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The contact angle of wetting of the solid phase of soil before and after chemical modification

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Abstract

Wettability of soil affects a wide variety of processes including infiltration, preferential flow and surface runoff. Wettability of surface is usually expressed in terms of contact angle (CA) measurement. If the CA between liquid and solid surface is less than 90°, the surface is called hydrophilic, otherwise the surface is called hydrophobic. If the CA of water droplet on hydrophilic surface is in a range of 0-30° this surface is called superhydrophilic. In case of superhydrophobic surfaces the CA exceeds 150° that means that these surfaces are extremely difficult to wet. CA of wetting of mineral soil particles depends on the overlying organic and iron compounds. The object of study is a sample of the humus-accumulative horizon of typical chernozem (Kursk, Russia) and two samples (horizons A1, B2) of red ferrallitic soils (Fr. Norfolk, NE Oceania). The soil samples were analyzed for organic carbon, forms of non-silicate iron and hydrophobic-hydrophilic composition of humic substances. CA of wetting was determined in the intact samples and after removal of organic matter (H_2O_2 treatment), amorphous and crystallized forms of iron. Static contact angles were determined with the sessile drop method using a digital goniometer (Drop Shape Analysis System, DSA100, Krüss GmbH, Hamburg, Germany). The contact angle was calculated by the Young–Laplace method (fitting of Young–Laplace equation to the drop shape). The measurements were repeated 10-15 times for every sample. Oxidation of organic matter (H_2O_2 treatment) causes an increase in the values of CA of wetting (in chernozem from 9.3 to 28,0-29.5º, in ferrallitic soil from 18.0 – 27.3 to 22.4 – 33.4º). CA remained constant for chernozem and slightly decreased in the case of ferrallitic soil, when the removal of amorphous and crystallized forms of iron was performed on samples pretreated with H_2O_2. CA increase occurs after successive removal of nonsilicate forms of iron from soil samples of chernozem (9.3 – 17,9 – 29.5º) and ferrallitic soils (27.3 – 30.6 – 33,4 and 18.0 – 29.0 – 29.2 º). Relative hydrophobicity of the soil solid phase surface after treatment by Mehra and Jackson (1957) occurs in parallel to the carbon content reduction. Loss of carbon in the samples after the extraction of iron is related to the solubility of the hydrophilic components of humic substances. These results indicate that the main factor, which determines the wettability of soil solid phase, is the organic substance.

Keywords: soil solid phase, contact angle, organic matter, hydrophobic-hydrophilic humic substances, nonsilicate iron forms.

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Introduction

Soil water repellency is a near surface phenomenon that has received much attention in recent years, most notably for its adverse effects on vadose zone processes. Wettability of surface is usually expressed in terms of contact angle (CA) measurement. If the CA between liquid and solid surface is less than 90°, the surface is called hydrophilic, otherwise the surface is called hydrophobic. If the CA of water droplet on hydrophilic

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surface is in a range of 0-30° this surface is called superhydrophilic. In case of superhydrophobic surfaces the CA exceeds 150° that means that these surfaces are extremely difficult to wet. Contact angle, or more specifically, water-air contact angle is an intrinsic property of solid-liquid-gas systems such as soils (Lu and Likos, 2004). Contact angle quantifies the physicochemical interactions at the liquid-solid interface (Letey, 1962). It is important for many physical processes involving the interaction of soil and water (Anderson et al., 1995; Doerr et al., 2000), water infiltration, redistribution, groundwater recharge, solute transport in unsaturated zones, compaction and aeration in variably saturated soils, and temperature-induced water redistribution (Bachmann and Ploeg, 2002; Grant and Salehzadeh, 1996).

In geotechnical engineering, contact angle is essential to the establishment of the SWCC, one of the fundamental concepts in unsaturated soil mechanics (Fredlund et al., 1994). Soil wettability, usually associated with hydrophobicity and water repellency, has been studied mostly in soils of high organic matter content. The variation in soil wettability has frequently been explained by vegetation types, organic matter quality and quantity, influence of mycoflora or other microorganisms and their secretions, soil texture and acidity (Bachmann et al., 2008; Doerr et al., 2000; Feeney et al., 2006; Franco et al., 2000; Goebel et al., 2005; Hubbert et al., 2006; Hurrass and Schaumann, 2006). However, throughout the literature contradictory findings on their correlations with wettability are frequently reported.

Mineral components of the soil (aluminosilicates -kaolin, illite, montmorillonite) and some free oxides such as Al_2O_3, Fe_2O_3 are hydrophilic, because their splitting (cleavage) does not occur with the rupture of ionic bond. The hydrophilicity of minerals, i. e. the affinity with water, increases along with the density of their charges and polar groups, mainly the OH- ones, on the surface. In nature, the surface of one mineral is frequently covered with another by adsorption or adhesion that leads to change of wettability of a surface of an initial mineral (Tschapek, 1984).

The aim of this paper is to analyse the influence of the amphiphilic components of soil HS and forms of free iron oxides in soils on the value of the contact angle determined using sessile drop method.

Material and Methods

The soil investigated in this study was typical chernozem ($A1_2$ horizon, 10 - 20 cm) and ferralitic soil (horizons A1, 0-10 cm and B2 125-145 cm). A typical chernozem from the territory of the Alekhin Central Chernozemic State Biospheric Reserves in Kursk oblast under the virgin herbaceous meadow steppe has been studied. Many data on the properties of this soil type can be found in published literature. In particular, this soil type is characterized by the high (up to 5% on the average) content of organic carbon in the upper 30 cm, the high water stability (up to 65% of water-stable aggregates larger than 0.25 mm), the very high microaggregation (up to 95% of microaggregates larger than 10 μ m), and light clayey texture (Afanasyeva, 1966; Kursk Encyclopedia, 2011; Margolina et al., 1988).

The ferrallitic soil from the subtropical volcanic islands in South-Western Pacific: Norfolk (Australia) - is an old (2-3 million years) island with the main plateau (about 140 m. a.S.L.) and two small mountains (318 m.) formed by black and gray basaltic lavas and tuffs. The soil of Norfolk Island studied under the evergreen litter forests (araucaria, hay-scented ferns, palms) were developed within the red or red-brown (cinnamonic) ferrallitic clays. The chemical and mineralogical composition of this soil testifies about very clear features of profound ferralitization: molecular ratio $Si0_2/Al_20_3$ – 2.0; $Si0_2/R_20_3$ - 1.3; total clay content - 50-90%; predominant minerals in clay and silt fractions are kaolinite, gibbsite and haematite (Targulian and Milanovskiy, 1999; Milanovskiy, 2009).

OC content, Fe and Al extraction. Total C content was measured with a CN analyzer (Vario EL, Elementar, Germany) on (i) bulk samples, (ii) after removal of free iron oxide and (iii) after oxidation of organic matter with H2O2. Inorganic C is not present in any sample, thus the total C analysed corresponds to organic C.

Iron from poorly crystalline oxides and bound to organic matter were extracted from bulk soil samples with 0.2 M NH_4 oxalate (pH 3) according to Schwertmann (1964). Total iron oxides were estimated by the dithionite–citrate–bicarbonate (DCB) method (20). The Fe in the extracts was determined with atomic absorption spectrophotometry (contrAA 300, Analytik Jena AG, Germany).

Ammonium Oxalate and Dithionite-Citrate Extractions was conducted on samples before and after oxidation of organic matter. After removal of the free forms of iron, samples were washed twice with deionized water, dialyzed against water in dialysis tubing (SERVAPOR (SERVA, Electrophoresis, Germany) and dried.

Oxidation of organic matter was performed at room temperature by suspending 1–2 g of soil in 10–20 ml of 50% H_2O_2. After the end of the sometimes intense initial reaction, samples were heated to 40 °C. Fresh H_2O_2 was added daily until frothing was no longer visible. This was usually achieved after 20–40 d. After oxidation the samples were washed twice with deionised water, dried and analyzed for the remaining OC concentration (Eusterhues et al., 2005).

For the sessile drop method, a microscope cover glass slide (2.2 cm×2.2 cm), cleaned with acetone and deionized water, was coated with sample following the procedure described by Wu (2001). For the coating, concentrated samples stock suspensions were first diluted with deionized water to a concentration of about 1–2% wt/vol, and stirred with a magnetic stir bar for several hours. Then, 1.5 µL suspension was placed on the microscope slide, evaporated for two days under laminar air flow, and finally dried in an oven at 105ºC for 12 h. Glass slides were kept horizontal during the drying process.

Static contact angles were determined with the sessile drop method using a digital goniometer (Drop Shape Analysis System, DSA100, Krüss GmbH, Hamburg, Germany). For contact angle measurements, the syringe needle was positioned 0.2 mm from the surface of the clay film, and a drop of the test liquid (2µL) was dispensed at a constant rate of 1.75 µLs-1 . The drop shape was monitored with a digital camera for 20 s, and contact angle, drop diameter, and volume were recorded. After dispensing, the drop shape was monitored with a digital camera for 20 s, and contact angle, drop diameter, and volume were recorded. To determine the contact angle, the drop contour was mathematically described by the Young–Laplace equation using DSA100, and the contact angle was determined as the slope of the contour line at the three-phase contact point. The measurements were repeated 10-15 times for every sample.

Total C content was measured with CN analyzer (Vario EL, Elementar, Germany) in (i) the original samples, (ii) after the removal of free forms of iron and (iii) after the oxidation of organic substances with H_2O_2.

Contact angles were determined on (i) bulk samples, (ii) after oxidation of organic matter with H_2O_2 and (iii) after removal of free iron oxide

Method of Hydrophobic Interaction Chromatography (HIC) was used to separate hydrophobic and hydrophilic components of humic substances (HS). HS was isolated from mineral soil horizons by the solution 0.1M $Na_4P_2O_7$+0.1N NaOH solution at the soil : solution ratio 1:10. The extract of humus substances was purified from mineral impurities by centrifugation (8000 rpm; 20 min) and filtration through a 0.45-µm membrane filter. Humus substances directly extracted from soils were fractioned.

Hydrophobic interaction chromatography was operated on Octyl Sepharose CL-4B (Pharmacia) at low pressure liquid chromatograph BioLogic LP (BioRad, USA). The sample volume was 0.1 ml; the rate of filtration was 1 ml/min; eluate was monitored at 280 nm; a 1 x 10 cm column was used. Elution of HS sorbed on a matrix gel was performed by a gradual attenuation of HS hydrophobic contacts with matrix gel (first with 0.05 M Tris-HCl buffer with a negative concentration gradient of $(NH_4)_2SO_4$, and then with increasing concentrations of Sodium Dodecyl Sulfate (SDS) in buffer. Last fraction was desorbed with 5 mM EDTA+0.2 n. NaOH solution). Features of the method used was described in Milanovskiy (2009). The first two fractions (fractions 1 and 2) eluted from the column in the presence of ammonium sulfate had predominantly hydrophilic properties (we shall name them hydrophilic fractions), and the following fractions (3, 4 and 5) were hydrophobic (Figure 1).

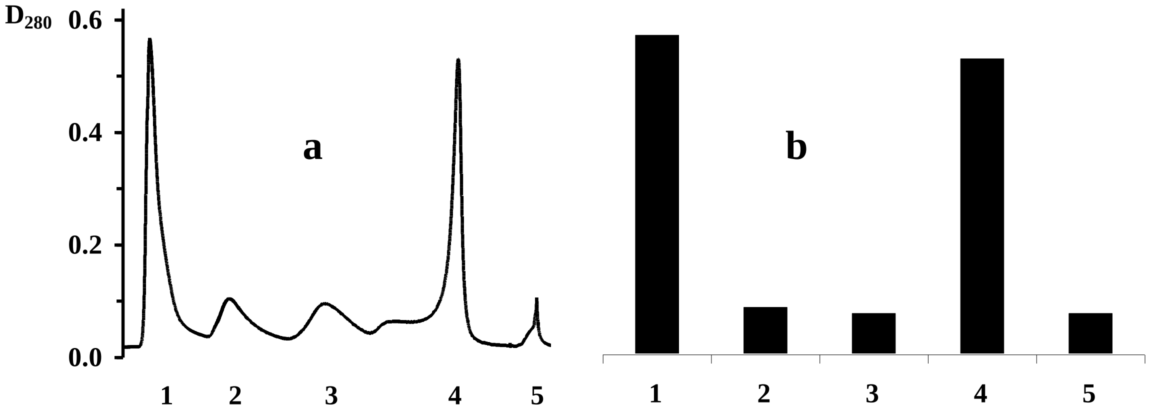

Figure 1. HS fractioning results as a chromatogram (a) and plot (b); 1 - 5 fractions of humus substances

Extraction and chromatographic fractionation of HS were performed on the initial samples, and after the removal of the free forms of iron. The optical density of chromatographic fractions were normalized by the sample weight and carbon content.

Results and Discussion

In soil, the presence of free iron oxide serve as important parameters in understanding its development and they are known to influence soil properties. Their distribution and amount in the soil are known to influence some soil properties such as anion adsorption, surface charges, specific surface area, nutrient transformation, swelling and aggregate formation and pollutant retention in soils (Enya et al., 2011).

Content of OM and Fe, extracted with sodium dithionite sodium citrate, and ammonium oxalate are shown in Table 1. Low content of free iron in the chernozem is caused by temporary reducing conditions in the spring, when there is moisture stagnating. In summer it is replaced by downdrafts, which remove free iron.

Table 1. Selected properties of bulk soils and after oxidation of organic matter (%): organic carbon concentration, Fe_{OX}—oxalate extractable Fe, Fe_{DCB}—dithionite-citrate-bicarbonate extractable Fe

Soils	Depth, (cm)	Bulk soils			After oxidation of OM			Resistant OM
		TOC	OC*/Fe $_{OX}$	OC*/Fe $_{DCB}$	OC	OC/Fe_{OX}	OC/Fe $_{DCB}$	% of TOC
Chernozem	10 - 15	4.03	3.75/0.2	1.79/0.2	0.48	0.45/0.9	0.18/0.2	11.9
Ferrallitic	0 - 10	9.14	8.60/0.7	7.34/11.2	1.43	1.40/1.4	1.12/14.5	15.64
	125 - 145	1.08	0.77/0.6	0.45/9.8	0.19	0.18/1.0	0.17/14.0	17.59

* Organin the sample after Oxalate and Dithionite–Citrate–Bicarbonate extracts

The main processes in ferralitic soil are desilication and iron accumulation. These processes are accompanied by a complete decay of the primary minerals and aluminosilicates of 2:1 type. Simultaneously with mobile soil elements removal, relative accumulation of iron oxides occurs.

The percentages of Fe were extracted by the dithionite citrate bicarbonate method was more than the percentage of Fe extracted by the acid ammonium oxalate method and this observation agrees with(20) that higher percentages of free iron oxides should be extracted by the dithionite citrate bicarbonate method.

Both in chernozem and in ferralitic soil, OM oxidation leads to an increased solubility of free iron.

This fact indicates that Fe is not fully exctractable in the presence of OS and that organic matter is tightly associated with soil Fe. OC content in soil samples after Fe_{OX} and Fe_{DCB} extraction decreases, indicating the SOM components solubility in Oxalate and Dithionite-Citrate-Bicarbonate solutions. This fact is confirmed by the results of the chromatographic fractionation of HS extracted from the original soil and after removal of the free iron (Figure 2 and 3).

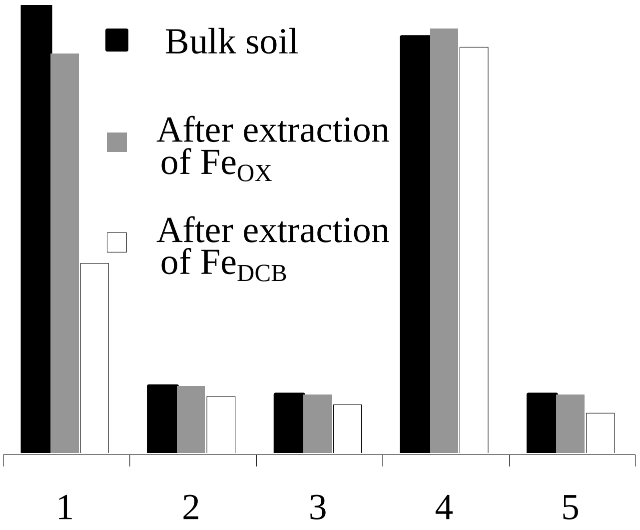

Figure 2. Relation of hydrophilic and hydrophobic components of HS in initial Chernozem and after extraction forms of free iron oxides,1 - 5 fractions of HS

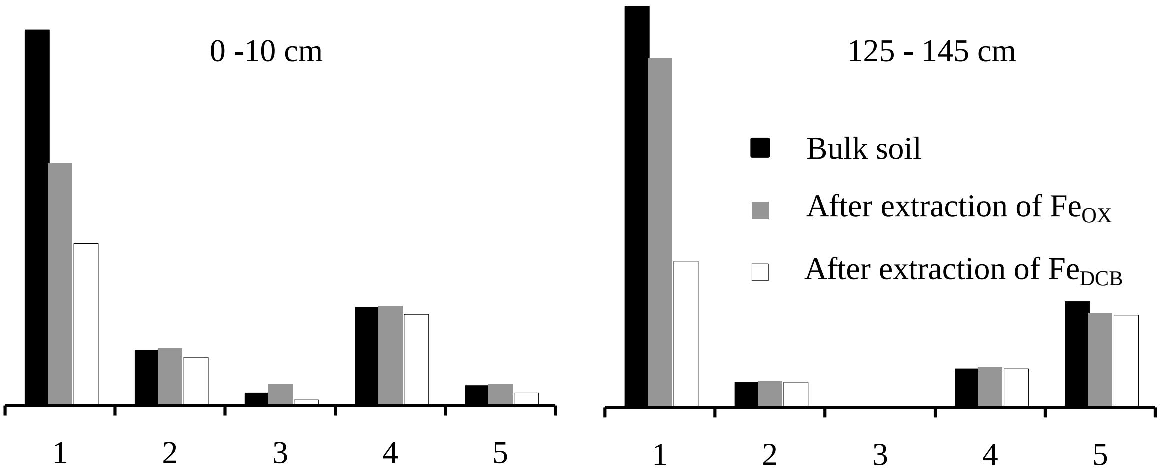

Figure 3. Relation of hydrophilic and hydrophobic components of HS in initial Ferrallitic soil and after extraction forms of free iron oxides,1 - 5 fractions of HS

Regarding contents of chernozem and ferralitic soil HS, removal of Fe_{OX} and Fe_{DCB} is accompanied with a significant decrease in the content of hydrophilic components of HS fraction 1. HS content in other fractions (2-5) stays almost the same. Variations of contact angle as compared to initial soil sample and after chemical exposure are shown in Figure 4.

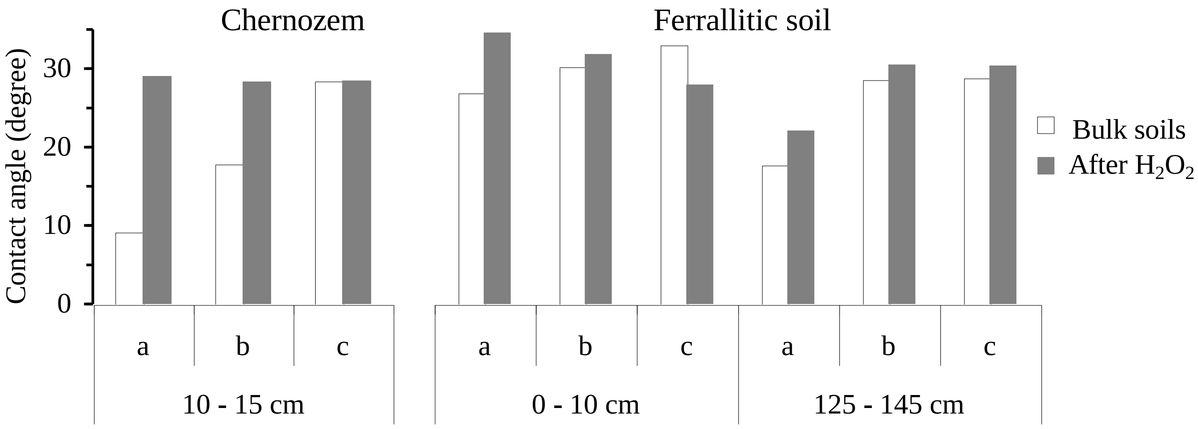

Figure 4. Change of a contact angle after chemical treatment: a - starting soil, b - after extraction of Fe_{OX}, c - after extraction of Fe_{DCB}

Removal of free iron from the initial samples and ferralitic soil causes a clear increase in the contact angle. In chernozem OM oxidation by H_2O_2 causes an increase in the contact angle, and it does not change after the removal of free iron.

In ferralitic soil removal of free iron from the horizon A1 (after H_2O_2) causes a contact angle decrease, whereas for a horizon $B2_2$ it leads to CA increase. Thus, all variants of chemical exposure causes a change in contact angle, but in some cases it is increased, while in others - decreases.

According to Eusterhues et al. (2005) oxidation-resistant organic matter is enriched in aliphatic C and there is a correlation between the oxidation-resistant carbon and total iron oxides (Fe_{DCB}). NMR spectra of H_2O_2-treated samples are best explained by lipids, waxes and other recalcitrant aliphatic biomacromolecules. Such structures are hydrophobic in nature.

On the other hand (Ivesona et al., 2004), CA values are defined by the ratio of goethite (CA ≈ 15-26 º) and hematite (CA ≈ 40-60º) in the sample. CA comparison for samples after OM oxidation indicates that in chernozem (with low FeOX and Fe_{DCB}) the value of CA is determined by hydrophobic oxidation-resistant organic matter. Types of ferriferous minerals of ferralitic soils could be responsible for the corresponding behavior. This type of soil was previously characterized by decreasing along with depth hematite and increasing goethite content (Milanovskiy, 2009).

These factors are responsible for the differences in the observed trends of contact angle variations.

For initial soil samples, the hydrophilicity of the surface increases with an increased charges density; in the case of uncharged surfaces, it increases with the density of polar groups such as -OH, -COOH, -NH_2, and decreases with the density of nonpolar groups such as -CH_3, =CH_2, -CH_3, etc. (Tschapek, 1984).

Liquid chromatography of hydrophobic interaction physically allows dividing a set of humus substances in extract on hydrophilic and hydrophobic components different in ability to enter in hydrophobic interactions with a gel matrix. Hydrophilic components of humus substances (1 - 2 fractions) are submitted in soils by indigenous (in structure of humification products in situ) and allochtonousy illuvial (lateral) forms. Hydrophilic products of humification contribute to modern metamorphism of soil mineral weight. Accumulation of hydrophilic HS occurs in structure of compounds of clay and humus as well as Fe and Al-humus substances. Hydrophilic HS are the most labile components of soil humus subjected to a microbiological and chemical mineralization.

Hydrophobic components of soil humus substances (3 - 5 fractions) are indigenous formations spatially dated for humification products of organic material in situ. Irrespective of type of a soil water mode, they are motionless in a structure, being collected on the place of fossil humification.

Chernozem with non-washing (periodically washing) type of a water mode and mainly intra-structure receipt of fossils as the basic source of humus substances, is characterized by prevalence of hydrophobic components in humus substances (fraction 4, figure 2). Formation and accumulation of hydrophobic humification products occurs in the structure of organic particles, which are not connected with a mineralogical matrix. Accumulation of hydrophilic humification products occurs in structure of compounds of clay and humus (fraction 1, figure2).

Ferralitic soils with washing type of water mode and mainly ground receipt of fossils as source of HS are characterized by prevalence of hydrophilic components in structure of humus substances. Hydrophilic humification products support acid hydrolysis of a silicate material, redistribution of Al and Fe through the soil structure of humid subtropical climate and form organic-mineral compounds

Visible CA increase after successive removal of nonsilicate forms of iron from soil samples of chernozem and ferrallitic soil is most likely caused by the selective dissolution of the most hydrophilic HS components localized on the mineral surface.

Thus, the surface hydrophobicity of samples may be caused both by the remaining hydrophobic HS components and by new surface properties of the mineral particles after the removal of the hydrophilic HS. These results indicate that the main factor, which determines the wettability of soil solid phase, is the organic matter.

Conclusion

Wettability of soil affects a wide variety of processes including infiltration, preferential flow and surface runoff. Determination of the wettability of a surface composed of soils and how it depends separately on the roughness and the surface chemistry presents significant challenges. Our study demonstrates that chemical treatment of soil solid phase surface causes the variation of its wettability. CA increase after OM oxidation is caused by hydrophobic properties of oxidation-resistant organic matter. HS fractioning by HIC method allowed to determine that the acid ammonium oxalate and dithionite citrate bicarbonate solutions selectively dissolve hydrophilic HS components as well as free iron oxide. The wettability of a soil solid phase surface after removal of the hydrophilic organic-mineral compounds decreases. These results indicate that the main factor, determining the wettability of soil solid phase, is the organic matter, namely oxidation-resistant organic matter and hydrophilic and hydrophobic HS components.

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