Measurement of Initial Soil–Water Contact Angle of Water Repellent Soils

M. L. K. Carrillo, J. Letey,* and S. R. Yates

ABSTRACT

Water repellent soils are common throughout the world. Water repellency significantly affects infiltration, evaporation, and other water–soil interactions. Various indices, such as the water–solid contact angle (θ), water drop penetration time (WDPT), and 90° surface tension (γ_{ND}), have been proposed to characterize the degree of water repellency. The water repellency of many soils is not stable, but changes with time after contact with water. No method is available to measure the initial soil-water contact angle. The purpose of this study was to establish a technique to measure the initial soil–water contact angle. We combined previously published theoretical relationships to develop the equations $\cos\theta = [(\gamma_{ND}/\gamma_w)^{1/2} - 1]$ and $h_p = 2[(\gamma_w\gamma_{ND})^{1/2} - \gamma_w]/r\rho g$, where γ_w is the water surface tension, h_p is the breakthrough pressure head, r is the pore radius, ρ is the water density, and g is the gravitational constant. The validity of these relationships was established by treating two sand materials with octadecylamine or solvent extracts from peat moss to create various levels of water repellency. An instrument was developed to measure h_p. A linear relationship was found between h_p and $\gamma_{ND}^{1/2}$, as specified by the equation. The value of r was computed from the slope h_p vs. $\gamma_{ND}^{1/2}$ curve, and this r value was combined with h_p in the capillary rise equation to compute $\cos\theta$. Good agreement was found between measured and predicted relationships between $\cos\theta$ and $\gamma_{ND}^{1/2}$. The major conclusion is that the value of θ can be determined by measuring γ_{ND}, which is easily done in the field or laboratory.

Water repellent soils have been reported in many countries and have been shown to cause preferential flow in field conditions (Ritsema et al., 1993; Hendrickx et al., 1993). Jamison (1945) reported the occurrence of hydrophobic sand in Florida that formed *dry bodies* in the subsoil beneath citrus trees. In California, DeBano et al. (1976) reported wild fires on chaparral watersheds produced water repellent soil. The burning litter produced volatile organic substances that moved into the underlying soil and caused the repellency. Soil fungi are also responsible for inducing hydrophobicity in soils. Fairy ring patterns found in turf are the result of mycelia from the Basidiomycete fungi which have a wax-like repellent surface (Bond and Harris, 1964). Prevalence of water repellent soils makes the development of methods to quantatively characterize the degree of repellency important.

Two methods of characterizing the magnitude of water repellency have been the liquid–solid contact angle (Letey et al., 1962; Emerson and Bond, 1963) and the water drop penetration time (WDPT) (Letey, 1969). The WDPT is the time it takes a drop of water to infiltrate a soil. Assuming soil pores can be characterized as capillary tubes, the capillary rise equation can be evoked.

$$H = \frac{2\gamma \cos\theta}{r\rho g} \quad [1]$$

where H is the height of capillary rise, γ is liquid–air surface tension (hereafter referred to as the liquid surface tension), θ is the liquid–solid contact angle, r is the capillary radius, ρ is the liquid density and g is the gravitational constant. When θ is >90°, H has a negative value and the liquid will not spontaneously enter the capillary tube. Therefore, if a drop is placed on the soil surface and does not spontaneously enter the soil, θ must be >90°. If the drop enters the soil after some time, it indicates that the values of γ and/or θ are changing with time. Thus, the WDPT allows one to determine whether the initial θ is greater or less than 90° and provides information on the stability of the water repellency. Traditionally, a soil has been considered to be water repellent if WDPT is >0, which specifies that the initial contact angle is >90°.

The liquid–solid contact angle measurement (Letey et al., 1962) compared the height of rise of water and ethanol in a soil column. The value of θ for ethanol was assumed to be 0, which allowed the calculation of r by Eq. [1] for the soil. The value of r and the measured H for water allowed the calculation of θ. This method requires the water to be in contact with the soil for some time so that the values of γ and/or θ have an opportunity to change. A computed θ, therefore, is not necessarily the initial value but is a resultant value after some time of interaction between water and the soil particle surface. Contact angles measured by this technique are in the range of 0 to 90°.

If θ is >90°, a positive pressure must be applied to force liquid into the capillary tube. This pressure will be referred to as the breakthrough pressure head and symbolized as h_p.

The degree of water repellency can be characterized by the 90° surface tension, γ_{ND} (Watson and Letey, 1970). The γ_{ND} is the surface tension of the liquid when the contact angle is 90°. The concept behind this test is similar to the one proposed by Zisman (1964) for the critical surface tension. Zisman, using a homologous liquid series and planar surface, found a linear relationship between θ and γ. He referred to the surface tension that created a contact angle equal to 0 as being the critical surface tension and found this to be a characteristic of the solid surface itself. Watson and Letey (1970) modified Zisman's approach by using the surface tension when the contact angle was 90° rather than 0. This was done by mixing ethanol with water to create a range of surface tensions. Drops of these solutions were placed on the soil surface. All low surface-tension solutions spontaneously enter the soil, and the high surface-tension solutions do not spontaneously enter the soil. The γ_{ND} was defined as the surface tension of the solution that represented a transition between the drop entering the soil vs. remaining balled on the soil. A variation of this test was developed by Ritsema et al. (1993), who characterized the degree of water repellency of sand dunes by using the amount of ethanol which needed to be added to water to reach the transition point, and who reported the results in terms of the molarity of this aqueous ethanol solution.

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Abbreviations: WDPT, water drop penetration time.

To date there is no method to measure the initial contact angle of water repellent soils. The objectives of this study were to (i) combine previously published theoretical relationships in order to obtain equations relating the breakthrough pressure head to γ_{ND} and the initial contact angle to γ_{ND}, (ii) experimentally test the validity of these relationships, and (iii) propose a technique to measure the initial contact angle of water repellent soils based on these relationships.

THEORY

Good and Girifalco (1960) showed that the interfacial tensions between the liquid and solid phases were given by

$$\gamma_{sl} = \gamma_{so} + \gamma_l - 2\Phi(\gamma_{so}\,\gamma_l)^{1/2} \qquad [2]$$

where γ_{sl} is the solid–liquid, γ_{so} is the solid–vacuum and γ_l is the liquid–vapor surface tension. The constant Φ is a function of the molecular properties of the solid and liquid and has empirical values ranging from 0.5 to 1.15 (Adamson, 1990, p. 144). For a water–hydrocarbon system, Φ is approximately unity. In these systems only the contribution from the dispersion forces on the surface tensions are taken into account (Adamson, 1990, p. 144). For more information regarding Φ the reader is referred to Girifalco and Good (1957).

Young's (1805) equation is given by

$$\gamma_l \cos\theta = \gamma_{sv} - \gamma_{sl} - \pi_e \qquad [3]$$

where γ_{sv} is the solid–vapor surface tension and $\pi_e = (\gamma_{so} - \gamma_{sv})$ is referred to as the equilibrium spreading pressure. Assuming that π_e is 0 ($\gamma_{so} = \gamma_{sv}$) and combining Eq. [2] and [3] results in

$$\cos\theta = 2\Phi\,(\gamma_{sv}/\gamma_l)^{1/2} - 1 \qquad [4]$$

Selecting γ_l so that $\theta = 90°$ ($\gamma_l = \gamma_{ND}$) in Eq. [4] produces

$$\gamma_{sv} = \gamma_{ND}/4\Phi^2 \qquad [5]$$

Eq. [5] is very similar to an equation derived by Miyamoto and Letey (1971) except that they assumed that Φ was equal to 1.

Substituting the Eq. [4] and [5] into Eq. [1] and assuming that the liquid is water results in the following equation:

$$h_p = 2\,[(\gamma_w\gamma_{ND})^{1/2} - \gamma_w]/r\rho g \qquad [6]$$

If for a given soil both h_p and γ_{ND} are known, then r can be calculated from Eq. [6], which allows the calculation of θ from Eq. [1].

The contact angle, θ, can be directly related to γ_{ND} by substituting Eq. [5] into Eq. [4], which for the case of water results in the following equation:

$$\cos\theta = [(\gamma_{ND}/\gamma_w)^{1/2} - 1] \qquad [7]$$

EXPERIMENTAL PROCEDURES AND RESULTS

Two different Carsitas gravelly sand (mixed, hyperthermic Typic Torripsamments) samples were obtained at the University of California Research Station in Coachella, CA. The soils were dry-sieved to remove particulates >2mm and wet-sieved to remove the fraction of material <0.05 mm. The particle-size distribution of the sand materials used in the study is presented in Table 1. These two samples will be designated as Sand 1 for the coarser sand and Sand 2 for the finer sand.

Table 1. Percent particle-size distribution for the sands used in the study.

Size	Sand 1	Sand 2
mm	%	%
0.05–0.1	2.6	6.2
0.1–0.25	1.3	17.4
0.25–0.5	3.2	25.9
0.5–1.0	77.3	41.4
1.0–2.0	15.6	9.1

The sands were made water repellent using octadecylamine. Sands were treated by mixing 200 g of sand with 100 mL of water containing either 0.06, 0.10, or 0.14 g of octadecylamine for Sand 1, and either 0.20, 0.21 or 0.22 g of octadecylamine for Sand 2. The sand–solution mixtures were shaken for 12 h and then dried in an oven at 70°C. These treatments provided sands with different degrees of very stable repellency.

Sand 1 was also made water repellent by treating it with ethanol or benzyl alcohol extracts of peat moss. The extracts were made by mixing 200 g of peat with 1.5 L of either solvent. The peat–solvent mixtures were shaken for 24 h and then filtered through a Whatman no. 3 filter. One thousand grams of sand were mixed with either 200 or 500 mL of the filtered ethanol extract, or with 250 ml of the filtered benzyl alcohol extract. The ethanol-extract treated sands were dried under a hood for 24 h and the benzyl alcohol treatments were dried in an oven at 100°C for 72 h. These treatments provided sand with different degrees of water repellency that was not completely stable after contact with water.

The breakthrough pressure head, h_p, was measured in the device illustrated in Fig. 1. It was constructed of 20-cm-long polypropylene tube that has 1.8-cm i.d. and a wall thickness of 0.3 cm. A fine wire screen was attached with aluminum tape at the bottom of the tube to retain the sand. Two ports located 6 cm from the bottom of the tube were used for water application and pressure measurements. Two electrodes were placed 3 mm below these ports. Tap water was applied by a Marriott bottle apparatus, and a pressure transducer (Micro Switch 143 PC 05 G, Honeywell Microswitch, Freeport, IL) measured the pressure head in centimeters of water. The pressure transducer output was monitored

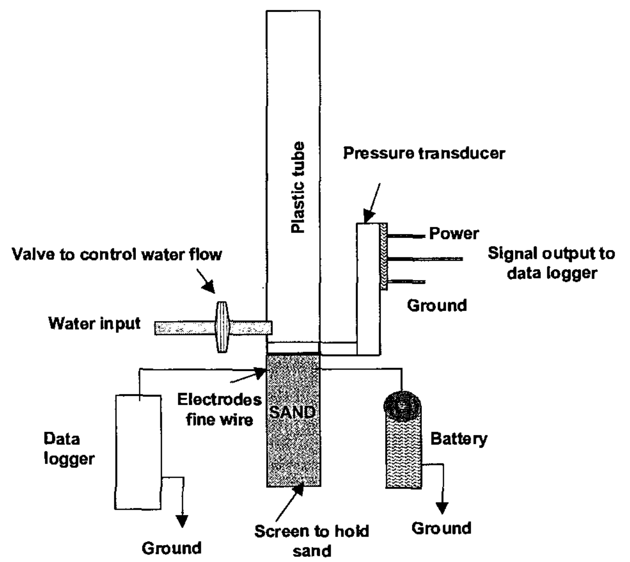

Fig. 1. Illustration of instrument used to measure breakthrough pressure head, h_p (not drawn to scale).

with a data logger. In order to measure the pressure head when the water penetrated the soil, one electrode was connected to a 1.5-V battery and the other was connected to the data logger input.

To prevent water from preferentially infiltrating between the sand and the wall, the tube was coated with a Teflon-based dry film lubricant before each measurement. The sand was packed by pouring 27 g through a funnel and then gently tapping the sides of the tube. The average bulk density of the packed sand was 1.42 g cm^{-3}. The sand level was between the electrodes and the ports for water application and pressure measurement. Water was applied at a constant rate and the pressure was measured as a function of time. When water penetrated the soil, the electrodes were shorted out and a signal was transferred to the data logger input. The data logger simultaneously collected the voltage and the pressure as a function of time. The breakthrough pressure head was the pressure when the voltage signal appeared on the data logger input. Figure 2 shows a typical run of the electrode and pressure data signals vs. time. The value of h_p was measured three times for each treatment.

The 90° surface tension (γ_{ND}) measurement was made by first mixing a series of aqueous ethanol solutions to create a range of surface tensions. A plot of percent ethanol vs. surface tension was produced by measuring the surface tension of each mixture using a surface tensiomat. Drops of each mixture were placed on the top of each sand treatment and the time of infiltration noted. The surface tension of the mixture that had a five second infiltration time was taken as γ_{ND}, as specified by Watson and Letey (1970).

The relationships between h_p and $\gamma_{ND}^{1/2}$ for both Sand 1 and 2 are shown in Fig. 3. The x-axis intercept was set at 0.27, which is the square root of the surface tension of water. According to Eq. [6], $h_p = 0$ when $\gamma_w = \gamma_{ND}$. The data were fit to a linear regression equation and the slope calculated. Sand 1 had a coefficient of determination equal to 0.92 and Sand 2 had a coefficient of determination equal to 0.84. The linear relationship between h_p and $\gamma_{ND}^{1/2}$ was consistent with Eq. [6]. The slope of the line is $2\ \gamma_w^{1/2}/r\rho g$ (Eq. [6]), which was used to compute an r value of 61.3 μm for Sand 1 and 38.7 μm for Sand 2. The values of h_p and r were used in Eq. [1] to calculate θ.

The relationship between cos θ and $\gamma_{ND}^{1/2}$ is illustrated in Fig. 4. The line represents the theoretical values predicted by Eq. [7] to which the experimental data were compared. The root mean square error (RMSE)

$$\mathrm{RMSE} = \left[\frac{\sum(P_i - O_i)^2}{N}\right]^{1/2} \qquad [8]$$

where P is predicted, O is observed, and N is the number of observations, was calculated to be 0.02 for the data presented

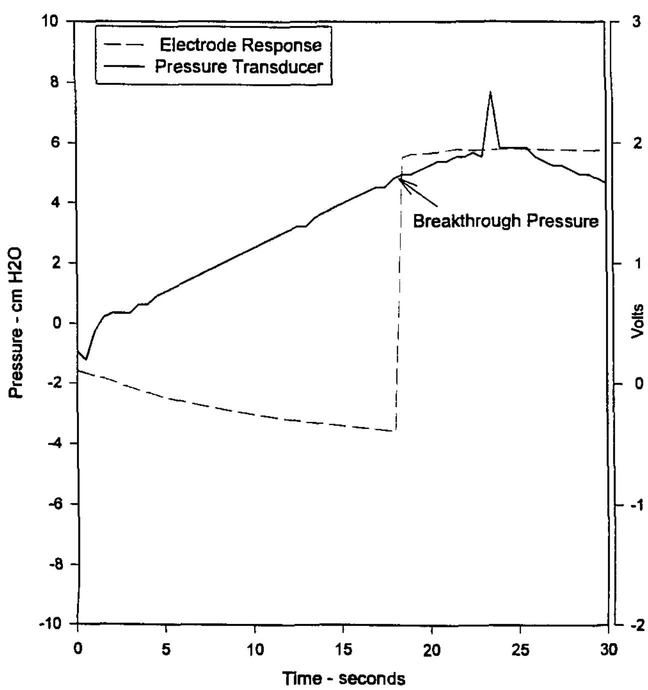

Fig. 2. Typical pressure transducer and electrode response during the measurement of breakthrough pressure head, h_p.

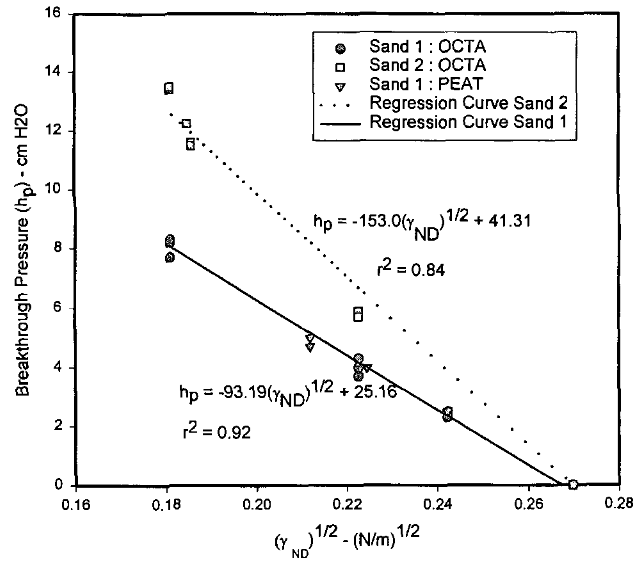

Fig. 3. The relationship between breakthrough pressure head, h_p, and the 90° surface tension, $\gamma_{ND}^{1/2}$, for the various treated sands.

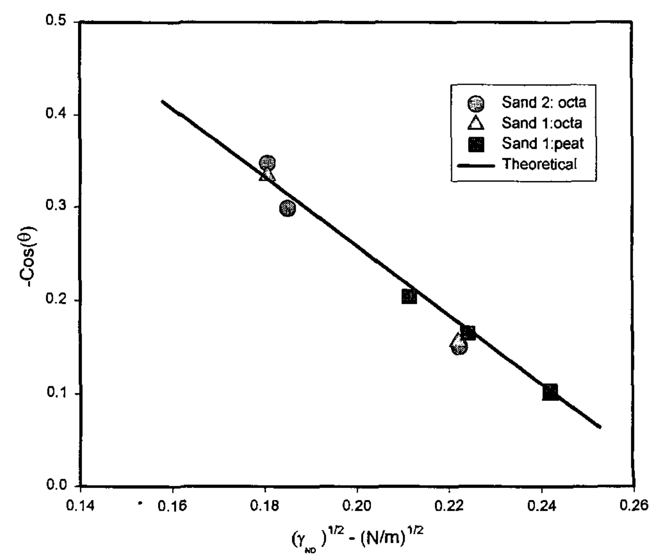

Fig. 4. The relationship between liquid–solid contact angle, cos θ, and the 90° surface tension, $\gamma_{ND}^{1/2}$, for the various treated sands.

in Fig. 4. Thus, there was very good agreement between experimental and theoretical data.

The values of h_p, γ_{ND}, θ, and WDPT are presented for all treatments in Table 2. Note that octadecylamine treatments provided a very stable water repellency, as indicated by an infinite WDPT. Conversely, the peat extracts provided an initial contact angle >90°, but this angle was not stable because the water drop penetrated the sand after some exposure. The procedure for measuring h_p was effective for sands having a WDPT as low as 1 min.

CONCLUSIONS

The validity of $\cos \theta = [(\gamma_{ND}/\gamma_w)^{1/2} - 1]$ was confirmed by data presented in Fig. 4. This finding provides a simple technique for measuring θ of soils with $\theta > 90°$ and represents the major contribution of this study. One needs only to measure γ_{ND} and use Eq. [7] to compute the value of θ. The value of γ_{ND} can easily be measured in the field or laboratory. Note that this procedure provides the initial θ value, which may change with time after exposure to water if the water repellency is not stable. The WDPT, which can be measured in the field or laboratory, provides information on the stability of the repellency.

The validity of Eq. [6] was confirmed by data presented in Fig. 3. Therefore, measurements h_p and γ_{ND} can be used to compute the pore radius. After the pore radius is found, the value of h_p can be calculated from γ_{ND} of the same soil material that received other treatments.

Table 2. Average breakthrough pressure (h_p), 90° surface tension (γ_{ND}), contact angle (θ), and water drop penetration time (WDPT) for the various treatments.

	Sand 1‡				Sand 2‡			
Treatment†	h_p	γ_{ND}	θ	WDPT	h_p	γ_{ND}	θ	WDPT
	cm	N m^{-1}	degrees	min	cm	N m^{-1}	degrees	min
Octa. 1	2.4	0.059	96	∞	5.8	0.050	100	∞
Octa. 2	4.0	0.050	100	∞	11.5	0.034	108	∞
Octa. 3	8.1	0.033	109	∞	13.4	0.033	109	∞
Peat 1	2.5	0.059	96	1				
Peat 2	4.0	0.050	100	10				
Peat 3	4.8	0.045	102	150				

† Treatments are with octadecylamine (Octa.) or with solvent extracts from peat moss (Peat).
‡ See Table 1 for particle-size distribution for these two samples.

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REFERENCES

Adamson, A.W. 1990. Physical Chemistry of Surfaces. 5th ed. John Wiley & Sons, New York.

Bond, R.D., and J.R. Harris. 1964. The influence of the microflora on physical properties of soils. I. Effects associated with filamentous algae and fungi. Aust. J. Soil Res. 2:111–122.

DeBano, L.F., S.M. Savage, and D.A. Hamilton. 1976. The transfer of heat and hydrophobic substances during burning. Soil Sci. Soc. Am. J. 40:779–782.

Emerson, W.W., and R.D. Bond. 1963. The rate of water entry into dry sand and calculation of the advancing contact angle. Aust. J. Soil Res. 1:9–16.

Girifalco, L.A., and R.J. Good. 1957. A theory for the estimation of surface and interfacial energies. I. Derivation and application to interfacial tension. J. Phys. Chem. 61:904–909.

Good, R.J., and L.A. Girifalco. 1960. A theory for the estimation of surface and interfacial energies. III. Estimation of surface energies of solids from contact angle data. J. Phys. Chem. 64:561–565.

Hendrickx, J.M.H., L.W. Dekker, and O.H. Boersma. 1993. Unstable wetting fronts in water-repellent field soils. J. Environ. Qual. 22: 109–118.

Jamison, V.C. 1945. The penetration of irrigation and rain water into sandy soils of central Florida. Soil. Sci. Soc. Am. Proc. 10:25–29.

Letey, J., J. Osborn, and R.E. Pelishek. 1962. Measurement of liquid-solid contact angles in soil and sand. Soil Sci. 93(3):149–153.

Letey, J. 1969. Measurement of contact angle, water drop penetration time, and critical surface tension. p. 43–47. *In* L.F. DeBano and J. Letey (ed.) Water-repellent soils. Proceedings of Symposium on Water-Repellent Soils. University of California, Riverside, CA. March 1969. University of California.

Miyamoto, S., and J. Letey. 1971. Determination of solid–air surface tension of porous media. Soil Sci. Soc. Am. Proc. 35:856–859.

Ritsema, C.J., L.W. Dekker, J.M.H. Hendrickx, and W. Hamminga. 1993. Preferential flow mechanism in a water repellent sandy soil. Water Resour. Res. 29:2183–2193.

Watson, C.L., and J. Letey. 1970. Indices for characterizing soil-water repellency based upon contact angle–surface tension relationships. Soil Sci. Soc. Am. Proc. 34:841–844.

Young, T. 1805. On the cohesion of fluids. Philos. Trans. R. Soc. London, A 84.

Zisman, W.A. 1964. Relation of equilibrium contact angle to liquid and solid constitution. p. 1–51. *In* R.F. Gould (ed.) Contact angle wettability and adhesion. Advances in Chemistry Series 43. American Chemical Society, Washington, DC.