Influence of a cyclodextrin on soil wettability**

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A b s t r a c t. The effect of various doses of the randomly methylated β-cyclodextrin on changes in surface free energy and wettability of a natural, and a humic acid enriched, loessial soil Orthic Luvisol was studied. A thin column wicking technique was used to determine the horizontal migration velocity vs. time dependence in the sample beds for a range of liquids of various surface tensions (surface free energies). From the latter dependencies the surface free energy and its components (water contact angles, works of adhesion and force of interparticle interaction via water layer) were estimated for the studied materials.

The dispersive component of the surface free energy was least affected by the added cyclodextrin, however for the natural soil this markedly increased after the highest (2.5%w/w) cyclodextrin addition. The polar, acid-base component decreased in general with the cyclodextrin dose increase. The contribution of the electron-donor interactions to the polar surface free energy component decreased after low cyclodextrin doses (0.1 and 0.5%) and increased after the highest (2.5%) dose. Generally, the opposite tendency was noted for the electron-acceptor contribution. The wettability of the soil decreased at low cyclodextrin concentration and increased again at the highest load. The increase in the cyclodextrin concentration decreased the effective radius of the soil bed which caused an increase in the average force of interaction between soil particles via water layer, despite the simultaneous decrease of adhesion forces of water to the soil.

K e y w o r d s: cyclodextrin, soil, surface free energy, wettability

INTRODUCTION

Cyclodextrins are crystalline, water soluble, non-reducing, cyclic, toroidially shaped oligosaccharides built from six to twelve glucopyranose units. The conformation of the-

se units is such that the outer part of the toroid is ringed with primary and secondary hydroxyl groups enabling the hydrophilic character of the molecule. However, inside the toroid cavity, the high electron density of the glucosidic oxygen creates a hydrophobic trap, into which a great variety of low-polar guest molecules of sufficient size can be encapsulated (Szejtli, 1998). Formation of such inclusion complexes markedly increases the apparent aqueous solubility and bioavailability of the guest molecules, allowing for the use of cyclodextrins in situ-flushing and/or biodegradation of a great number of soil organic contaminants (Allenza *et al*., 1992; Fava and Grassi, 1998; Gruiz and Kriston, 1995; Gruiz *et al*., 1996; Mc Cray and Brusseau, 1998; Szejtli, 1992; Wang *et al*., 1998; Wang and Brusseau, 1993).

Strong interaction of natural and synthetic mineral phases with cyclodextrins (Kijima, 1986; Sopkova and Mezes, 1999; Zhao and Vance, 1998) suggest that the properties of the soils may also be seriously affected by these oligosaccharides, which may have an influence on soil remediation processes. However, little is known about the response of soil solid phase to cyclodextrin addition. Józefaciuk *et al*. (2001) studied the effect of the randomly methylated β-cyclodextrin (commercial name RAMEB) on surface and pore properties of common clay minerals: bentonite, illite and kaolinite. Pure RAMEB sorbed huge amounts of water, however the energy of its interaction with water vapour was low. Contrary to what was expected, when increasing amounts of RAMEB were added to the minerals, the water sorption decreased and adsorption energy increased, suggesting RAMEB's interaction with clay minerals is strong. These results suggested that RAMEB addition might affect water properties of mineral soils. To check this

hypothesis we studied the effect of the addition of the RAMEB on changes in surface free energy and wettability of a loessial soil.

Soil wettability is a very important factor governing water retention and transport processes (Kramers and De Bano, 1965). Wettability of a solid can be characterized by the solid-liquid contact angle, which in turn depends on surface free energies of the liquid and the solid (Bernett *et al.*, 1959; Emmerson and Bond, 1962). The surface free energy of a solid can not be determined directly (Van Oss, 1994). The direct measurement of the contact angle, particularly on granular materials (soils) is hardly possible either. For estimation of the above values one can use migration data of a range of polar and apolar liquids in the horizontal mineral bed using thin column or thin layer wicking techniques (Chibowski, 1992; Chibowski and Hołysz, 1992).

THEORY

Let us recall only some basic dependencies necessary to follow the general idea of our thin column wicking studies. For detailed methodical and theoretical background, the interested reader should study: Chibowski, 1992; Chibowski and Hołysz, 1992; Chibowski and Gonzalez-Caballero, 1993; Hajnos and Matyka-Sarzyńska, 1996; Hajnos, 1999; Van Oss, 1994.

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

$$\gamma_L \cos \theta = \gamma_S - \gamma_{SL}, \qquad (1)$$

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 apolar 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):

$$\gamma = \gamma^{LW} + \gamma^{AB}, \qquad (2)$$

where γ^{AB} is a geometric mean of electron-acceptor (Lewis acid) γ^+ and electron-donor (Lewis base) γ^- components:

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

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

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

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

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

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):

$$x^2 = (rt/2\eta)\Delta G, \qquad (6)$$

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.

The effective capillary radius is calculated from the migration data of n-alkane on the surface covered with an equilibrium liquid film (the so-called duplex film formed at saturated vapour pressure) assuming that in this case $\Delta G = \gamma_L$ (Chibowski, 1992) and that r is 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}):

$$\Delta G_b = W_a - W_c, \qquad (7)$$

where $W_a = \gamma_S + \gamma_L - \gamma_{SL}$.

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:

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

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 vapour of this liquid, is usually expressed as the work of spreading W_s (J m^{-2}):

$$\Delta G_b - \Delta G_p = W_s, \quad (9)$$

where ΔG_p holds for the free energy of the interaction of the liquid with the solid surface covered by the vapour 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 vapour covered solid is expressed as:

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

$$2\left(\gamma_L^+\gamma_S^-\right)^{1/2} - 2\gamma_L. \quad (10)$$

Knowing γ_S^{LW} and solving the Eq. (10) using experimental migration data for at least two polar liquids on the bare and on the vapour 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 from Eq. (1).

Using water contact angle values and knowing water surface tension γ_w, one can find the force of interaction F (N) occurring between soil solid particles joined via water layer of a defined shape (Adamson, 1982). For the present calculations we assumed that the plane surfaces of the soil particles are joined by a water film in the shape of a circle having the diameter d (m) and the thickness h (m). In this case (Jañczuk et al., 1993):

$$F = \frac{1}{2}\gamma_w\left(\pi d^2 h^{-1}\cos\Theta - \pi d\right). \quad (11)$$

The h value should be equal to the distance between soil particles, therefore this was approximated by the equivalent pore diameter ($2r$) of the sample bed. The d value should correspond to the magnitude of the interacting particles. Because in the studied loessial soil the silt fraction dominates, the d value was taken as 10 µm, which corresponds to the diameter of the silt 2-20 µm fraction (Day, 1965), as well as being convenient for the calculation.

MATERIALS AND METHODS

Sample of 0-20 cm depth A horizon of a loess-derived soil Orthic Luvisol (Elizówka, Poland) was studied. The dominant clay mineral in this soil was illite. The soil had CEC of 21.2 cmol kg^{-1} and an organic matter content of 0.73%. Part of the soil sample was enriched with humic acid (HA) obtained from the sodium humic acid salt (Riegel,

Germany). The HA was precipitated with HCl from the solution of the reagent and cleaned by centrifugation with an additional 4 doses of HCl and then with water until it started to peptize. The wet sediment was added to the water-saturated soil in order to arrive at the final concentration of the organic matter equal to 2.5% and equilibrated during 2 weeks. The ash content of the cleaned HA was 3.4% w/w (dry mass).

The natural and the HA enriched soil samples were air-dried, crushed, 2 mm sieved and amended with the randomly methylated β-cyclodextrin (RAMEB, Wacker Chemie, Germany) in order to arrive at the final RAMEB soil content of 0.1, 0.5 and 2.5% w/w. The RAMEB was added to the soil samples as solutions of the same volume (1:1 soil: solution ratio) containing different amounts of the RAMEB. Water was added to the soils without RAMEB addition (controls), used as a reference materials. The resulting suspensions were slowly dried at room temperature. At the end of the drying process the samples were carefully mixed with a glass rod to minimize nonuniform RAMEB distribution. Dry samples were crushed, 1 mm sieved and used for the further studies.

Thin column wicking experiments were performed using water, formamide, n-octane and n-decane. Dry soil samples (bare solid) and soil samples previously introduced to the vapour of the given liquid (vapour covered solid) were used. The samples were placed in 10 cm long horizontal glass columns and put into contact with a given liquid via a cellulose wick immersed in the bulk liquid. The surface of the liquid was on the same level as the centre of the column. The migration distance and time were measured in three replicates, which differed no more than 4%. From the migration data, surface free energies of the samples, water contact angles and the interparticle forces were calculated. The average values of the replicates are discussed further.

RESULTS AND DISCUSSION

The dependencies of migration time on the square of the migration distance in the thin column wicking experiment are exemplarily presented in Fig. 1 for the migration process of water. From similar dependencies, the slopes of the regression lines of the migration time vs. distance were calculated for all studied systems. The reciprocal values of these slopes, which relate to the (distance dependent) liquid migration velocities (Eq. (6)) are shown in Fig. 2 for all solids and liquids studied. In general the migration velocity of a given liquid at any distance is lower on the bare (dry) surface than on the vapour covered (wet) surface. Nonpolar liquids migrate faster in the studied systems than the polar ones. No well defined tendencies in migration velocities due to the addition of the RAMEB were noted, because migration velocities reflect not only changes in surface free energy during the migration but also the radius of the pore in which

a

b
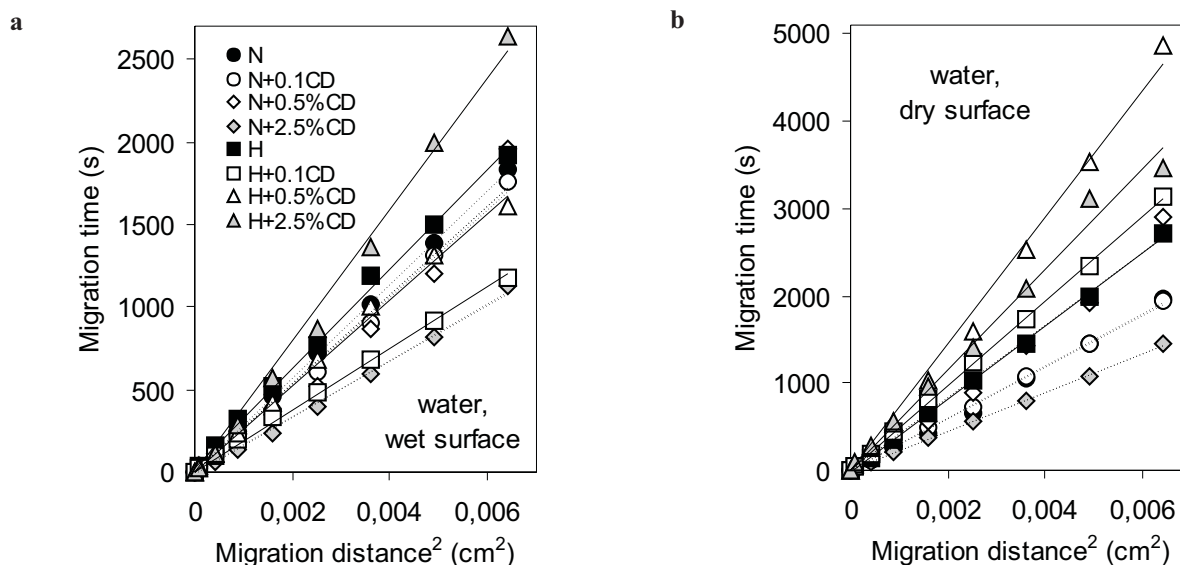
Fig. 1. Dependence of water migration time on the square of the migration distance in a thin column wicking experiment for natural (N) and humic acid enriched (H) soil as dependent on the RAMEB (CD) dose for: a) vapour covered solid (wet surface), and b) bare solid (dry surface).

the liquid moves. However, one can observe that the migration velocities of the studied liquids markedly change with the RAMEB addition and differences between wet and dry material occur. This indicates that the transport of water as well as of liquid organic pollutants in natural soils can be seriously affected by addition of a cyclodextrin and also by wetting-drying periods.

Based on the migration data, solid surface free energies and their components were calculated. Values of these parameters for control samples of the natural and humic acid amended soil are presented in Table 1. This table also includes the calculated values of the effective pore radii (Eq. (6)), the water contact angles (Eq. (1)), and the force of interactions between mineral plates via the water layer (Eq. (11)).

The surface free energy of the studied soil exhibits a high contribution of Lifshitz van deer Waals interactions. The contribution of the acid-base γ^{AB} component is markedly lower due to low contribution of the electron-acceptor (Lewis acid) γ^+ component, despite the fact that electron-donor (Lewis base) γ^- interactions are high. Of course, the presence of the γ^- component seriously affects the interaction of the polar liquids with the studied surfaces. Because the electron-acceptor γ^+ component of the surface free energy is below 1 mJ m^{-2} for all solids studied, the studied surfaces may be considered in practice as monopolar electron donors. A strong preponderance of electron-donicity is a common feature of most natural surfaces (Van Oss, 1994).

It can be seen that the addition of humic acid to the natural soil leads to its slight hydrophobization (increase in water contact angle and decrease of the work of spreading)

and loosening of structure (increase in the average pore radius). The addition of the humic acid to the studied soil, however, causes an increase in the input of the dispersive and acid-base surface free energy components. The contact angle of water on the HA enriched soil is only slightly higher than before humic acid addition. Usually, natural soil organic matter has contact angles around 90°, and its presence makes the soil much more hydrophobic. However, the organic compounds present in the soil extracts may be more polar than soil organic matter as a whole, because most charged and most polar particles are extractable. Therefore the addition of the HA, being an extractable form of soil organic matter, may cause smaller changes in hydrophobic character of the soil as those induced by natural soil organic compounds.

Changes of the parameters characterizing the natural and the HA enriched soil (shown in Table 1) after various RAMEB additions are summarized in Fig. 3. In this figure, the ratio of a given parameter for the RAMEB treated soil to its value for the control soil is presented on the y-axis.

For the natural soil, after addition of the RAMEB the dispersive component of the surface free energy, γ^{LW}, initially increases slightly and decreases after the highest RAMEB addition (Fig. 3a). The initial increase in the dispersive component can indicate that RAMEB nonpolar centres become exposed. The final drop in dispersive Lifshitz van der Waals interactions may be due to a covering of the surface by RAMEB in such way that the hydrophilic parts of the cyclodextrin molecules are exposed, as well as to the reorientation of the organic matter (and added HA)
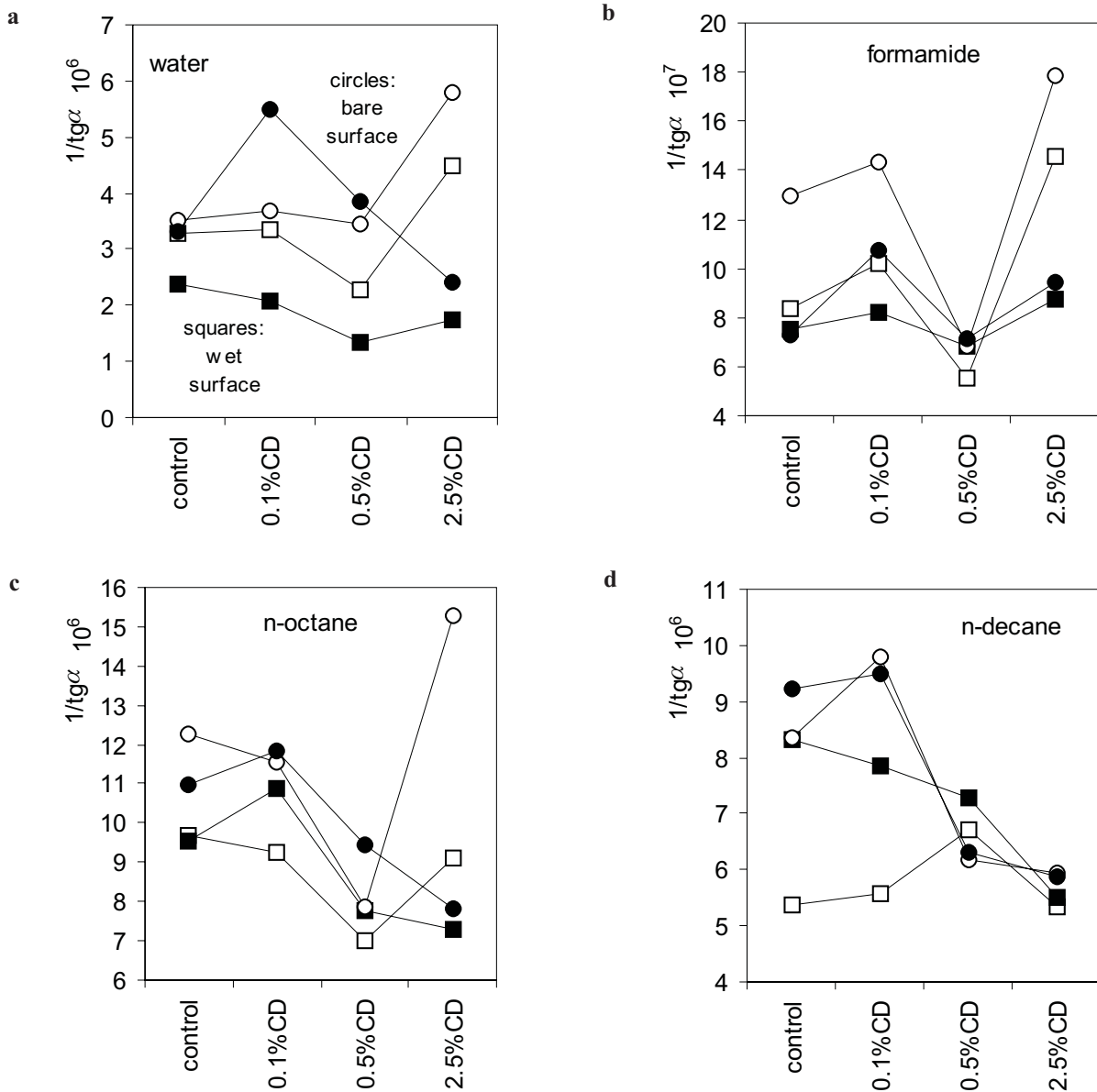
Fig. 2. Distance-dependent migration velocities for the studied liquids: water (a), formamide (b), n-octane (c), and n-decane (d) in a thin column wicking experiment for natural (white points) and humic acid enriched (black points) soil as dependent on the RAMEB (CD) dose and the initial moisture of the sample.

molecules caused by RAMEB. The most hydrophobic chains of the organic molecules can enter into the RAMEB hydrophobic cavity leading to the exposure of their hydrophilic groups and the simultaneous decrease in the overall amount of apolar interactions. For the HA enriched soil smaller changes in the dispersive SFE component are noted.

The electron donor interactions markedly drop with the increase of the RAMEB load (Fig. 3a), which can be due to the RAMEB properties in itself. The γ^- component of the RAMEB may be low as indicated by the low values of γ^-

(around 20 mJ m^{-2}) reported for non-methylated cyclodextrins (Van Oss, 1994).

A high increase in the electron donor component in both soils at the highest RAMEB load could be due to the previously described entering of hydrophobic organic matter chains into RAMEB and the contribution of the exposed polar groups. The contribution of these groups to polar interactions may be more pronounced in the HA enriched soil because the overall amount of organic matter in this soil is high.

T a b l e 1. Effective capillary radius *r,* surface free energy components: Lifshitz van der Waals γ^{LW}, electron-donor γ^-, electron acceptor γ^+ and acid-base γ^{AB}, water contact angle Θ_W, force of interaction between soil particles via water meniscus *F* and work of spreading W_S for natural (N) and humic acid enriched (H) soil

Soil	r (μm)	$\gamma^{LW}*$	γ^-*	γ^+*	γ^{AB}	$\Theta_W(°)$	W_s*	F (mN)
N	0.64	42.4	62.4	0.24	7.8	8.3	-0.76	5.2
H	0.71	44.9	50.3	0.80	12.7	17.6	-3.41	4.2

* values in mJ m^{-2}.
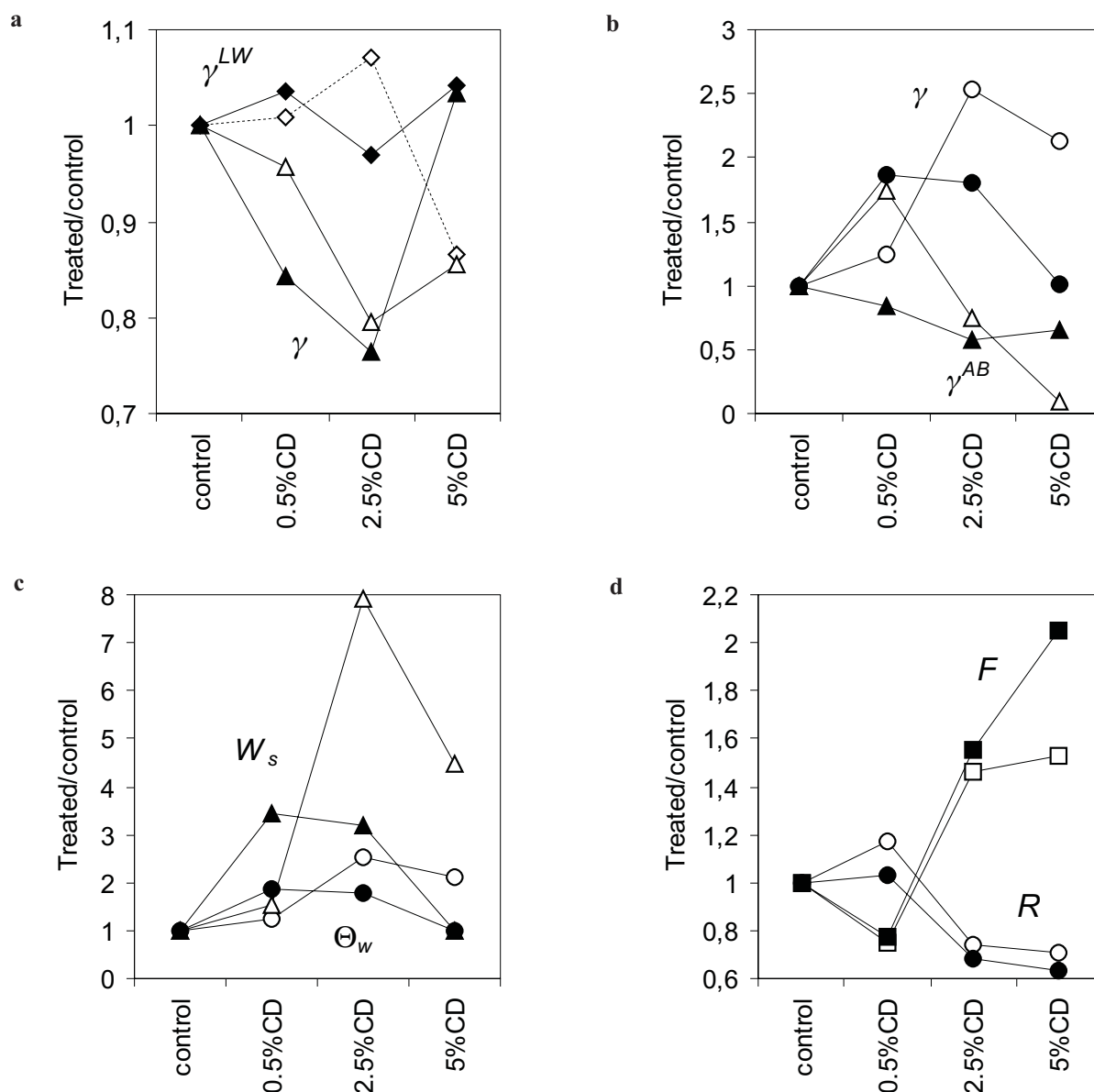
Fig. 3. Changes in: a) dispersive (γ^{LW}) and the electron-donor (γ^-) surface free energy component, b) electron acceptor (γ^+) and acid-base (γ^{AB}) component, c) work of spreading (W_s) and contact angle (Θ_w) of water, d) effective pore radius (R) and the force of interaction of soil particles via water layer (F) for natural (white points) and humic acid enriched (black points) soil as dependent on the RAMEB dose. On the y-axis the ratio of a given parameter for the RAMEB treated soil to its value for the control soil is presented.

The opposite trend to that of the electron donor interactions is observed for the electron acceptor contribution due to a RAMEB concentration increase. The electron acceptor interactions initially increase and decrease at higher RAMEB loads, which is illustrated in Fig. 3b. This figure also shows changes in the overall contribution of the acid-base interactions which generally decrease with the increase of RAMEB content (the exception is the natural soil amended with the lowest RAMEB dose). The decrease in acid-base component indicates that the studied solids become generally less polar.

The behaviour of water in RAMEB enriched soil may be described based on the work of spreading and the contact angle of water on the studied solids. More negative work of spreading and a higher contact angle indicate a smaller adhesion of water to the studied solid, a higher hydrophobicity and therefore less water retention. Figure 3c, showing the above parameters, illustrates that at low RAMEB concentrations both soils become more hydrophobic and return to more hydrophilic at the highest RAMEB concentration.

The addition of the smallest dose of the RAMEB leads to slight loosening of the soil structure as indicated by the rise of the effective pore radius (Fig. 3d). A further rise in the RAMEB load leads to a marked decrease in the pore radius, which may be caused by strong interactions of the RAMEB with the soil solid components leading to the shrinking of soil pores and moving the soil particles closer. The latter phenomenon is a reason that, although interactions of water with the RAMEB enriched soil are weaker, the force attracting soil particles via water layer may be higher (Fig. 3d), which can lead to an increase in soil structure stability.

CONCLUSIONS

Soil wettability by water as well as soil structure and its stability are markedly altered by the cyclodextrin. Complex processes may affect these changes, among which a reorientation of the soil organic matter molecules at the presence of RAMEB as well as the strong interaction of the RAMEB with soil solid phase seem to play an important role. At high RAMEB doses the effect of the RAMEB properties themselves may be increasingly important. The observed phenomena indicate that the water retention and transport processes may be retarded in cyclodextrin bioremediated mineral soils.

To find a more detailed picture of the cyclodextrin effect on soil surface free energy and wettability, more studies are necessary. These should include more cyclodextrin concentrations, a larger concentration range and more soil types.

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