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Effect of solid phase wettability on water transport and retention in peat enriched soil affected by freezing/thawing**

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Abstract. Samples of A and B horizons of arable loessial soil, with and without the addition of c.a. 9% of peat and subjected to six freezing/thawing cycles, were studied. Surface free energies and water contact angles were determined using a thin layer wicking technique. The water retention curving relating soil moisture to the pressure head was measured by combining the suction plate and pressure chamber methods. The addition of the fresh (non-dried) peat increased soil wettability in both horizons, which increased further after cyclic temperature changes. The amount of water retained at high pressure head values (in the low moisture region) decreased with the decrease in soil wettability, i.e., with the decrease in the work of spreading of water and the increase of the contact angle. However, the amount of water retained at low pressure head values (in the high moisture region) depended on the pore volume of the soils. It was concluded that the value of the surface free energy has an important effect on water retention at low soil moistures, whereas at high moistures, macroscopic soil characteristics (such as porosity or bulk density) govern the water retention.

Keywords: wettability, water retention, freezing/thawing, soil

INTRODUCTION

Soil wettability is a very important factor governing water retention and transport processes (Emmerson and Bond, 1962; Kramers and De Bano, 1965; Moseley and Dhir, 1996). The wettability of the solid can be characterized by the solid-liquid contact angle, which depends in turn on the surface free energies (surface tensions) of the liquid and of the solid (Van Oss, 1994). Because direct measurement of the contact angle, particularly for water on granular materials (soils) is almost impossible, one can calculate this from experiments on migration of a range of polar and non-polar liquids in the horizontal soil bed using a thin column wicking technique (Chibowski, 1992; Chibowski and Hołysz, 1992). This method allows for finding the surface free energies of the solid and solid-liquid interface from migration experiments for a few different liquids and then to estimate water contact angles. The surface free energy of the solid cannot be determined directly. The surface free energy of the soil, and its change due to immersion in water, constitute the driving force responsible for water transport in the porous soil body (Emmerson and Bond, 1962). Water retention in soils is the basic factor governing growth and yield of crops (Walczak and Zawadzki, 1979; Walczak *et al*., 1997). This is characterized via water retention curves (pF-curves) relating soil moisture to the overall force of water binding to the soil solid phase, i.e., the pressure head (or water potential) value (Kutilek and Nielsen, 1994; Walczak, 1984; Walczak and Witkowska-Walczak, 1990). Soil fully saturated with water is classically defined as being in equilibrium with a free water level, strictly at the suction pressure of 1cm of water (pF=0), which is equal to 98.1 Pa pressure head. The higher the pressure head the drier the soil. Usually for characterizing soil water retention, full wettability (zero contact angle) of a solid phase is assumed (Walczak, 1984).

Enrichment of the soil with peat has been a commonly used procedure to increase soil fertility. In general the peat addition increases the cation exchange capacity and creates better conditions for the development of soil biota. Dry peats

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are hydrophobic (Tschapek, 1973), thus if the soil is overdried, there exists a risk of the negative effect on soil water properties via an increase of soil hydrophobicity and decrease of wettability. However, the wettability in peat enriched soils increases over a period of time due to the reorientation of organic particles and formation of organo-mineral compounds (Michel *et al*., 1998).

Freezing of the soil is an important soil forming factor influencing soil structure, water properties and/or vertical movement of soil particles (Bac, 1934; Bullock *et al*., 1988; Bryk *et al*., 2001; Fitz Patric, 1956; 1971; Kok and McCol, 1990). Thus freezing/thawing periods may have an important influence on soil wettability and water properties.

The aim of this study is to examine the effect of peat addition and freezing/thawing on soil wettability and water retention.

THEORY

Because the theory of water retention (pF-curves) is generally known to the community of soil physicists, to whom the paper is addressed, and well elaborated in handbooks (Kutilek, 1966; Kutilek and Nilsen, 1994) let us recall briefly only the theory of wettability.

Wetting of a solid by a liquid depends on the force balance at the interface (Fowkes, 1964) which can be described by this general equation of Young's:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL}, \tag{1}$$

where θ (°) is the solid-liquid contact angle, γ_S (J m^{-2}) is the surface free energy of the solid *S*, γ_{SL} (J m^{-2}) is the surface free energy of the solid-liquid *SL* interface and γ_L (J m^{-2}) is the surface free energy of the liquid *L* (surface tension).

In general the surface free energy is expressed as a sum of two components, responsible for non-polar γ^{LW} (J m^{-2}) (Lifshitz van der Waals) and polar γ^{AB} (J m^{-2}) (acid-base) interactions (Good and Chaudhury, 1991; Norris *et al*., 1992; Van Oss *et al*., 1988):

$$\gamma = \gamma^{LW} + \gamma^{AB}, \tag{2}$$

where γ^{AB} is a geometric mean of electron-acceptor (Lewis acid) γ^{+} and electron-donor (Lewis base) γ^{-} components (Chibowski, 1992; Van Oss *et al*., 1988):

$$\gamma^{AB} = 2\left(\gamma^{+}\gamma^{-}\right)^{1/2}. \tag{3}$$

The Lifshitz van der Waals component of the interfacial free energy, γ_{SL}^{LW}, is given as:

$$\gamma_{SL}^{LW} = \left(\left(\gamma_S^{LW}\right)^{1/2} - \left(\gamma_L^{LW}\right)^{1/2}\right)^2 \tag{4}$$

and the polar component of the interfacial free energy, γ_{SL}^{AB}, is given as:

$$\gamma_{SL}^{AB} = 2\left(\left(\gamma_S^{+}\gamma_S^{-}\right)^{1/2} + \left(\gamma_L^{+}\gamma_L^{-}\right)^{1/2} - \left(\gamma_S^{+}\gamma_L^{-}\right)^{1/2} - \right.$$
$$\left. -\left(\gamma_L^{+}\gamma_S^{-}\right)^{1/2}\right). \tag{5}$$

The migration of the liquid in a porous body placed in the thin horizontal tube (column) can be described by the Washburn equation modified by Chibowski and Hołysz (1988):

$$x^2 = \left(rt / 2\eta\right)\Delta G, \tag{6}$$

where *r* (m) is an effective average radius of the capillary system in a porous body, *t* (s) is the time of migration of a liquid to the distance *x* (m), η (Pa s) is the viscosity of the liquid and ΔG (J m^{-2}), defined for convenience to be positive, is the change in free energy accompanying the wetting process of the unit area of the solid. Equation (6) assumes that the porous body is a set of parallel capillaries of average radii *r*. A flat migration front is assumed. This model neglects pore tortuosity and/or percolation thresholds. However, this has been satisfactorily applied in the description of migration of liquids in thin porous layers and thin column beds (for example in thin-layer or column chromatography).

The effective capillary radius is calculated from the migration data of n-alkane on the surface covered with an equilibrium liquid film (so-called duplex film formed at saturated vapor pressure) assuming that in this case $\Delta G = \gamma_L$ (Chibowski, 1992). The *r* value is taken to be the same for all other solid-liquid systems.

Generally, for the migration of a liquid on a bare solid, the free energy change accompanied by the liquid migration ΔG_b is expressed as a difference between the work of adhesion, W_a (J m^{-2}) of the liquid to the solid and the work of cohesion of the liquid W_c (J m^{-2}):

$$\Delta G_b = \left(W_a - W_c\right), \tag{7}$$

where $W_a = \left(\gamma_S - \gamma_L - \gamma_{SL}\right)$.

From the migration data of nonpolar liquids (e.g., n-alkanes which interact only by dispersion forces, for which $\gamma_L = \gamma_L^{LW} > 0$ and $\gamma^{AB} = \gamma^{+} = \gamma^{-} = 0$) on the bare solid one can easily find the dispersion component of the solid surface free energy using:

$$\Delta G_b = 2\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{1/2} - 2\gamma_L. \tag{8}$$

The difference between the free energy of the migration of a high surface tension liquid on a bare solid and on a solid covered by a vapor of this liquid, is usually expressed as the work of spreading W_s (J m^{-2}):

$$\Delta G_b - \Delta G_p = W_s, \tag{9}$$

where ΔG_p holds for the free energy of the interaction of the liquid with the solid surface covered by the vapor and $W_s = (\gamma_S - \gamma_{SL} - \gamma_L)$. Combining Eqs (4), (5) and (8) the difference in free energies of the migration processes on the bare and on the vapor covered solid is expressed as:

$$\Delta G_b - \Delta G_p = 2\left(\gamma_S^{LW}\gamma_L^{LW}\right)^{1/2} + 2\left(\gamma_S^{+}\gamma_L^{-}\right)^{1/2} + 2\left(\gamma_L^{+}\gamma_S^{-}\right)^{1/2} - 2\gamma_L. \tag{10}$$

Knowing γ_S^{LW} and solving a set of Eqs (10) using experimental migration data for at least two polar liquids on the bare, and on the vapor covered solid, one can find the surface free energy (SFE) of the solid and its components. The values of SFE, γ^{LW}, γ^+ and γ^- for a number of various liquids are well known and available in the literature (Van Oss, 1994). Knowing the surface free energy components of the solid, the water contact angle can be calculated using Eq. (1).

MATERIALS AND METHODS

For the present investigations samples of A and B horizons of a loessial Typic Eutrochrept soil (Elizówka) and their mixtures with 8.7% w/w of a peat Eutric Histosol (Polesie Lubelskie) were used. The original soils and their mixtures with the peat were moistened at 25% of their field water capacity and subjected to six cyclic changes of temperature. Each cycle consisted of a one-week treatment at 30°C following by one week at minus 35°C.

Thin column wicking experiments were performed in three replicates using water, formamide, n-octane and n-decane. Soil samples were uniformly placed in 10 cm long and 0.3 cm diameter glass columns and dried in a vacuum for 2 days (bare solid). Part of these was previously introduced to the vapor of the given liquid by 48 h (vapor covered solid). The columns with the respective samples were positioned horizontally and put into contact with a given liquid via a cellulose wick, and immersed in the bulk liquid. The surface of the liquid was on the same level as the center of the column. The columns were placed on a scale marked at every centimeter and the migration time at a given distance was measured with a stop-clock. From the migration data, surface free energies and their components, water contact angles and work on spreading of water were calculated. The migration data differed no more than 6% for the replicates. The average values calculated from each replicate are discussed further.

The soil's water retention at a given water potential value was measured by weighing and expressed on the dry mass basis. The dry mass was measured after completing the experiment for 24 h/105°C oven-dried samples. For measurements of soil moisture at low water potentials the suction plate method was applied (Richards, 1949). Water retention at high water potentials was measured using the pressure-chamber method (Walczak, 1984). All measurements were performed in triplicate, which differed by less than 7%. The water potential was expressed in SI units via the suction pressure head p (Pa). The p value was defined to be positive.

The total volume of the soil pores ranging in radii between c.a. 0.04 to 10 mm was measured in duplicate by mercury intrusion porosimetry using Carlo Erba 2000 equipment. The differences between the duplicates were less than 2%.

RESULTS AND DISCUSSION

Neither migration of different liquids in the thin layer wicking experiment, nor the water retention (water potential curves for natural soil samples) were affected by the freezing/thawing cycles. Therefore the respective data is not considered in the following discussion.

The dependence of migration time on the square of the migration distance in the thin column wicking experiment is presented completely in Fig. 1. Because water properties of the studied soils are of primary interest in the present studies, the migration process is illustrated using the data for water. The dependencies of the migration time vs. square of the migration distance are linear. The higher the slope of the aforementioned line the lower the migration velocity at a given distance. The migration velocity of water at any distance is lower on the bare (dry) surface than on the vapor covered (wet) surface, which is true of any other liquid. As compared to the A horizon, the water migration in the B horizon samples was faster, with the exception of the soil with the peat addition (CP). Water migration velocities for peat-enriched soil were significantly lower than for the initial soil for both soil horizons and these markedly increased after freezing/thawing cycles. This indicates that the addition of a peat as well as wetting/drying and freezing/thawing periods can seriously alter the transport of water in soils. Changes in the velocity of water transport result from a complex set of variables (see Eq. (6) and the following) including free energy change (being the driving force during the migration), liquid viscosity and/or the pore radius of the migration medium. The migration velocity for the other liquids also depends on the horizon, peat addition and freezing/thawing cycles.

Water retention in the studied soils vs. water potential dependencies is shown in Fig. 2. The retention of water differs slightly among both natural soil horizons. The moisture of the soils in the whole water potential range studied increases due to the peat addition. Compare this to the fact that peat enriched soils and the upward and downward changes in water retention in different water potential ranges were noted for frozen/thawed samples.

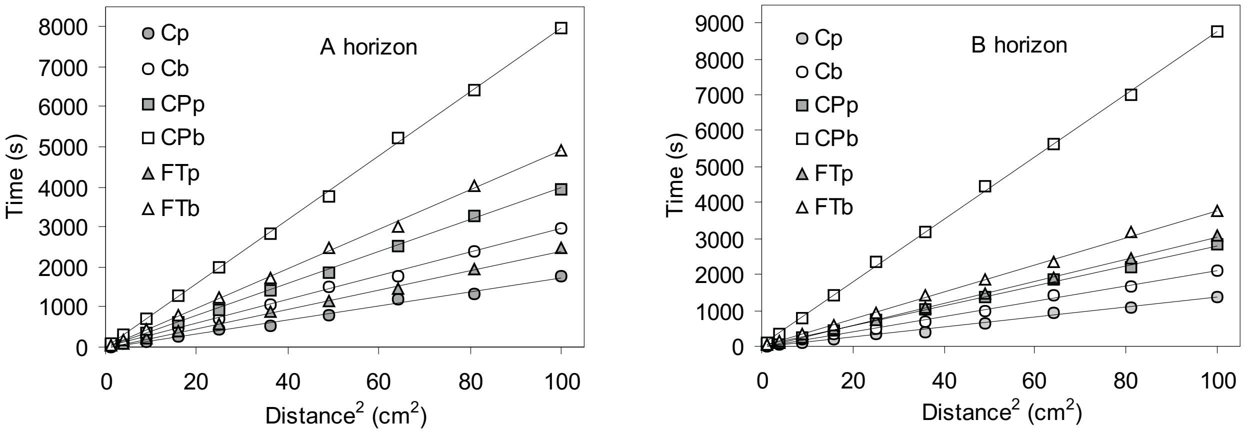

Fig. 1. Time of water migration vs. distance dependencies on bare and precontacted surfaces of A and B horizons as dependent on the peat addition and freezing/thawing cycles. Abbreviations: C - control soil, CP - soil + peat, FT - soil + peat after freezing/thawing cycles, b-bare solid, p-vapor covered solid.

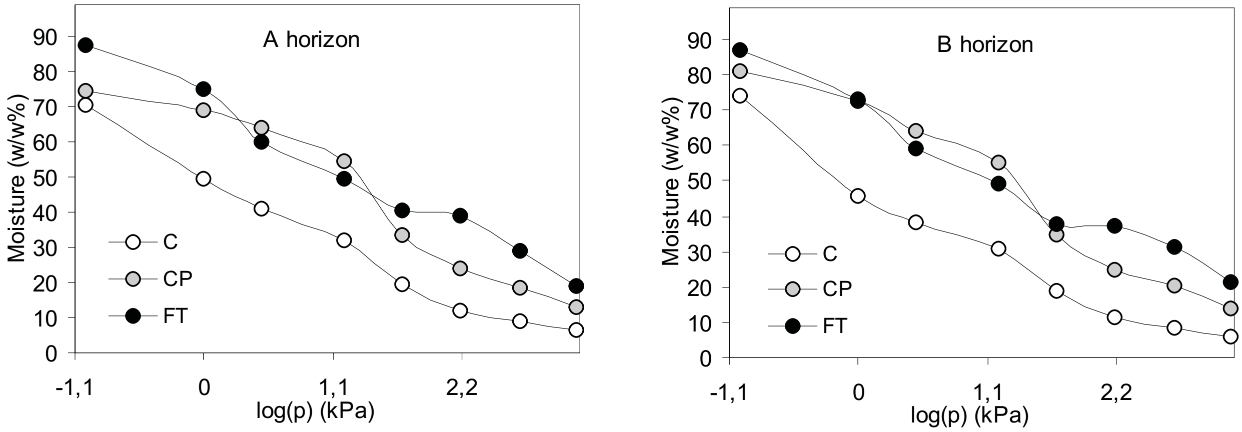

Fig. 2. Water retention curves (sample moisture vs. pressure head). Explanations as in Fig. 1.

Components of solid surface free energies calculated based on the migration data of various liquids in the thin column wicking experiment are presented in Table 1. This table also includes the calculated values of the effective pore radii, the water contact angles, work of spreading, the water retention data at minimum and maximum water potential values obtained from pF-curves and pore volumes from mercury intrusion experiments. Particularly, the work of spreading of water and the contact angle relate directly to hydrophobic character of the solid. More negatively, W_S and a higher contact angle indicate worse wettability.

The surface free energy of the studied soil in both horizons exhibits high contribution of Lifshitz van deer Waals interactions. The contribution of the electron-donor (Lewis base) γ^- interactions is high, however the electron-acceptor (Lewis acid) γ^+ component is very low. Of course, the presence of the γ^- component seriously affects the interaction of the polar liquids (water) with the studied soils. The acid-base γ^{AB} component (see Eq. (3)) is low due to low contribution of the γ^+ component.

The addition of the peat induces a slight decrease of the dispersive surface free energy component in A horizon and

T a b l e 1. Effective radius of capillary *r,* components of the SFE: dispersive γ_i^{LW}, electron acceptor γ_i^{+}, electron donor γ_i^{-}, water contact angle θ_w, work of spreading W_s, water retention at the highest water potential $V_{pF_{max}}$, difference between water retention at the lowest and the highest water potentials $\Delta V_{(pF)}$, and pore volume from mercury intrusion TCV for the studied soil samples

Soil	r (μm)	γ_i^{LW} (mJ m^{-2})	γ_i^{+} (mJ m^{-2})	γ_i^{-} (mJ m^{-2})	θ_w (°)	W_s (mJ m^{-2})	$V_{pF_{max}}$ (w/w%)	$\Delta V_{(pF)}$ (w/w%)	TCV (mm^{3}g^{-1})
				Horizon A (0-5cm)					
C	0.46	45.0	0.98	37.9	31.6	-20.8	6.5	64.1	130
CP	0.37	42.0	0.38	44.3	32.7	-17.8	13.0	61.6	101
FT	0.54	46.2	0.07	54.6	20.9	-7.5	18.9	68.7	159
				Horizon B (5-25 cm)					
C	0.54	38.3	2.54	36.9	31.0	-26.5	6.0	68.2	132
CP	0.61	41.4	1.04	44.7	26.6	-18.0	13.9	67.1	121
FT	0.42	46.8	0.03	59.4	17.3	-3.8	21.3	65.8	90

Abbreviations: C - control soil, CP - soil + peat, FT - soil + peat after freezing/thawing cycles.

its increase in B horizon. The contact angle of water on the peat enriched soil slightly increases in the A horizon and decreases in the B horizon after the peat addition, however the work of spreading increases in both cases, indicating an increase in the hydrophilic character of the soil. It is frequently reported that natural soil organic matter, including peat, has contact angles around 90°, and its addition should make the soil more hydrophobic. However, such high values of contact angles were measured for dry organic matter (Tschapek, 1973). Dry peat can have a high contact angle because during drying the conformation of soil organic molecules changes and their most hydrophobic parts become exposed. In our studies fresh, nondried peat was added to the soil and, in this state, this can have a hydrophilic character (Wershaw, 1994). The dispersive component of the SFE increases after freezing/thawing cycles for both horizons indicating some reorientation of peat molecules due most probably to formation of organo-mineral compounds. Formation of organo-mineral compounds between soil mineral phase and peat organic substances (Zhang and Hartge, 1992) leads to loosening of soil structure which causes an increase in soil permeability and aeration.

For both soil horizons, after addition of the peat the electron-donor γ^{-} component of the SFE markedly increases. This certifies that the added peat has a hydrophilic character, as suggested above. The freezing/thawing cycles lead to a further increase of the electron donor component suggesting the further exposure of the hydrophilic parts of the peat molecules. The opposite trend to the electron donor interactions is observed for the electron acceptor γ^{+} contribution. Due to peat addition and the freezing/ thawing cycle the electron acceptor interactions markedly decrease in both horizons. As the overall amount of the polar interactions depends on the product of the electron acceptor and electron donor components, the overall effect is a decrease in acid-base polar SFE component due to the peat addition and the freezing/thawing.

Composite effects influencing changes in the surface free energy components described the above result in changes of the wettability of the studied soils. As seen from the increase of the work of spreading, soils become generally more wettable due to the addition of the peat and consecutively more wettable after freezing/thawing periods. The migration of water in the horizontal soil bed is directly related to the wettability of the solid as the latter governs the ΔG value being the driving force in transport processes (see Eq. (6)). However, the dependence of the migration velocity and wettability in the soil cannot be simply linear because the former also depends on the radius of the soil bed in which water moves. The equivalent radii of the soil pore depend on both the peat addition and freezing/thawing cycles (see Table 1). The thinner the pore, the slower the migration velocity. The soil wettability reflects the interaction forces of the water molecules and the solid surface. Therefore not only the transport but also the retention of water, at least at low moistures (where these interactions play an important role), should be related to parameters of soil wettability. The dependence of the amount of soil water retained at high water potential on the work of spreading and on the contact angle is presented in Fig. 3 for all samples studied. From this figure it is clearly seen that the increase in water retention in the low moisture region is directly related to the decrease of the contact angle and the increase in the work of spreading.

The total amount of the retained water, e.g., that measured at the lowest water potential follows the same order in the samples studied as the water retained at high potentials. The total amount of the retained water should be higher in

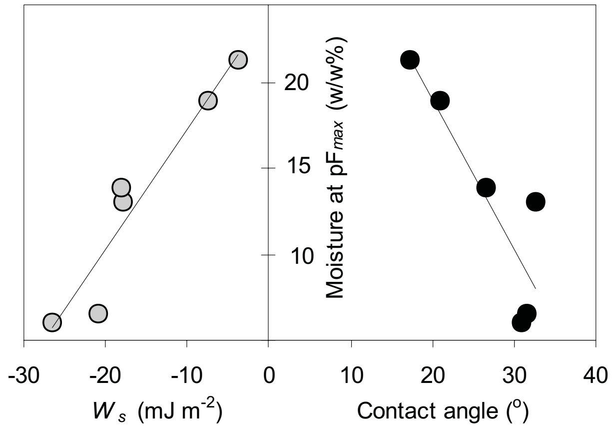

Fig. 3. Dependence of soil moisture at high water potential on the work of spreading (left) and on the water contact angle (right) for all soil samples studied.

soils of higher total porosity and lower bulk density, because more space is available for water. Usually, the total soil porosity is highly correlated with the total pore volume measured by mercury intrusion porosimetry (Konstankiewicz and Stawiński, 1976). However, in the studied soils, the total amount of the retained water seems not to be related to the mercury intrusion pore volume. The latter value seems to correlate positively with the difference between the total amount of the retained water and the amount of water retained at the highest water potential. The dependence between the above values is different in A and B horizons. The water retention at high potentials relates to the strongly bound water, present as adsorbed molecules and thin water films. Therefore the difference mentioned above may be considered as the gravitational water plus capillary water, and indeed this may better correlate with the soil porosity than the total amount of soil water.

CONCLUSIONS

Soil wettability by water is markedly altered by the addition of peat and freezing/thawing cycles. The parameters responsible for the soil wettability govern water transport processes and water retention at high water potentials, i.e., in low soil moisture range.

Addition of the peat to the soil can increase its water retention, which can be important, particularly in urban areas where the present infrastructure favors the rainwater outflow and diminishes its retention.

The studies reported included too small an amount of samples to verify statistically the described results and should therefore be treated as preliminary investigations. To find a more detailed picture of the effect of soil surface free energy and wettability on soil water properties, more studies are necessary including more on different soil samples. Such studies are planned in our future work.

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