s⁻¹), A = parameter (m² s⁻¹), η = viscosity of water (N s m⁻²), G = the pore shape factor (–), λ = the penetration coefficient (m s^{-1/2}), ρ , g, σ , α , r = as defined in equation (1).

The penetration coefficient (λ) represents the advance of the visible wetting front on the horizontal axis per square root of time. Parameter K may be thought of as the hydraulic conductivity

of a capillary tube that has an equivalent behaviour to that of the considered porous medium. The shape factor (G) for circular capillaries of the uniform diameter has a theoretical value equal to 8 (Childs 1969). Analogous to a capillary tube, the value of the shape factor in a porous medium must be divided by water-filled porosity (Malik et al. 1984).

The values of the parameters A and K were determined by fitting the equation (2) to the experimental data. The fitting was done using the Marquardt algorithm with the STATGRAPHICS program (STSC 1996). Then the values of the soilwater contact angle were calculated from the definition of A.

In the calculations of the contact angle the following parameter values were assumed: surface tension of water and ethanol equal to 0.0727 Nm⁻¹ and 0.0230 N m⁻¹, respectively; density of



Fig 2. Relationship between contact angle, bulk density and gravimetric moisture content.

water and ethanol equal to 998.203 kg m⁻³ and 789.5 kg m⁻³, respectively. Gravitational acceleration is equal to 9.81 m s^{-2} and viscosity of water was assumed as equal to $0.00096 \text{ N s} \text{ m}^{-2}$.

RESULTS AND DISCUSSION

The example of the measured rate of capillary rise of water and ethanol during a long-term experiment, and the calculated contact angle values using the Letey et al. (1962) method, are presented in Fig. 1. From this figure it can be seen that calculated contact angle values differ depending on the time at which equilibrium is assumed. Large differences occur during the first 24 hours of the experiments and then the value of the contact angle is nearly constant. Based on the curve in Fig. 1b, the equilibrium height of the capillary rise occurred after 120 hours. The choice of this time was somewhat arbitrary, however, as it was noted that movement of liquid after 120 hours was negligible.

The results of contact angle measurements using the equilibrium height of the capillary rise method, together with physical properties of the soils, are presented in Table 1. The soil-water contact angles determined with the Latey et al. (1962) method varied from 64.2 to 83.1 with the average value equal to 72.5 degree for the 19 soils studied. There were only minor differences in the contact angle values between considered soil kinds. The contact angle values measured in peat-moorsh soils confirm that these soils exhibit some degree of hydrophobicity at all water contents and packed densities.

The values measured here of the wetting angle are in fact apparent contact angles, which cannot be related directly to the contact angle at the liquid-solid interface. According to Philip (1971) the apparent contact angle is determined not only by the true liquid-solid contact angle, but also by properties of the internal geometry of the medium. As a result, the measured values of the bulk density and initial moisture content of the soils were included in the multiple regression analysis as parameters influencing porous medium geometry.

Soil	Number of samples	Moisture content (g g ⁻¹)	Bulk density (g cm ⁻³)	Contact angle (°)	
				equilibrium method	dynamic method
Moorsh (turf layer) 6	1.080 (0.503–1.638)*	0.338 (0.202-0.603)	72.8	88.2 (87.0–89.5)
Moorsh	7	1.189 (0.814–1.506)	0.296	72.7 (67.8–83.1)	88.2 (86.3–89.8)
Reed peat	4	1.495 (0.730–2.296)	0.220 (0.129–0.338)	71.1 (64.2–78.9)	87.6 (86.6–88.0)
Alder peat	2	0.873 (0.158–1.588)	0.371 (0.212–0.530)	74.1 (67.9–80.4)	88.8 (88.2–89.4)

* = minimum and maximum values



Fig. 3. Measured and fitted (according to Malik et al. 1984 equation) values of height of water capillary rise for two cases (a = the best fitting case, b = the worst fitting case).

As a result of performed multiple regression analysis the following equation was determined:

$$\alpha = 75.38 + 11.13\rho - 5.23\theta$$
 R² = 0.457 (5)

where α = contact angle (°), ρ = bulk density (g cm⁻³), θ = gravimetric moisture content (g g⁻¹), R = coefficient of correlation (–).

The obtained value of the R-squared statistic indicated that the fitted model explains 45.7% of the variability in the wetting angle. Performed analysis of the t-statistics showed that bulk density and initial moisture content in equation (5) are statistically significant variables at probability levels of 0.75 and 0.96, respectively.

Measured and predicted with equation (5) values of the contact angle are presented in Fig. 2. It was seen that an increase in the soil bulk density caused an increase in the contact angle, whereas a decrease in the soil moisture content values resulted in increasing contact angle.

The observed values of the height of water capillary rise versus time, measured during short term experiments, were used to calculate contact angle values according to the dynamic capillary rise method proposed by Malik et al. (1984). The measured and fitted relationships between the height of the capillary rise and the time for the two cases are shown in Fig. 3. The values of coefficient of determination (R^2) for the best fitting case (a) is 99.65% and for the worst fitting case (b) is 80.27%. The close match between the measured and predicted values of the height of the capillary rise verifies the validity of equation (2) and

provides some basis for application of the dynamic capillary rise approach to these soils for determination of contact angle values. The soil-water contact angles determined with the Malik et al. (1984) method varied from 86.3 to 89.8 with the average value equal to 88.1 degrees for the 19 soils studied (Table 1).

The comparison of data representing contact angle values, determined according to the Letev et al. (1962) method with contact angle values determined according to the Malik et al. (1984) method, is presented in Fig. 4. Comparison of the experimental results showed that the values of the contact angles obtained using the dynamic capillary rise approach were about 12% higher than the values obtained from the equilibrium capillary rise method. This difference can be explained by the fact that the final soil-water contact angle is measured in the equilibrium height of the capillary rise technique; this is in contrast to the dynamic capillary rise method in which the contact angle is determined for the early stage of capillary rise.

CONCLUSIONS

The following conclusions can be drawn:

— the soil-water contact angle in peat-moorsh soils from the Biebrza River Valley, with equilibrium height of the capillary rise method, varied from 64.2 to 83.1 degrees with the average value equal to 72.5 degree. However,



Fig. 4. Comparison of contact angle values determined according to the equilibrium height of capillary rise method with the values determined using the dynamic capillary rise method.

with the dynamic capillary rise method, the angle varied from 86.3 to 89.8 with the average value equal to 88.1 degree,

- comparison of experimental results of contact angle measurements using two different indirect methods showed that the dynamic capillary rise approach gives the values of the contact angle as about 12% higher than the values determined from the equilibrium height of the capillary rise method,
- the determined multiple regression equation, relating the apparent contact angle to moisture content and bulk density, showed that the increase in the soil bulk density value causes an increase in the contact angle, whereas a decrease in the soil moisture content value results in an increase in the contact angle.

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