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Extended methodology for determining wetting properties of porous media

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Abstract

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Keywords

soil wettability, contact angle, capillary rise, Wilhelmy plate method

Disciplines

Agriculture | Hydrology | Soil Science | Statistical Methodology

Comments

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Extended methodology for determining wetting properties of porous media

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[1] Because most methods for assessing the wettability of porous materials are restricted in their applicability, we developed two new methods for measuring contact angles and particle surface energy. The proposed methods (the Wilhelmy plate method (WPM) and the modified capillary rise method (MCRM)) were tested on 24 soils. For comparison, the water drop penetration time test (WDPTT) and the sessile drop method (SDM) were also applied. It was found that advancing contact angles, measured either with WPM or MCRM, agreed well in the range of 0° to 142° . Sessile drop contact angles were within the domain enclosed by the range of advancing and receding contact angles as determined with WPM. WDPTT, however, was only sensitive in the narrow range of 85° to 115° . We conclude that both WPM and MCRM are reliable methods for determining contact angles and particle surface energy over a wide range of porous material wettabilities. *INDEX TERMS*: 1875 Hydrology: Unsaturated zone; 1866 Hydrology: Soil moisture; *KEYWORDS*: soil wettability, contact angle, capillary rise, Wilhelmy plate method

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1. Introduction

[2] Natural soils show variable degrees of water repellency. Our understanding of water repellency and its impact on other soil properties has significantly improved during the past decade [De Bano, 2000]. Soil organic matter is considered to be a major reason for water repellency [Roy and McGill, 2002]. It changes the interfacial energy of the three-phase system in partly saturated soils. The moisture-retention relation of such soils is significantly affected by changes in the interfacial energy [Demond and Roberts, 1991]. Extreme soil water repellency can lead to a complete loss of infiltration capacity, enhancing soil erosion, and the occurrence of landslides [Robichaud and Hungerford, 2000]. Water repellency (or hydrophobicity) also favors preferential soil moisture flow and forces soil water into soil macropores, leading to persistent nonuniform soil wetting patterns [Dekker et al., 2001]. Soil wetting patterns, in turn, implicate a rapid transfer of solutes into the groundwater [de Rooij and de Vries, 1996]. The wetting ability of a liquid is a function of the surface energies of the solid-gas interface, the liquid-gas interface, and the solid-liquid interface. The surface energy across an interface (or the surface tension at the interface) is a measure of the energy required to form an additional unit area of new

surface at the interface. For a consistent presentation, we use the terminology of surface energy [J m^{-2}] throughout this article.

[3] To better understand phenomena involving immersion and liquid sorption, knowledge about interfacial interaction of solid soil particles with liquids is indispensable. Both the solid-liquid contact angle and the surface energy can be used to characterize the interaction between the solid, liquid and gaseous interfaces in partly saturated porous media. Contact angles are rarely discussed in the soil water literature. Because they are difficult to measure, often a contact angle of zero degree is assumed. However, this frequently does not apply and contact angle measurements and their interpretation are a challenging task, because of geometrical and surface roughness effects [Philip, 1971; Morrow, 1975, 1976; Hazlett, 1993] and spatial chemical heterogeneity [Dettre and Johnson, 1964; Drehlich, 1997]. Such effects may lead to deviations from the equilibrium, and thermodynamically defined, intrinsic contact angle [Chibowski and Perea-Carpio, 2002], which is measured on clean and smooth surfaces [Adamson, 1990].

[4] Because clean and smooth surfaces of soil material are rare, it is difficult to determine the intrinsic contact angle of such materials. Numerous effects, like surface roughness, chemical heterogeneity, fluid dynamics, particle shape, and gas adsorption, give rise to contact angle hysteresis, e.g., larger contact angles for an advancing wetting front, and smaller contact angles for a receding wetting front, as

compared with the intrinsic contact angle. This also holds for contact angles in porous media, as shown, for example, by *Morrow* [1975, 1976]. Morrow used PTFE (polytetrafluoroethylene) as a test material, from which both smooth plates and rough capillaries, as well as a porous medium, were prepared. By using smooth plates, rough capillaries, and a porous medium of the same material, Morrow was able to demonstrate the systematic dependence of the advancing contact angle θ_a and the receding contact angle θ_r on the intrinsic contact angle θ . Results were consistent and were independent of tube diameter. Morrow further showed that changes in capillary-pressure-saturation relations, measured by using liquids with different surface energies, suggest that operative contact angles, which cannot be measured directly within porous media, were in reasonable correspondence with contact angles measured in roughened tubes. He concluded that drainage and imbibition curves of the porous PTFE medium were proportional to the cosine of receding and advancing contact angles observed at rough surfaces. For details we refer to Morrow's original work and also to the work of *She and Sleep* [1998].

[5] Because it is nearly impossible to measure the surface energy of irregularly shaped solid particles (such as soil particles) directly, often indirect methods are applied [*Wallis and Horne*, 1992; *Letey et al.*, 2000]. These methods include the water drop penetration time test (WDPTT), as used by *Letey* [1969] or *Dekker and Ritsema* [2000], and the molar ethanol droplet test (MEDT). In MEDT the molarity of water and ethanol mixtures is varied repeatedly, until droplets of the mixture infiltrate into the dry soil in a pre-given length of time [*Watson and Letey*, 1970; *King*, 1981; *de Jonge et al.*, 1999]. A penetration time of five seconds for a droplet defines a contact angle of ninety degrees. From the volume fraction of the ethanol in the mixture, the corresponding surface energy of the liquid is determined and defined as the ninety-degree surface energy σ_{ND} [*Letey et al.*, 2000]. *Roy and McGill* [2002] suggested a standardized procedure for MEDT to improve its reproducibility.

[6] Both MEDT and WDPTT are useful because of the easy application, especially in the field. However, both methods have disadvantages. WDPTT possibly alters the solid surface during the measurement. Therefore the result is likely affected by both the impact of the initial contact angle and the persistence of the repellency [*Roy and McGill*, 2002]. Moreover, dissolution of soil organic and inorganic compounds during the measurement may change the liquid surface energy either to smaller [*Anderson et al.*, 1995] or larger values [*Hartge*, 1958]. MEDT is somewhat unsatisfactory, because of its empirical nature and the lack of a rational foundation.

[7] The methods discussed so far assess the contact angle and surface energy of porous materials in an indirect way. Other methods aim at measuring contact angles directly. *Bachmann et al.* [2000], for example, proposed using a one-grain layer of sieved soil particles on a flat surface to measure the contact angle of sessile water droplets. Unfortunately, because of capillary forces, a thin layer wicking effect on wettable samples can occur, and therefore this so-called sessile drop method (SDM) is restricted to hydrophobic particles. However, experiments applying pressed powder pellets [*Valat et al.*, 1991; *Chibowski and Perea-Carpio*, 2002] showed that SDM can provide reasonable results.

[8] An alternative procedure for determining contact angles examines the imbibition rate of porous materials by a specific liquid. The capillary rise method (CRM) is such a procedure [*Siebold et al.*, 1997]. It has become an accepted technique for measuring advancing contact angles of powders and for deriving other parameters of solid surfaces [*Michel et al.*, 2001]. A major disadvantage of CRM is that the testing fluid does not rise into the sample, if the liquid-solid contact angle is larger than 90° . This excludes hydrophobic soil material, when water is used as the testing liquid.

[9] In summary, existing methods for measuring contact angles and surface energies of partly saturated porous media are restricted in their application. To our knowledge, no single method has been developed to date that can be applied over the entire wettability range and yet be accurate and sensitive. Our objective is therefore to introduce a novel concept for determining contact angles of soil material over the entire range of contact angles. Specifically, our objective is to introduce the so-called Wilhelmy plate method (WPM), which basically can be used over the entire range of contact angles [*Spelt and Vargha-Butler*, 1996; *Ramé*, 1997]. We will compare contact angle values determined with WPM to those obtained with CRM, MCRM and WDPTT. CRM will be used for contact angles $<90^\circ$ and MCRM for angles $>90^\circ$; MCRM will also be used for contact angles $<90^\circ$ for comparison to CRM values. The comparison is important to assess the effect of, because of different sample preparation techniques, different testing liquids and, importantly, different physical principles involved in the measurement. We will compare our results also with WDPTT data. WDPTT data are widespread in the literature, but their interpretation in terms of contact angles is somewhat ambiguous. For our tests, soil samples were used that vary considerably in texture, parent material, soil depth, and geographic origin. Knowledge of interfacial energies is necessary for the general understanding of wetting phenomena. As will be shown, MCRM not only allows the determination of the contact angle θ , but also the ninety-degree surface energy σ_{ND} . As well, the critical surface energy σ_c of the soil material can be estimated with this method. Interfacial energies determined with MCRM will also be compared with surface energies evaluated from the hysteresis of the advancing and receding contact angles determined with WPM.

2. Theory

[10] Wettability of dry or partly saturated porous media, such as soils, is mainly determined by two factors, i.e., the surface energies of the interfaces and the geometry of the pore space. As the surface energy of inorganic soil particles is high in relation to water, soil material is expected to be wettable. In soils, however, coatings of organic matter generally lower the surface energy, and particular nonpolar hydrophobic groups like $-CH_3$ are likely to decrease the wettability and to cause hydrophobicity [*Tschapek*, 1984]. Surface wettability is determined by the nature and the packing of the outermost molecules and not by the nature and arrangements of atoms inside the solid substrate that are 10 to 20 Ångström ($1 \text{ \AA} = 10^{-10} \text{ m}$) below the surface [*Zisman*, 1964].

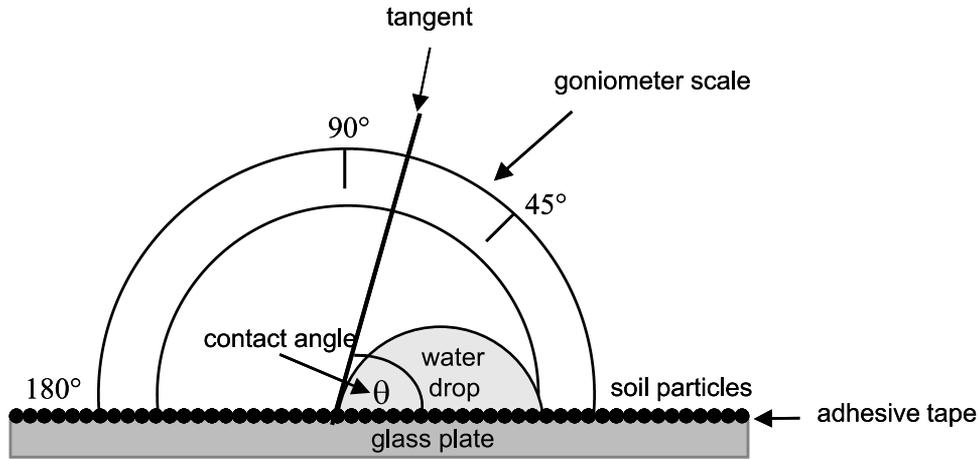


Figure 1. Schematic representation of a device for measuring static contact angles θ of soil particles with the sessile drop method (SDM), as proposed by *Bachmann et al.* [2000].

[11] The solid-air interfacial energy σ_{sv} is a fundamental thermodynamic property, which affects the wetting behavior of the surface. The extent of hydrophobicity of three-phase systems (gas-liquid-solid) can be quantified by the contact angle θ , which is the angle between the fluid wetting front and the solid surface (see Figure 1). A complete wettability of solid surfaces in contact with a liquid and a gas phase may be defined as the ability of the liquid to spread over a surface, which occurs at a contact angle of zero degrees, i.e., at $\cos(\theta) = 1$ [*Letey et al.*, 1962]. A formal expression relating contact angle and interfacial energies was established by *Young* [1805] and is therefore known as the Young equation. It can be given as:

$$\cos(\theta) = \frac{\sigma_{sv} - \sigma_{sl}}{\sigma_{lv}} \quad (1)$$

In equation (1) θ is the (intrinsic) contact angle [degrees], σ the surface energy [mJ m^{-2}], and the indices s, v, and l denote the solid, gas and liquid phase, respectively.

[12] From equation (1) it can be seen that the behavior of a liquid on a solid surface is controlled by competition between the interfacial energies σ . Equation (1) was initially based on empirical considerations; later, *Dupré* [1869] provided a theoretical treatment. *Zisman* [1964] stated that the surface of a solid is wetted by a liquid, when the surface energy of the liquid is smaller than the so-called critical surface energy σ_c of the solid. This critical surface energy σ_c is characterized by a contact angle of zero degrees and can be determined by using, repeatedly, liquids of different surface energy. In natural soils, contact angles vary somewhere between 0° (completely wettable) and 140° (extremely water repellent).

[13] Equation (1) has only limited practical significance in soil water studies. It cannot be used directly to determine the contact angle θ . It can correctly be applied only to ideal solids, whose surfaces are homogeneous, isotropic, smooth, and rigid. Real surfaces, particularly in soils, however, are rough, heterogeneous, anisotropic, elastic, deformable, and may react with a wetting fluid [*Drehlich*, 1997].

[14] Although the application of equation (1) to soil material seems to be restricted, *Bachmann et al.* [2000] used a small glass plate ("slide") as shown in Figure 1. The

glass plate was covered with a double-sided adhesive tape and a homogeneous one-grain layer of soil particles of similar diameter was pressed onto it.

[15] Droplets of water were then placed on the surface with a syringe. *Bachmann et al.* [2000] measured the contact angle of each droplet using the tangent of a special goniometer fitted microscope (OCA, Data Physics). The authors refer to the method as the sessile drop method (SDM).

[16] The capillary rise method (CRM) for determining contact angles uses a completely different physical principle. This method has become a standard method for analyzing advancing contact angles of powders, especially in physical chemistry and pharmacology. Although *Michel et al.* [2001] applied it to peats, CRM has not yet been reported as a routine method for soil analysis. The air-dry and sieved (<2 mm) material to be studied is packed in a glass tube, which is closed at the lower end with a filter. The base of the upright tube is brought into contact with a test fluid in a reservoir, and the mass gain of the tube can be recorded with an electronic balance. The maximum height h_m that is reached by the wetting front can be expressed as

$$h_m = \frac{2\sigma_{lv} \cos \theta_{st}}{\rho g R_{st}} \quad (2)$$

where h_m is the height of the wetting front above the base of the tube [m], σ_{lv} is the surface energy of the liquid-air interface [mJ m^{-2}], ρ the density of the fluid [Mg m^{-3}], g is the acceleration due to gravity [m s^{-2}], R_{st} is the mean static radius of pores for an idealized bundle of parallel capillaries [m], and θ_{st} is the static contact angle [degrees]. Equation (2) cannot be used to determine the contact angle θ directly because h is a function of the two unknown parameters R_{st} and θ_{st} . *Washburn* [1921] [see also *Siebold et al.*, 1997, 2000] expressed the rate of the rise of the wetting front in the powder-filled glass tube (dh/dt) by means of Poiseuille's law, i.e., as

$$\frac{dh}{dt} = \frac{R_d^2 \Delta P}{8\eta h} \quad (3)$$

where R_d is the mean hydrodynamic pore radius [m], η is the dynamic viscosity of the fluid [$\text{kg m}^{-2} \text{s}^{-1}$], and ΔP is the hydrostatic pressure difference [Pa], which can be expressed as the sum of the capillary pressure and the hydrostatic pressure. Substitution for ΔP in equation (3) yields:

$$\frac{dh}{dt} = \frac{R_d^2}{8\eta h} \left(\frac{2\sigma_{lv} \cos \theta}{R_{st}} - \rho gh \right) \quad (4)$$

Washburn [1921] integrated equation (4), disregarding the hydrostatic pressure in the air-dry material, and derived the following expression:

$$h^2 = \frac{r\sigma_{lv} \cos \theta}{2\eta} t \quad (5)$$

where $r = R_d^2/R_{st}$ is the effective capillary radius. Equation (5) was modified by introducing a geometric, soil-specific factor c , that lumps the effective capillary radius r and the porosity by inserting the mass gain w [kg] instead of the height of the wetting front h , i.e.,

$$w^2 = c \frac{\rho^2 \sigma_{lv} \cos \theta}{\eta} t = mt \quad (6)$$

Equation (6) suggests a linear relationship between w^2 and t , with the slope being denoted by m . This applies to a wetting agent that partly wets, such as water, as well as to wetting agent that completely wets, such as n-hexane ($\cos(\theta) = 1.0$). The soil-specific factor c of equation (6) can be determined using a fluid like n-hexane. Once the factor c is known, the capillary rise (wetting front) experiment can be carried out with water as the wetting agent, from which the contact angle θ for water can then be determined. The parameter c can be derived from the slope of the function $w^2 = mt$ and the physical properties ($\rho(T)$, $\eta(T)$, $\sigma_{lv}(T)$) of the completely wetting fluid, where T denotes temperature. The equations for the contact angle θ with CRM are therefore:

$$c = m_h \cdot \frac{\eta_h}{\sigma_{lv,h} \rho_h^2} = m_h \cdot F_h(T), \quad (7)$$

where it is assumed that $\cos(\theta_h)$ for n-hexane is equal to one. For water,

$$\cos(\theta_w) = \frac{m_w}{c} \cdot \frac{\eta_w}{\sigma_{lv,w} \rho_w^2} = \frac{m_w}{c} \cdot F_w(T), \quad (8)$$

which in turn can be written as

$$\cos(\theta_w) = \frac{m_w}{m_h} \frac{F_w(T)}{F_h(T)}, \quad (9)$$

where m and F are functions as described by equations (6)–(8), and where the subscripts h and w stand for n-hexane and water. From equation (9) the contact angle θ_w for water can be calculated. Equation (6) applies only to contact angles $<90^\circ$. Finally, for details regarding proper packing of the column, we refer to *Siebold et al.* [1997] and *Michel et al.* [2001].

[17] Besides an expression for the contact angle θ , an equation for the solid-gas surface energy σ_{sv} is needed for a basic representation of the solid surface properties. According to *Girifalco and Good* [1957], the liquid-solid interfacial energy σ_{sl} (equation (1)) can be approximated as

$$\sigma_{sl} = \sigma_{sv} - \pi^0 + \sigma_{lv} - 2\phi \sqrt{\sigma_{sv} \cdot \sigma_{lv}}, \quad (10)$$

where π^0 [mJ m^{-2}] is a correction for the adsorption of vapor on the liquid-solid interface and ϕ , which is a dimensionless parameter describing interactions between the two phases, is often set equal to one [*Adamson*, 1990]. In many studies, either this term is ignored, or the experimental conditions are held constant, to fix the error caused by ignoring π^0 . Substitution of the simplified equation (10) into equation (1) yields (π^0 is neglected):

$$\cos(\theta) = -1 + 2 \sqrt{\frac{\sigma_{sv}}{\sigma_{lv}}} \quad (11)$$

The term $\cos(\theta)$ can now be expressed as a linear function of $(\sigma_{lv})^{-0.5}$, which leads to

$$\cos(\theta) = b_0 + b_1 \sigma_{lv}^{-0.5} \quad (12)$$

Alternatively, *Zisman* [1964] proposed a linear relation between $\cos(\theta)$ and σ_{lv} , e.g.,

$$\cos(\theta) = b_0 + b_1 \sigma_{lv} \quad (13)$$

where b_0 and b_1 are fitting parameters. When depicted graphically, equation (13) has been called a *Zisman plot*. It can be noted that in case $\cos(\theta) = 0$, or $\theta = 90^\circ$, equation (11) reduces to

$$\sigma_{sv} = \sigma_{lv}/4 = \sigma_{ND} \quad (14)$$

The term σ_{ND} in equation (14) is frequently defined as the ninety-degree (ND) surface energy.

[18] Finally, for a contact angle of zero degrees, $\cos(\theta) = 1$ and equation (11) yields:

$$\sigma_{sv} = \sigma_{lv} = \sigma_c \quad (15)$$

where σ_c is the previously mentioned critical surface energy of the solid surface [*Zisman*, 1964]. This approach is considered as semiempirical, especially for heterogeneous systems like soil materials and for the soil solution as the wetting agent [*Roy and McGill*, 2002]. Both equations (14) and (15) can be used to evaluate σ_{sv} .

[19] In physical chemistry [*Adamson*, 1990, p. 390; *Spelt and Vargha-Butler*, 1996, p. 388] the Wilhelmy plate method (WPM) is used to assess contact angles. To our knowledge, this method has not yet been applied in soil studies. A schematic representation of the method is shown in Figure 2a.

[20] Consider a thin plate or slide (thickness ≈ 0.1 cm) with an area of about 10 cm^2 ($4 \text{ cm} \times 2.5 \text{ cm}$). The plate (e.g., of platinum) hanging on a thread (Figure 2a) is connected to an electronic balance and can be lowered into a reservoir filled with a test liquid. In soil studies, a small glass slide as shown in Figure 2, with adhesive tape and a

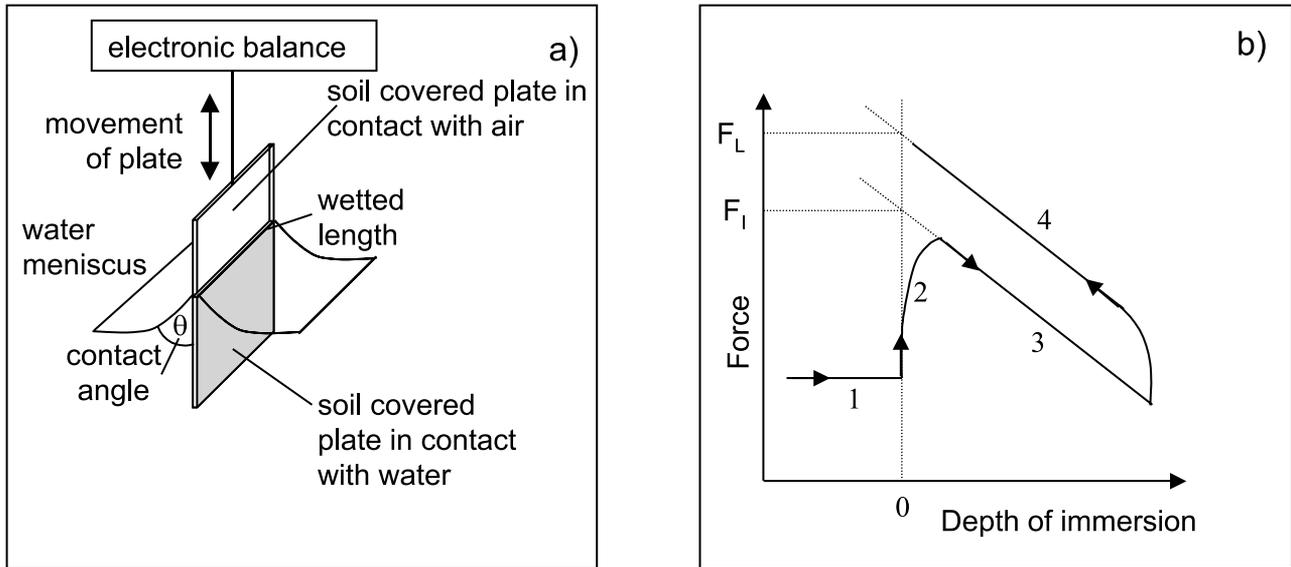


Figure 2. The Wilhelmy plate method (WPM) for measuring contact angles: (a) schematic representation of the experimental setup and (b) the forces acting on the plate while it is immersed (F_I) into or lifted (F_L) from a reservoir with a test fluid (definition of stage 1 to 4 see text).

one-grain layer of soil particles on both sides, could be used for this purpose. If the plate is slowly lowered into the liquid, three forces are acting on the plate, i.e., gravity, buoyancy, and the meniscus force, caused by the interfacial energies at the three-phase boundary (Figure 2a). The contribution of surface and line forces along the smallest dimension of the plate and impact of viscous forces acting on the plate under dynamic conditions, are usually ignored. For a rigorous treatment of the impact of viscosity, we refer to *Ramé* [1997]. The buoyancy force F_b increases linearly with the plate's depth of immersion. The wetting force F_w , that arises because of the curved meniscus around the plate, initially increases the total force F_t acting on the plate (after partly immersion, contact angle $<90^\circ$), but decreases as the plate is being immersed completely. The four stages are illustrated in Figure 2b. Stage 1: sample above the liquid; stage 2: sample hits the surface; stage 3: sample immersed; buoyancy force increases and causes a decrease in force on the balance; mode for measuring advancing contact angle θ_a . Stage 4: after having reached the desired depth, the sample is pulled out of the liquid (receding angle, θ_r). At any stage, while the plate is partly immersed, the total force F_t that is acting on the plate can be given as

$$F_t = W - F_b + F_w = W - V\rho g + l_w\sigma_{lv}\cos(\theta) \quad (16)$$

The symbol W [kg] in equation (16) denotes the weight of the plate, V [m³] is the volume of the part of the plate that is immersed, and l_w [m] is the wetted length of sample. If the balance is tared, $\cos(\theta)$, and hence the contact angle θ , can be calculated from

$$\cos(\theta) = \frac{(F_t + V\rho g)}{l_w\sigma_{lv}} \quad (17)$$

For an evaluation of the contact angle θ , the wetting force F_w has to be determined through a linear regression of the

recorded weight curve as a function of time (Figure 2b) and by extrapolation to zero-depth immersion for F_I (buoyancy corrected wetting force for the advancing cycle) or F_L (buoyancy corrected wetting force for the receding cycle, see Figure 2b). For a rigorous treatment of the interfacial tensiometry theory we refer to *Rusanov and Prokhorov* [1996].

[21] For a proper understanding of transport processes in partly saturated porous media, knowledge about the energy of the solid-gas interface (σ_{sv}) is indispensable. A straightforward assessment of σ_{sv} is still a problem. *Chibowski et al.* [2002] proposed an indirect approach employing contact angle hysteresis,

$$\sigma_{sv} = \sigma_{sl} + \sigma_{lv}\cos\theta_a \quad (18)$$

$$\sigma_{sf} = \sigma_{sl} + \sigma_{lv}\cos\theta_r \quad (19)$$

where θ_a and θ_r are the advancing and receding contact angle, respectively, and σ_{sf} is the film-covered solid surface energy, which can be expressed as:

$$\sigma_{sf} = \sigma_{sv} + \pi \quad (20)$$

where π [mJ m⁻²] is the film pressure. Combination of (18) to (20) yields:

$$\pi = \sigma_{lv}(\cos\theta_r - \cos\theta_a) \quad (21)$$

Defining the parameter k as the ratio of the dispersive interaction of the work of adhesion W for both advancing (a) and receding (r) modes (for the advancing and receding wetting front; ϕ referred to equation (10)), we can express k as [*Girifalco and Good, 1957*]

$$k = \frac{W_a}{W_r} = \frac{2\phi\sqrt{\sigma_{sv}\sigma_{lv}}}{2\phi\sqrt{\sigma_{sf}\sigma_{lv}}} \quad (22)$$

Table 1. Soils and Some Selected Properties Used in This Study

Soil Horizon	Parent Material/Origin	Soil Order ^a	Texture Number ^a	Maximum Grain Size, mm	Organic Carbon Content, %	Remarks
INC_Ah	Mesozoic	inceptisol	sandy clay	<2	8.26	soil profile "Steinkreuz" described by <i>Kaiser et al.</i> [2002]
INC_Bv	sandstone/central Europe		loam	<2	0.98	
INC_Bv1			loam	<2	0.30	
INC_Bv2			loam	<2	0.14	
INC_IIIcV			sandy loam	<2	0.11	
INC_IVcV			sandy loam	<2	0.05	
ALF_Bv	Weichselian loess/central Europe	alfisol	silt	<0.063	0.07	described by <i>Bachmann et al.</i> [2002]
ALF_BvS ^b			silt	<0.063	0.08	
MOL_Ah2 ^c	Weichselian loess/central Europe	mollisol	silt	<0.063	0.73	silane treated ^c
MOL_Ah1 ^d			silt	<0.063	0.47	
SPO_Ah1	glacial sand/central Europe	spodosol	loamy sand	<2	6.23	described by <i>Bachmann et al.</i> [2000]
SPO_Ah2			loamy sand	<2	2.33	
SPO_C			loamy sand	<2	0.91	
SPO_AG3			sand	<2	2.40	
SPO_AG4b			sand	<2	3.05	
SPO_GP7b			sand	<2	4.18	described by <i>Springob and Kirchmann</i> [2002]
SPO_GP17			sand	<2	2.29	
SPO_RG2			sand	<2	1.12	
SPO_CP12a			sand	<2	1.64	
ENT_C	dune sand/central Europe	entisol	sand	<2	0.00	
INC_Lsy	volcanic ash/west Java	inceptisol	clay	<2	0.29	
INC_LSdv			clay	<2	0.37	
OXI_B	volcanic ash/west Java	oxisol	silty clay	<2	0.81	
INC_Ahc	mesozoic carbonate rock/west Java	inceptisol	clay	<2	3.42	
adhesive tape						used for WPM and SDM

^aSoil order and texture class according US Soil Taxonomy.

^bTreated with 9.0 mL dichlorodimethylsilane per 100 g soil.

^cTreated with 4.2 mL dichlorodimethylsilane per 100 g soil.

^dTreated with 8.4 mL dichlorodimethylsilane per 100 g soil.

From equation (22) we can derive k^2 as

$$k^2 = \frac{\sigma_{sv}}{\sigma_{sf}} = \frac{\sigma_{sv}}{\sigma_{sv} + \pi} \quad (23)$$

and subsequently σ_{sv} as

$$\sigma_{sv} = \frac{\pi k^2}{1 - k^2} \quad (24)$$

Using the classical definition for the work of adhesion [Adamson, 1990] and defining k again by using the classical definition of the work of adhesion, k can also be expressed as

$$k = \frac{W_a}{W_r} = \frac{1 + \cos \theta_a}{1 + \cos \theta_r} \quad (25)$$

Equation (25) then leads to our final notation for σ_{sv} , i.e.,

$$\sigma_{sv} = \sigma_{lv} \frac{(\cos \theta_r - \cos \theta_a) \cdot (1 + \cos \theta_a)^2}{(1 + \cos \theta_r)^2 - (1 + \cos \theta_a)^2} \quad (26)$$

For a thorough discussion of this approach, we refer to *Chibowski and Perea-Carpio* [2002]. This expression for σ_{sv} in equation (26) contains three measurable parameters. These are the advancing and receding contact angles θ_a and θ_r (which reflect the hysteresis of the contact angle), as well as the liquid-surface energy σ_{lv} . We applied equation (26);

values of σ_{sv} as calculated with equation (26) will be presented in the section Results and Discussion.

3. Materials and Methods

3.1. Materials

[22] Twenty-four materials, 17 were soils varying in texture, organic carbon content (C_{org}), profile depths, parent material, and geographic origin, and 7 were soil like materials, were used in this study. The soils had developed in parent materials that included both quaternary and Mesozoic sediments as well as young volcanic deposits. They were mainly from central Europe, but included some soils from west Java (Indonesia). With the exception of the inceptisol soil from west Java, with a $CaCO_3$ content of 0.3%, all samples were free of carbonate. A list of the soils and some of their properties is shown in Table 1.

[23] The organic carbon content (C_{org}) of the samples (see Table 1) ALF_Bv, ALF_BvS, MOL_Ah1, MOL_Ah2, SPO_Ah1, SPO_Ah2, SPO_C, INC_Lsy, INC_LSdv, OCI_B and INC_Ahc was measured conductometrically by dry combustion with a Wösthoff apparatus (H.WÖSTHOFF GMBH. MESSTECHNIK, Bochum, Germany) at 1050°C. Values of C_{org} for the gleyic soil profile (with the horizons INC_Ah, INC_Bv, INC_Bv1, INC_Bv2, INC_IIIcV, INC_IVcV) were taken from the work of *Rumpel et al.* [2002], whereas those for the samples SPO_AG3, SPO_AG4b, SPO_GP7b, SPO_GP17, SPO_RG2, and SPO_CP12a were taken from *Springob and Kirchmann* [2002]. For a reference material that is completely wettable, we used a sand which had been heated

to 1000°C for several hours. For a nonwetable material, a hydrophobized silty material treated with different amounts of dichlorodimethylsilane was used.

[24] Before the materials were used for contact angle and surface energy measurements, they were air-dried and sieved <0.063 mm (silt samples) or sieved <2 mm (all other samples). These samples were then used as follows.

3.2. Methods

3.2.1. Capillary Rise (CRM) and Modified Capillary Rise Method (MCRM)

[25] Capillary rise experiments were used for determining the contact angle of wettable soil with contact angles <90° (CRM), where both n-hexane and deionized water were used as the wetting agents. The modified capillary rise method (MCRM) was carried out for soils with a contact angle >90° (hydrophobic soils). In this case methanol-water mixtures of varying composition (and varying surface energies) were used instead of pure water as wetting agents.

[26] Air-dry, sieved soil material (with a diameter <2000 µm) was used for both methods. A glass tube (6 cm height and 0.9 cm inside diameter) with a sintered glass bottom covered by filter paper was filled with 1 to 2 gram of air-dry soil. The glass tube was hung from an electronic balance, which was attached to a personal computer. To make a CRM measurement, a reservoir with a test liquid (either n-hexane or water) was lifted until the bottom of the glass tube touched the liquid surface. Two replicate measurements with both n-hexane and water were recorded for each soil material. From the mean of these values the contact angle θ was calculated using equation (9).

[27] To achieve reproducibility, the bulk densities in each tube had to be similar [Siebold *et al.*, 1997]. Similar densities were obtained by tapping the soil-filled glass tubes 30 times before a measurement. The weight increase of a test tube during imbibition (equation (6)) was measured with a dynamic contact angle tensiometer (DCAT 11, DATA PHYSICS, Filderstadt, Germany), with a data acquisition rate of 10 to 30 measurements per second and a mass resolution of 10^{-5} g. The room temperature was recorded ($\pm 0.1^\circ\text{C}$ precision) during each measurement to adjust σ , ρ , and η of the test liquid (see equations (7), (8), and (9)) to the ambient room temperature.

[28] For soil material with a contact angle >90°, the modified capillary rise method (MCRM) was used. The experimental setup was the same as for CRM, but now a series of methanol-water solutions as test liquids of varying molarity and liquid surface energy σ_{lv} was used. To evaluate the data from such MCRM experiments, either equation (12) or equation (13) can be used instead of one single water measurement.

3.2.2. Wilhelmy Plate Method (WPM)

[29] The Wilhelmy plate method [Wilhelmy, 1863] enables the assessment of dynamic advancing or receding contact angles. Assessments are made through gradually immersing a soil-covered glass plate (Figure 2) down to a certain depth into a test liquid and then subsequently lifting the plate in the reverse direction. As mentioned earlier, the plate is attached to an electronic balance, which is connected to a personal computer (Figure 2) and tared. Glass plates were 4 cm long, 2.55 cm wide, and 0.1 cm

thick. In our study, two plates of each soil were investigated. Each glass plate was covered with double sided adhesive tape on all sides. The adhesive tape was covered with a one-grain layer of soil particles. Measurements of advancing and receding contact angles were made with the previously mentioned precision tensiometer (DCAT 11, DATA PHYSICS, Germany). The contact angle was evaluated with the software SCAT 12 (DATA PHYSICS). Theoretically, WPM allows the determination of contact angles in the range from 0° to 180°.

3.2.3. Sessile Drop Method (SDM)

[30] As shown in Figure 1, the contact angle of a water droplet can be measured by placing the droplet on a plane, homogeneous surface. The preparation of a quasi-plane surface of closely packed, uniformly shaped particles permits the determination of the static contact angle for soils with large contact angles [Bachmann *et al.*, 2000]. To prepare a slide, we used the particle size fraction of 63–100 µm. We sprinkled and subsequently pressed this sieved fraction on a glass slide covered with double-sided adhesive tape to get a thin, one-grain layer of soil particles of similar diameter. After preparation, five water droplets were placed on the surface with a syringe. The contact angle on both sides of each drop was then determined directly using the goniometer scale of a contact angle microscope (OCA, DATA PHYSICS; see Figure 1). Contact angles in the range from 0 to 180° can be generally assessed. For details we refer to Bachmann *et al.* [2000]. The range of applicability of SDM is limited primarily by the grain size of the soil particles, because the grain diameter has to be considerably smaller than the diameter of the drop.

[31] It seems appropriate to discuss briefly the accuracy and the sensitivity of both MCRM and WPM. Using the dynamic contact angle tensiometer DCAT 11, we achieved a precision of about <5° with MCRM. With WPM, which allows a large number of replicate measurements in a short time without too much effort, we achieved an accuracy on the order of 3–5°. Both MCRM and WPM theoretically allow contact angle measurements over the entire range from 0° to 180°. One disadvantage of WPM is that large soil particles and soil aggregates cannot be handled. The same applies to SDM [see Bachmann *et al.*, 2000]; for not-too-large particles or aggregates, contact angles can be determined with an accuracy on the order of <6°.

3.2.4. Du Noüy Ring Method

[32] The surface energy of the water-methanol mixtures was determined using the Du Noüy ring method [Adamson, 1990]. A platinum ring attached to an electronic balance (precision 10^{-5} g) was lowered to the liquid surface, which was detected automatically. The ring was slowly lifted and the force and the displacement of the ring were measured simultaneously with the aforementioned computer controlled dynamic tensiometer. The whole unit was housed in a rigid container, which provided protection and optimized temperature control. The resolution was better than 0.01 mJ m^{-2} , and the accuracy was better than 0.04 mJ m^{-2} .

3.2.5. Water Drop Penetration Time Test (WDPTT)

[33] WDPTT has been widely used to phenomenologically describe the wetting behavior of soil material

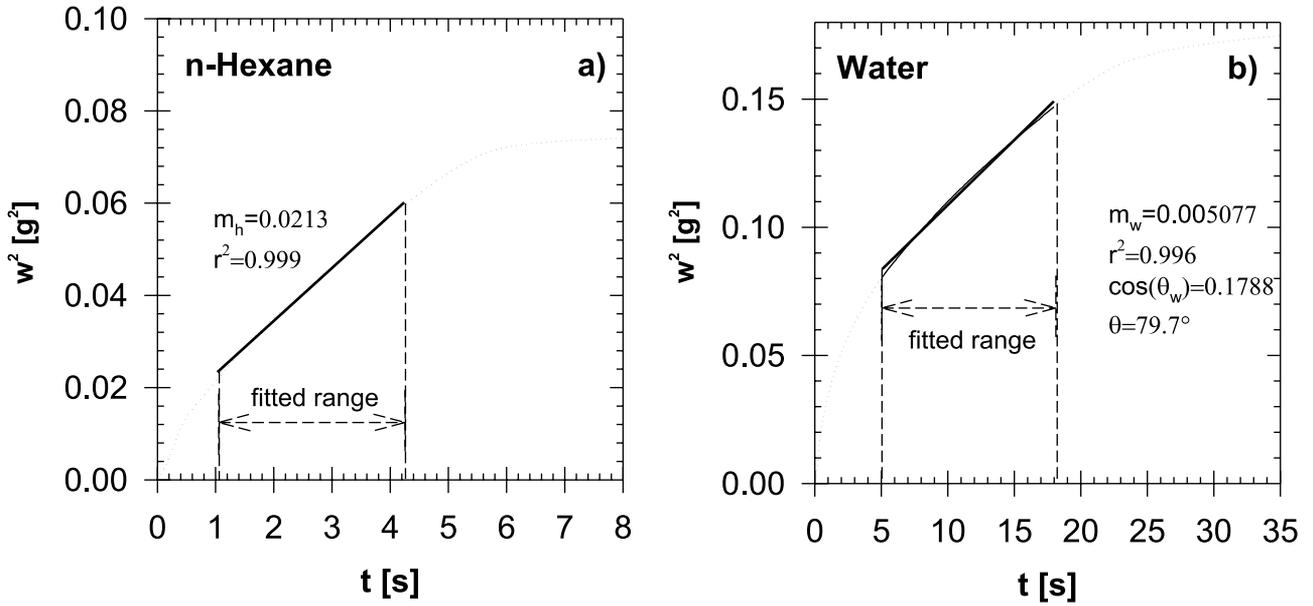


Figure 3. Plot of w^2 versus t (see equation (6)), for the conventional capillary rise experiment (CRM) with soil INC_Bv2, (a) with n-hexane as the wetting agent and (b) with water as the wetting agent. Soil INC_Bv2 represents a slightly repellent soil.

[Dekker and Ritsema, 2000]. WDPTT consists of placing a droplet of water on the soil surface and recording the time required for the water to infiltrate. For WDPTT, we placed approximately 100 g of air-dried soil <2 mm upon a dish, and smoothed the surface by hand. Three water droplets, each of 0.05 mL, were randomly placed on the air-dry sample. The median value of the infiltra-

tion time of the three droplets was considered as being representative.

4. Results and Discussion

[34] Figure 3 shows the relation between w^2 versus time t (see equation (6)) for a capillary rise experiment with the

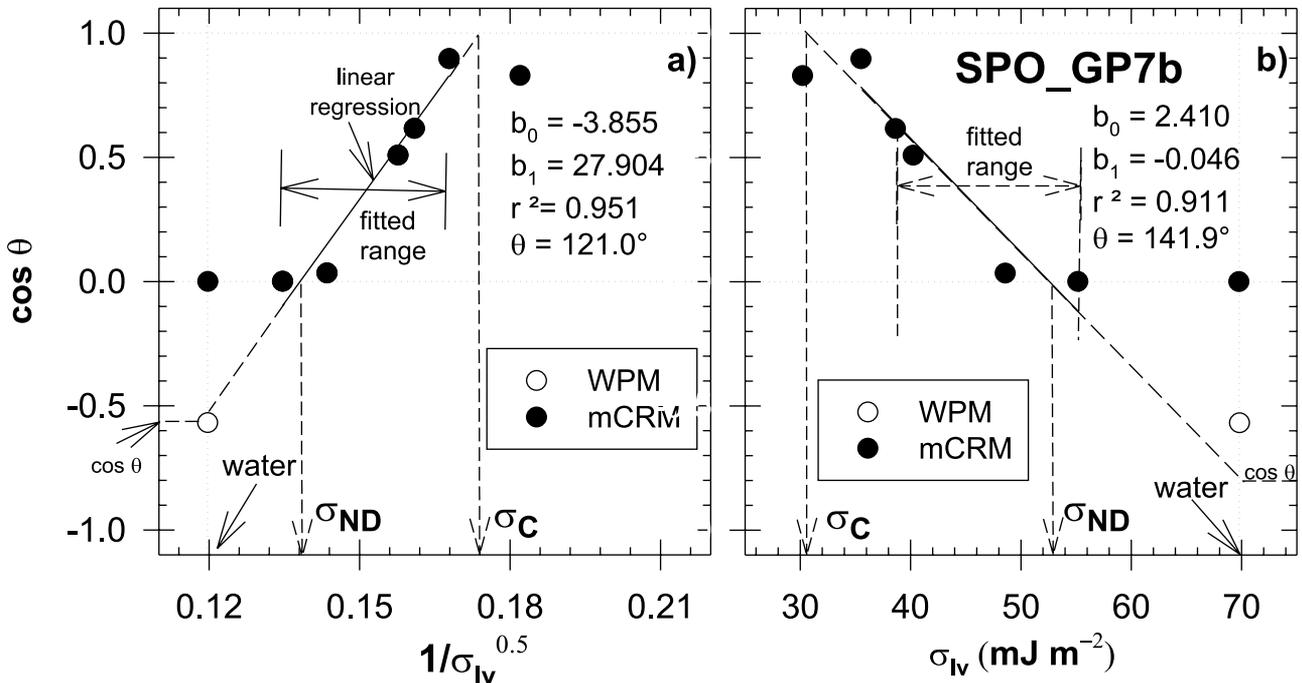


Figure 4. Sample data (SPO_Gp7b) from a capillary rise experiment (MCRM) with methanol-water solutions to determine the cosine of θ of a soil material having a contact angle $>90^\circ$; in this case also σ_{ND} and σ_c of the soil material can be determined from linear regression, calculated for $\cos(\theta) > 0$. Soil SPO_Gp7b represents a water repellent soil.

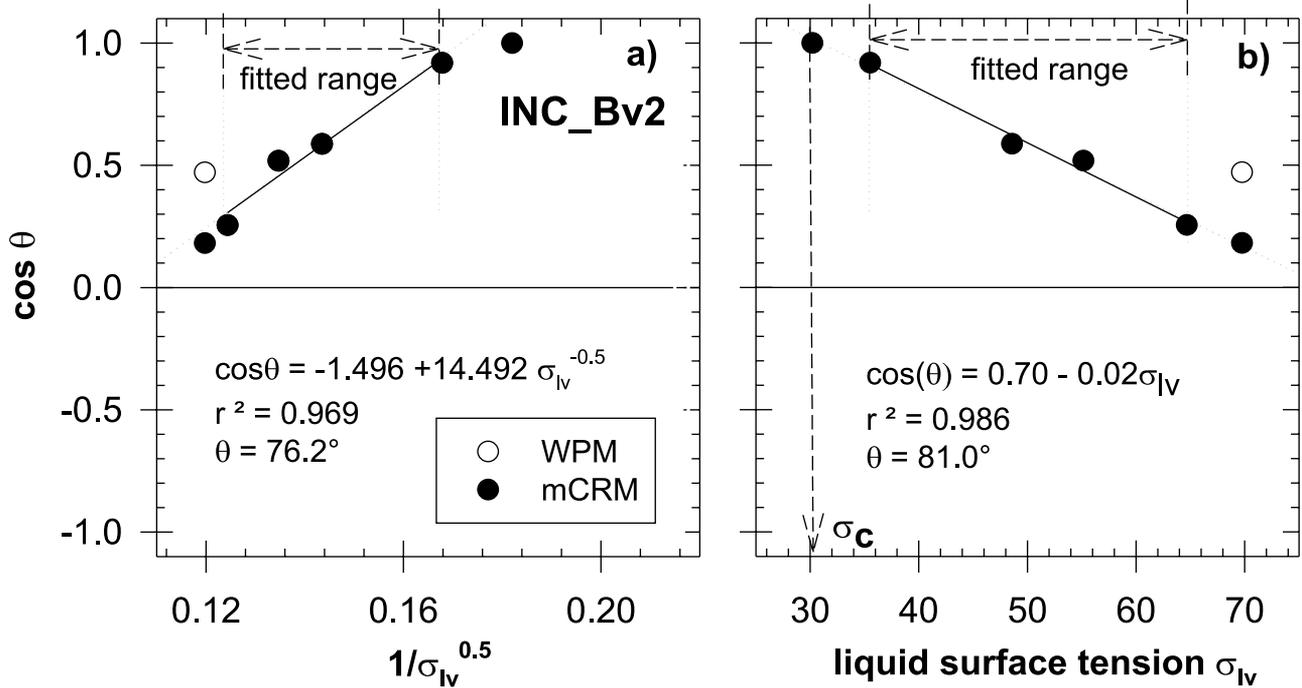


Figure 5. Sample data (soil INC_Bv2) from a capillary rise experiment (MCRM) with methanol-water solutions to determine the contact angle θ of a soil material having a contact angle $<90^\circ$.

wettable soil sample INC-Bv2, both with n-hexane and with water as the wetting liquid. From the part of each curve that is approximately linear (Figure 3), the corresponding slope was calculated. For n-hexane this value was 0.0213 and for water it was 0.005077. With equation (9) a value of 0.1788 for $\cos(\theta_w)$ was calculated and, correspondingly, $\theta = 79.7^\circ$ for water. For the other soils contact angles were determined similarly; results will be presented in the next section.

[35] Results from the MCRM for the hydrophobic soil SPO_GP7b are shown in Figure 4. For Figure 4a, equation (12) was applied and in Figure 4b a typical Zisman plot, obtained with equation (13), is shown. Also given in Figures 4a and 4b are the regression coefficients b_0 and b_1 , as well as the coefficient of determination r^2 . It can be seen that r^2 for equation (12) is slightly higher than for equation (13), suggesting that equation (12) describes the relation between $\cos(\theta)$ and σ_{IV} better than equation (13). This result, however, is an exception. For the other soils we found opposite results, but the difference in r^2 -values was always small. We will return later to this aspect.

[36] Also indicated in Figures 4a and 4b is how from the extended regression line a negative value for $\cos(\theta)$, i.e., $\theta > 90^\circ$, can be obtained for $\sigma_{IV} = 69 \text{ mJ m}^{-2}$, the surface energy for water at 25°C . This procedure allows the simple estimation of the (with conventional CRM not measurable) contact angle for water in hydrophobic media using water-alcohol mixtures with a lower liquid surface energy than water and by using the extrapolation of the regression in the contact angle range $<90^\circ$. In case of Figure 4a we estimated $\theta = 121.0^\circ$ and in case of Figure 4b the estimate was $\theta = 141.9^\circ$. Additionally, it is shown how for $\theta = 90^\circ$ ($\cos(\theta) = 0$) a value for σ_{ND} can be obtained; in the case of Figure 4a this value is derived from $(\sigma_{ND})^{-0.5}$ and is $\sigma_{ND} = 52.4 \text{ mJ m}^{-2}$. For Figure 4b it is $\sigma_{ND} = 53.2 \text{ mJ m}^{-2}$.

Finally, in both Figures 4a and 4b the value for $\cos(\theta)$ (symbol: open circle) is indicated, as determined with the Wilhelmy plate method (WPM). For soil material SPO_GP7b an advancing contact angle θ_a of 141.3° ($\cos(\theta) = -0.78$) was determined, and for the receding contact angle θ_r it was 44.0° using WPM. Other values, as determined with both MCRM and WPM for the other soils, will be presented and discussed in the next section.

[37] As noted earlier, MCRM can also be applied to soils that have a contact angle $<90^\circ$. In this case the procedure is the same as for soils with a contact angle $>90^\circ$. Also in this case either equation (12) or equation (13) can be used to process the data. An advantage of MCRM, as compared to CRM, is that MCRM gives additional information. This is shown in both Figures 4a and 4b, which indicate how both the 90-degree surface energy σ_{ND} as well as the critical surface energy σ_c of the soil material can be estimated. Similarly, we determined $\sigma_c = 30.8 \text{ mJ m}^{-2}$ for the wettable soil INC_Bv2 from the Zisman plot (Figure 5b). As in Figures 4a and 4b the regression coefficients b_0 and b_1 are given in Figure 5, as well as the coefficient of determination r^2 . For soil INC_Bv2 equation (13) appears to describe the data slightly better than equation (12). As mentioned earlier, this observation was made for nearly all the other soils that were analyzed. From Figure 5a a contact angle $\theta = 76.2^\circ$ was determined, and from Figure 5b a contact angle $\theta = 81.0^\circ$ was calculated. Also $\cos(\theta)$, as determined by WPM (as discussed next) is shown (open circles).

[38] Results obtained for the 24 soils that were studied are summarized in Table 2. Shown are contact angles θ , obtained either with CRM, MCRM, WPM, (both advancing θ_a and receding contact angle θ_r), and SDM, as well as penetration times (in seconds), as obtained with WDPTT. The results reveal that most soils that we examined were wettable or partly wettable, as indicated by contact angles

Table 2. Contact Angles Obtained With the Capillary Rise Method (CRM), Modified Capillary Rise Method (MCRM), Wilhelmy Plate Method (WPM), Sessile Drop Method (SDM), and Results of the Water Drop Penetration Time Test (WDPTT)

Soil	CRM θ , deg	MCRM θ^a , deg	WPM		WDPTT Time, s	SDM θ , deg	Rank for Figure 9
			θ_a , deg	θ_r , deg			
INC_Ah	>89.9	92.6, 94.3	115.6	0	109	42.0	16
INC_Bv	59.0	60.5, 59.0	44.9	0	<2	0	4
INC_Bv1	66.6	79.3, 81.4	65.6	0	<2	0	10
INC_Bv2	79.7	75.2, 81.0	61.9	0	<2	0	8
INC_IIIcV	69.1	80.0, 82.5	62.0	0	<2	0	9
INC_IVcV	43.9	44.4, 46.9	42.0	0	<2	0	3
ALF_Bv	54.6	67.8, 74.5	52.9	0	<2	0	6
ALF_BvS	80.5	83.4, 90.1	96.7	0	>3600	72.0	12
MOL_Ah2	>89.9	n.d., n.d.	141.3	72.0	>3600	135.0	23
MOL_Ah1	>89.9	102.3, 128.3	129.3	78.0	>3600	135.0	22
SPO_Ah1	>89.9	118.0, 138.4	128.0	40.0	>3600	109.0	18
SPO_Ah2	>89.9	103.7, 121.9	109.3	0	150	77.0	15
SPO_C	74.4	84.3, 93.6	100.9	0	11	52.0	14
SPO_AG3	>89.9	114.4, 135.3	131.5	49.0	>3600	85.0	20
SPO_AG4b	57.4	n.d., ^b n.d. ^b	72.2	0	<2	0	11
SPO_GP7b	>89.9	121.0, 141.9	141.3	44.0	>3600	89.0	19
SPO_GP17	>89.9	111.9, 125.1	124.6	70.0	>3600	129.0	21
SPO_RG2	67.2	n.d., ^b n.d. ^b	92.1	0	n.d.	29.0	13
SPO_CP12a	83.5	n.d., ^b n.d. ^b	115.7	0	n.d.	54.0	17
ENT_C	0	0, 0	0	0	<2	0	1
INC_Lsy	0	n.d., n.d.	0	0	<2	0	2
INC_LSdv	59.4	58.7, 59.4	54.6	0	<2	0	7
OXI_B	73.9	n.d., n.d.	49.2	0	<2	0	5
INC_Ahc	85.1	n.d., n.d.	0	0	<2	0	-
tape	n.d. ^b	n.d., n.d.	90.1	0	n.d. ^b	95.0	-

^aThe first value is estimated with equation (12), and the second value is estimated with equation (13); n.d. is not determined.

^bNot enough material for modified capillary rise method (MCRM).

smaller than 90° and WDPTT-values <2 s. Most often penetration times less than 2 s were measured, but frequently also penetration times larger than 3600 s were recorded; only a few values were within the range >2 s and <3600 s. We grouped our values accordingly in three classes. We measured a wide spectrum of contact angles, ranging from $\theta = 0^\circ$ for soil INC_Lsy and for the ignited sand ENT_C, up to contact angles around 140° for soils SPO_GP7b and SPO_Ah1. The data indicate that most soils feature some degree of repellency and thus that the zero degrees contact angle assumption of many soil physics textbooks [e.g., *Jury et al.*, 1991] is not confirmed. It is also interesting to note that some samples, identified by WDPTT-values <2 s, have advancing contact angles larger than 60° . Hence WDPTT values <2 s do not necessarily imply unrestricted wettability.

[39] The contact angle values, listed in Table 2, can be used for an evaluation of the methods of analysis. In Figure 6 the sensitivity of the water drop penetration time test (WDPTT) is examined. In Figure 6 the logarithm of the penetration time (in seconds) is plotted as a function of the contact angle θ , as determined by MCRM (Figure 6a) and WPM (Figure 6b). Both Figures 6a and 6b suggest that WDPTT is only sensitive in a rather narrow range around $\theta = 90^\circ$. The hydrophilic zone is defined by WDPTT <2 s, the hydrophobic domain by WDPTT >3600 . The transition domain zone was defined for all values >2 s and <3600 s, respectively. The significance of the transition domain proposed in Figure 6b is unknown. However, Figure 6b shows additional contact angle-WDPTT data presented originally by *King* [1981]. *King* calculated contact angles using capillary rise data. According to Figure 6b, *King's* data

are in general agreement with our findings, i.e., samples with WDPTT times within the proposed interval >2 s and <3600 s had contact angles within 70° and 90° which is within the defined transition domain.

[40] In Figure 7 additional results obtained with MCRM are shown. Figure 7 contains a series of Zisman plots (see also Figure 4b), illustrating the wide range of applicability of the method for determining contact angles. The values for $\cos(\theta)$ range from 0.70 ($\theta = 45.6^\circ$) to -0.70 ($\theta = 134.4^\circ$). In each plot also the value of the contact angle θ_a as determined with WPM is shown. The WPM data (accuracy 3° – 5°) were not used for the calculation of the linear regression for the σ_{lv} - $\cos(\theta)$ relation measured with MCRM. In general (but not always) there is a close agreement between θ as determined with MCRM and WPM. Coefficients of determination r^2 were >0.90 , except for the samples INC_IV Cv and MOL_Ah2 with r^2 values >0.62 . For the wettable or medium repellent soils (plots shown in the top row of Figure 7), the WPM values were within the confidence interval (95%) determined by the linear regression.

[41] This close agreement in general can also be demonstrated in a different way. Contact angles determined with both MCRM or WPM were compared (Figure 8). This is done for both models (equations (12) and (13)) that we used to describe θ as a function of σ_{lv} . Both Figures 8a and 8b suggest a linear relation, with the coefficient of determination r^2 for the model of equation (13) being slightly higher than for equation (12). Our results thus are in agreement with those of *Zisman* [1964]. We are aware that our approach is not entirely comparable to that of *Zisman*, because *Zisman* used a series of homologous liquids to

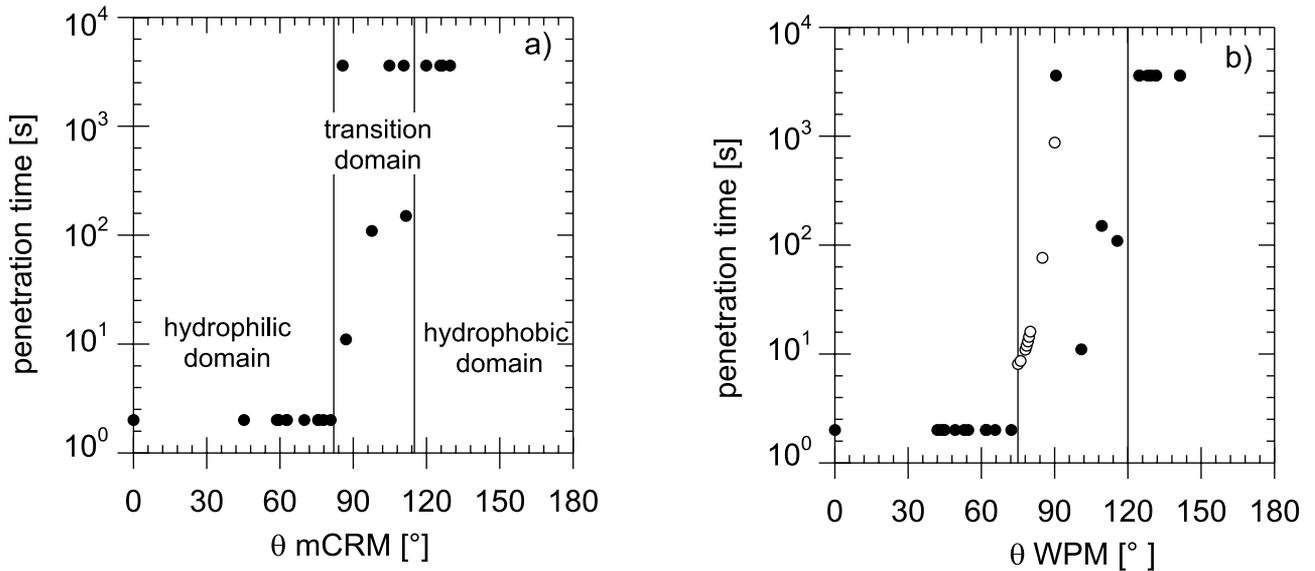


Figure 6. Log of water drop penetration time (WDPTT), (a) as tested against MCRM and (b) as tested against WPM. Solid circles represent data from soils used in this study, while open circles represent data reported by King [1981].

derive his relation. However, Zisman stated that, even when a variety of nonhomologous liquids was used, the graphical points did fall close to a straight line or in a narrow rectangular band. Our results suggest that this is even true for weakly defined and chemically heterogeneous soil particles. Although equation (13) exhibited a slightly closer fit to data, Table 2 shows contact angle data (θ for water at

25°C, $\sigma_{lv} = 69.8 \text{ mJ m}^{-2}$) that were determined with equations 12 and 13.

[42] One of the most interesting results, in our opinion, is presented in Figure 9. Plotted is $\cos(\theta)$ as a function either of the advancing contact angle θ_a (as long as the receding contact angle $\theta_r = 0^\circ$), or as a function of θ_r , in case $\theta_r > 0^\circ$ (see Figure 9). Additionally plotted is the cosine of the static

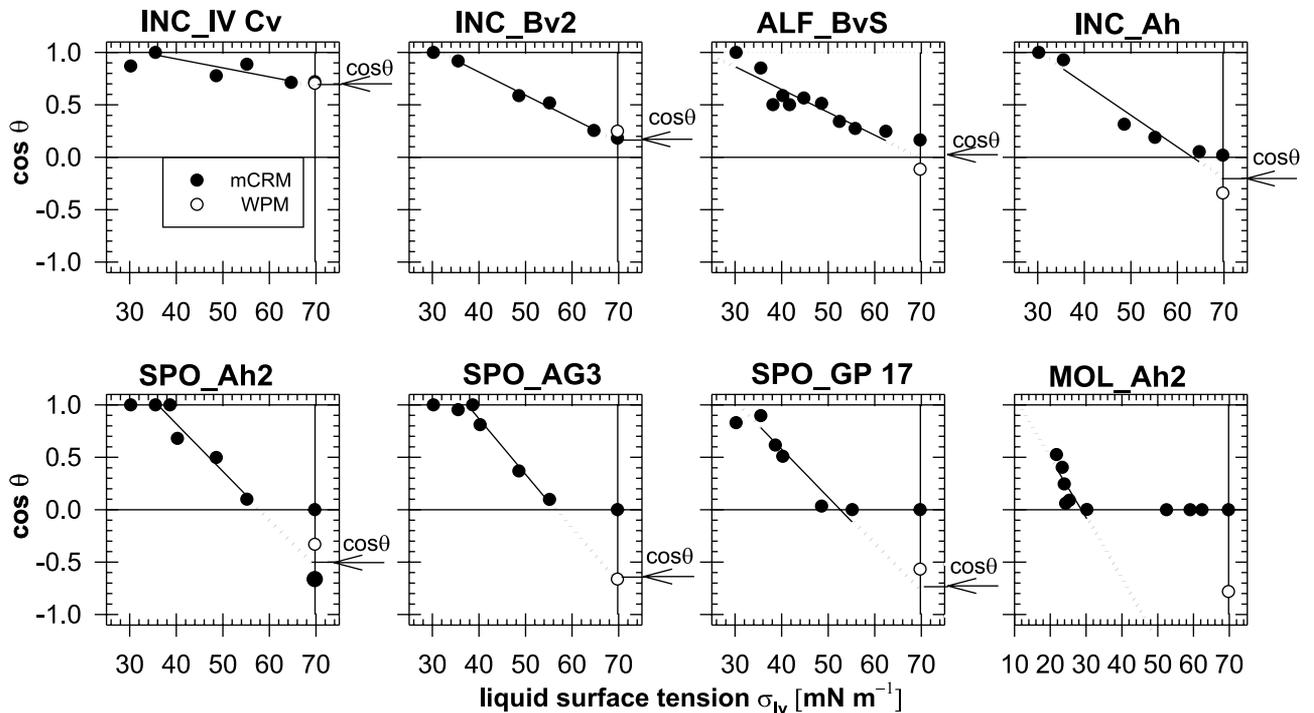


Figure 7. Contact angles (MCRM and WPM) as a function of the liquid surface energy (Zisman plots) for eight soils with contact angles varying from 45° to 140°; open circles are contact angles determined with WPM.

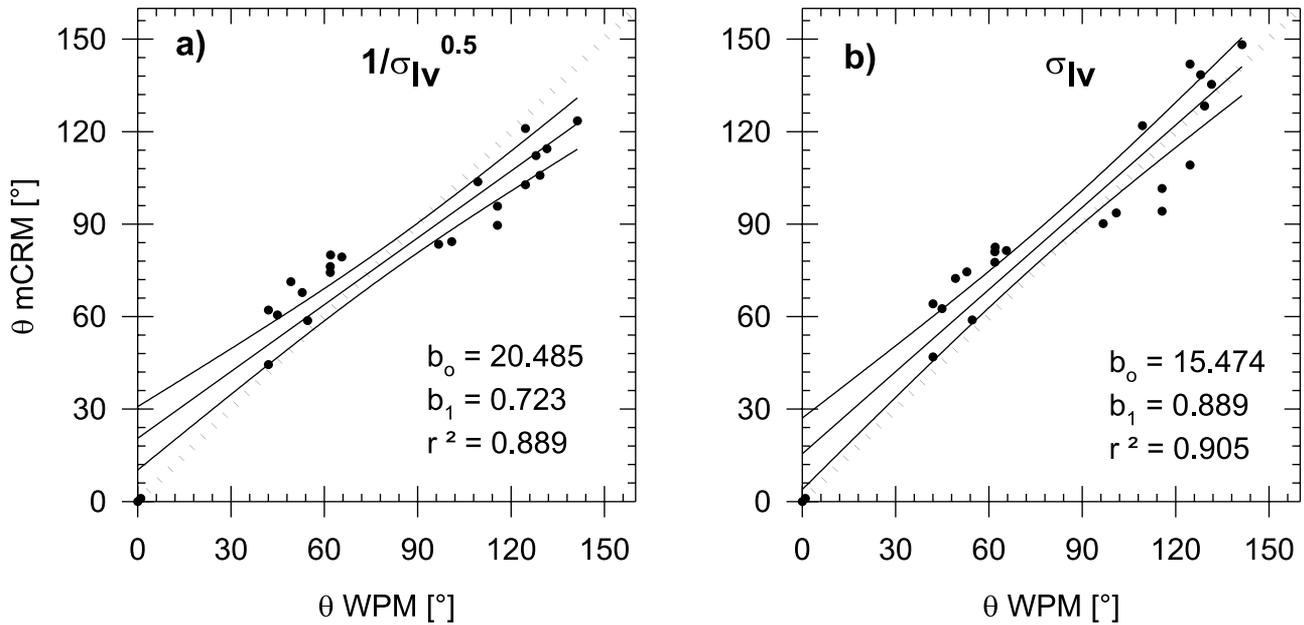


Figure 8. Contact angles determined with the modified capillary rise method (MCRM) versus contact angles determined with the Wilhelmy plate method (WPM); the MCRM values were calculated with equation (12) and (13).

contact angle (of the corresponding soil), as determined with SDM. The rank order presented (see also Table 2) was defined by increasing θ_a values because WPM provided a complete contact angle spectrum from 0° to $>140^\circ$. Figure 9 shows that the cosine values of the receding and advancing contact angle enclose a domain that suggests hysteresis. The domain includes the contact angle values as determined with SDM. As can be derived from Figure 9, the latter values in the range between 60° and 120° are about midway between the corresponding advancing and receding contact angle. This finding may support the hypothesis of *Johnson and Dettre* [1964] that SDM-values (static) are closer to the thermodynamic equilibrium than dynamic contact angles.

[43] Finally, some results will be presented that concern the solid-gas interfacial energy σ_{sv} of the soil materials. Figure 10 shows values obtained with equation (14) for $\cos(\theta) = 0$, i.e., $\theta = 90^\circ$, where σ_{sv} is estimated as $\sigma_{lv}/4$ ($= \sigma_{ND}$). The contact angle hysteresis determined with WPM allows an alternative way to estimate surface free energy [Chibowski and Perea-Carpio, 2002]. Such values were determined with equation (26). These values are also depicted in Figure 10. The 2nd order regression shows clearly differences for both methods, except for the area between 80° and 100° . It is interesting to note that this contact angle range is almost identical with the maximum of sensitivity of the water drop penetration time test WDPTT. As indicated by the confidence intervals of both regressions, differences are significant for all contact angles, except for contact angles around 110° . In the present state it is not possible to decide which values are closer to the true interfacial energy.

5. Conclusions

[44] Interfacial energies of the three-phase system of solids, water, and air in the vadose zone govern the capillary

pressure-saturation relationships. They also affect soil moisture movement in the unsaturated zone. For a better understanding of soil water phenomena in the unsaturated zone, it is therefore necessary to investigate the interfacial energies in this zone. However, methods of assessing interfacial energies to date have been only partly developed and have

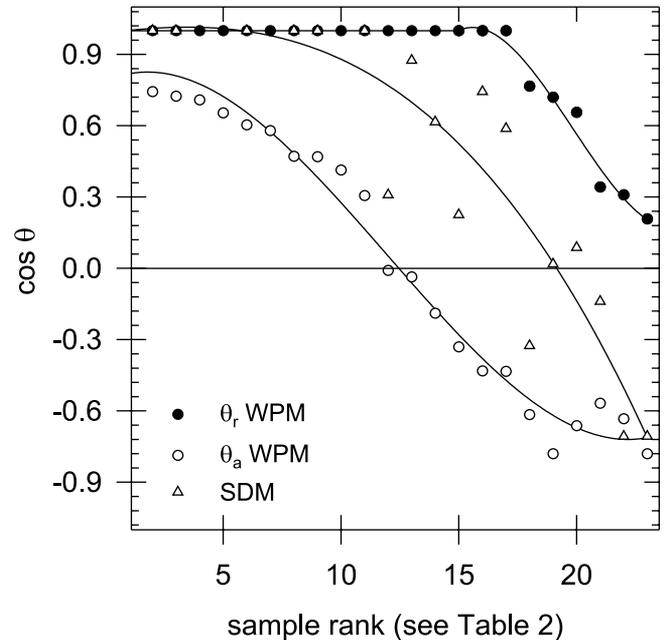


Figure 9. Values of $\cos(\theta)$ for the materials listed in Table 2 as measured with WPM (for both θ_a and θ_r) and SDM. As long as $\theta_r = 0^\circ$, the contact angle θ_a determines the ranking, whereas the contact angle θ_r determines the ranking for all values of $\theta_r > 0^\circ$ (see Table 2).

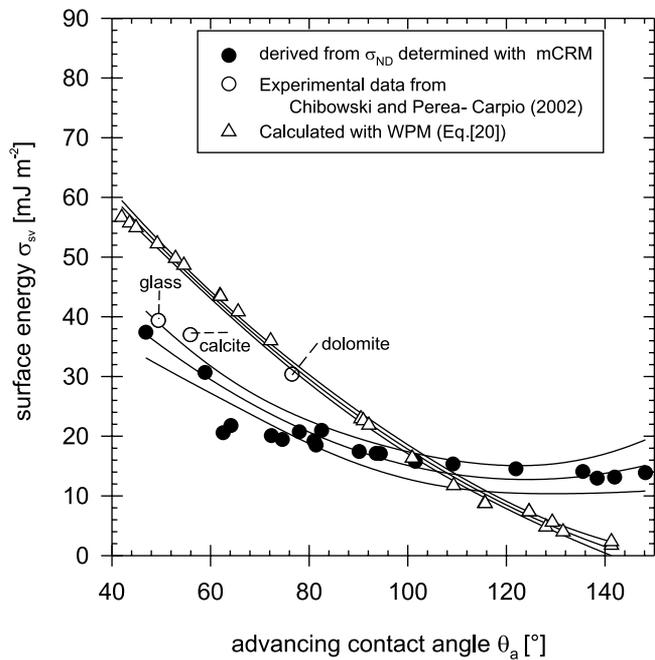


Figure 10. Surface energy σ_{sv} of soil particles as a function of the advancing contact angle θ_a as determined with MCRM (equation (15), solid circles) or with WPM (equation (20), triangles); also shown are values from Chibowski and Perea-Carpio [2002] (open circles).

limitations. For that reason we have described two methods that apparently have not been applied in vadose zone research to determine contact angles and from which interfacial energies can be derived. These are the modified capillary rise method (MCRM) and the Wilhelmy plate method (WPM). The first one consists of two parts: for contact angles less than about 85° MCRM is performed with n-hexane and deionized water, whereas for contact angles larger than 85° the test fluids are n-hexane and methanol-water mixtures of varying composition instead of pure water. In the latter case a graphical procedure is applied to estimate the soil's contact angle for pure water.

[45] The proposed methods were tested on 17 soils and 7 additional granular soil-like materials. Contact angles between 0° and 142° were measured. Measured values were compared with results obtained with hitherto considered standard methods such as the sessile drop method (SDM) and the water drop penetration time test (WDPTT). Agreement and differences were noted. With WPM, for example, dynamic contact angles, i.e., contact angles associated with an advancing or receding wetting front, are measured, whereas SDM assesses static contact angles. However, we found that SDM-values for the soils we examined were always in the domain enclosed by the corresponding values as measured with WPM. We also found that the contact angles of the soils studied usually differed from zero degrees and that most of these soils thus seemed to be slightly, partially, or fully water repellent. Furthermore we found evidence that the water drop penetration time test (WDPTT) is only sensitive in a rather narrow contact angle range around 90 degrees. The newly proposed methods, MCRM and WPM, seem to cover the entire range of

possible contact angles from 0 to 180 degrees. We conclude therefore that both MCRM and WPM appear to be valuable tools to study the behavior of soils that show various degrees of water repellency.

[46] With the capillary rise method (CRM) it seems possible to assess repellencies in the range from 0° up to approximately 85° , with a high degree of accuracy. It seems reasonable to set the limit at $\cos(\theta) > 0.09$, which excludes the contact angle domain between $85-90^\circ$, to improve linearity between $\cos(\theta)$ and σ_{lv} . For larger values, MCRM and WPM are able to provide reproducible results. Dissolution effects, swelling, or chemical reactions between solid and liquid were generally ignored in this study. Particularly for samples with weak soil structure or with high clay content, the possibility of swelling or dispersion of micro aggregates in contact with water has to be considered. Both effects may reduce the liquid uptake rate into the CRM sample, which results in increasing contact angles. The sample INC_Ahc indicates such a swelling effect, because the CRM contact angle is around 85° whereas the corresponding value for WPM (and SDM) is zero.

[47] It appears that the assessment of contact angles, i.e., dynamic or static contact angles of porous materials, can lead to different results depending on the applied methods. However, a comparison of dynamic contact angles determined by the (modified) capillary rise method and the Wilhelmy plate method showed reasonable agreement. These two methods seem useful for the determination of surface properties of irregularly shaped solid particles. WPM allows for the assessment of contact angle hysteresis and uses pure water (or soil solution) as the testing liquid. It appears probable that results from MCRM can be used to estimate contact angles for soil - soil solution systems, if the surface tension of the soil solution is known. Further studies on the usefulness of both methods for hydrological processes are needed.

[48] **Acknowledgments.** Financial support provided by the "Deutsche Forschungsgemeinschaft DFG" (Priority program "Soils as source and sink for CO_2 - mechanisms and regulation of organic matter stabilization in soils," SPP 1090) for this study is appreciated. We greatly appreciate the recommendations of Rienk R. van der Ploeg and the unknown reviewers for improvements to the manuscript.

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