Estimation of surface properties of Kostroma region soils formed on the Triassic clay deposits

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Abstract. The main indicators characterizing the surface properties of soils formed on the eluvium of Triassic clays of the Kostroma region have been studied. The categories of specific surface area and the degree of soil hydrophilicity have been calculated. Levels of sorption capacity and parameters of ultraporosity of the solid phase of the investigated soils have been identified.

1. Introduction

Generalized concepts and definitions used in genetic soil science often do not carry some information about the soil as a physical body, within which the processes of transfer of substances and energy occur. Surface phenomena can be basis for fine diagnostics processes, occurring in the soils. The study of the geometry, the energy state together with properties of interfacial surfaces, the composition of soil solutions, as well as chemical compounds introduced into the soil, enable to build real models of soil aggregates and to associate surface phenomena with the basic macroscopic properties of soils, to find ways to improve and optimize them. The study of surface phenomena in soil actually is the study of processes and properties of soil and their management at the molecular level.

2. Characteristic of surface phenomena in soils

One of the main physical characteristics of the surface of the soils’ solid phase is the specific surface area of the soil, calculated by BET and Farrer methods [1]. However, values of total, external and internal specific surface area are not always sufficient to describe the physical and chemical processes occurring in soils. A very important characteristic of the surface of the solid phase of soils is its hydrophilicity. To assess the quality of the soil surface, its hydrophilicity it is necessary to know the quantitative characteristics of the phenomenon of soil wettability – the value of the contact angle.

Modern methods of determining the contact angle do not always allow a comparative evaluation of the obtained data because of the complexity of the object of study and the features of preparation of sample for analysis. In our work we propose to consider another approach to the quantitative assessment of the phenomenon of soil wettability. It is based on a thermodynamic assessment of the state of water in the moment of formation of the first layer of wetting liquid. From the Young equation the cosine of the contact angle can be obtained as the difference of values of surface tensions at the solid–gas and solid–liquid interfaces.

$$\gamma_{s-g} - \gamma_{s-l} = \gamma_{l-g} \cdot \cos \alpha$$  \hspace{1cm} (1)
Simultaneously $\cos \alpha$ can be obtained from isotherms of water vapor sorption. For drop, lying on a horizontal smooth surface, the area of wetted surface $dS_{\text{solid-liquid}}$ can be a variable value. Increasing of the liquid-solid contact area by the amount $dS$ leads to decreasing of the solid-gas contact area by the same value. Thus,

$$dS_{s-g} = dS_{s-g}$$  \hspace{1cm} (2)

In this way the surface of liquid – gas contact will increase by the value of $dS_{l-g}$. The surface free energy of the system at the equilibrium state can be described as follows:

$$dG_{\text{surf}} = \gamma_{l-g} \cdot dS_{l-g} + \gamma_{s-l} \cdot dS_{s-l} - \gamma_{s-g} \cdot dS_{s-g} = 0$$  \hspace{1cm} (3)

From equation 3 it follows

$$\gamma_{s-g} - \gamma_{s-l} = \frac{dS_{l-g}}{dS_{s-l}} = \cos \alpha$$  \hspace{1cm} (4)

Assuming that $dS_{s-g} = S_s$, i.e. is proportional to the value of the water monolayer – $W_m$ according to BET. $dS_{l-g} = S_s$ ($dS$ liquid–gas=$S_s$) and is proportional to $(W_m)$, – the value of the water monolayer according to Farrer. In this way the equation (4) can be written like

$$\frac{(W_m)}{W_m} = \cos \alpha$$  \hspace{1cm} (5)

For a more precise assessment of the surface quality it is desirable to have an idea about the character of ultraporosity soils.

Various adsorptents can be divided into a number of basic structural types [2].

Each of these types of adsorptents according to Kiselev is characterized by its own vapor sorption isotherm and by its’ own distribution of the pores’ volume by the effective radius. Therefore, it is possible to assess the structural features of the adsorbent surface by sorption isotherms.

Isotherms of studied soils can be considered across classification Kiselev after the analysis of the curves of distribution of volumes of ultraporosity on effective radiuses.

The thermodynamics of volume absorption of vaporous moisture is most fully described in [3].

Since the volume of sorbed water ($W$) is a function of the mean radius of the capillary ($r$), the ultraporosity can be represented as a curve, obtained by differentiating the experimentally determined sorption isotherm by $r$, i.e:

$$\frac{dW}{dr} = f(r)$$  \hspace{1cm} (6)

The size of the radius $r$ is determined from the Thomson equation.

$$\ln \left( \frac{P}{P_0} \right) = \frac{2M \sigma}{\rho RT}$$  \hspace{1cm} (7)

From equation 8 we can express the radius of the capillary $r$:

$$r = \frac{2M \sigma}{\rho RT \cdot \ln \left( \frac{P}{P_0} \right)} = \frac{2V \sigma}{RT \cdot \ln \left( \frac{P}{P_0} \right)}$$  \hspace{1cm} (8)

where $P$ is the vapor pressure over the concave meniscus; $P_0$ is the saturated vapor pressure over a flat surface; $T$ is the absolute temperature; $R$ is universal gas constant; $\sigma$ is the surface tension; $V$ is the molecular volume of the liquid ($V=M/Q$), where $M$ is the molecular weight of the liquid, $Q$ is its density where $P$ is the vapor pressure over the concave meniscus; $P_0$ is the saturated vapor pressure over a flat surface; $T$ is the absolute temperature; $R$ is the universal gas constant; $\sigma$ is the surface tension; $V$ is the...
molecular volume of the liquid ($V = M/\rho$, where $M$ is the molecular weight of the liquid, $\rho$ is its density).

The aim of this work is to give quantitative and qualitative characteristics of surface properties of soils of the Kostroma region formed on clay deposits of Triassic.

3. **Objects and methods**

The objects of study – soils of slopes of the Northern Ridges, formed on the Triassic clays – the Mollic Gleyic Umbrisols Loamic and Mollic Gleyic Umbrisols Aric Loamic. Water vapor desorption isotherms of studied soils were determined by the sorption equilibrium method (relative pressure of water vapor 0.15; 0.32; 0.55; 0.86; 0.98). The total specific surface area was calculated by the BET method, the external specific surface area – by Farrer method [1]. The content of carbon was determined by coulometric titration on an-7529 Express analyzer. Particle size distribution was measured by laser diffraction method.

4. **Results and discussion**

All studied soils had a clayey texture, which was inherited from parent rocks – eluvium of Triassic clays. The Mollic Gleyic Umbrisols Loamic in comparison with two other soils had the most clayey texture with the increasing of the content of clayey particles down the profile from 50.14% in the upper humus layer to 67.42% in the gleyic lower horizon. Mollic Gleyic Umbrisols Aric Loamic (1) gleyed layer at a depth of 70-90 cm had more heavy composition, the content of physical clay reached 65.33%. The lightest composition from the considered soils had Mollic Gleyic Umbrisols Aric Loamic (2), where the content of physical clay did not exceed 55.62%.

The studied soils were significantly differentiated by the content of organic carbon. The maximum content of the organic matter was noted in the upper horizon of Mollic Gleyic Umbrisols Loamic – 17.7%. This organogenic horizon was differed in all parameters of the solid phase, including surface properties.

Granulometric composition and organic carbon content largely determine the surface properties of soils, first of all – the sorption capacity [3, 4]. Figures 1A and 1B show desorption isotherms for two types of soils.

![Figure 1](image-url)

**Figure 1.** Water vapor desorption isotherms: a – Mollic Gleyic Umbrisols Loamic; b – Mollic Gleyic Umbrisols Aric Loamic.

The shape of water vapor desorption isotherms of almost all soils samples have indicated the transition type of ultraprosity from non-porous to mixed, inhomogeneous-porous. And only the desorption isotherm of the horizon Ah of Mollic Gleyic Umbrisols Loamic (Figure 1A) have indicated
pure mixed type of ultraprosity. According to the concept of A.V. Kiselev, this fact gave us the opportunity to determine the total specific surface area of the soil by BET [1].

Character and features of ultraporosity of the studied soils is illustrated in figures 2A and 2B. The organogenic horizon Ah of Mollic Gleyic Umbrisols Loamic have differed from others. The volume of sorbed water \( (dw/dr) \) in the thinnest pores (1-2 micron) here was the maximal and exceeds 100 units. In the mineral horizons of these soils ultraporosity is significantly reduced (Figure 2A). Ultraporosity of Mollic Gleyic Umbrisols Aric Loamic was fundamentally different. The maximum value of sorbed water in the finest pores was presented in gley horizon Cg, and the minimum value – in the arable horizon AP (Figure 2B).

Figure 2. Ultraporosity of soil: A – Mollic Gleyic Umbrisols Loamic; B – Mollic Gleyic Umbrisols Aric Loamic.

A similar approach to the evaluation of ultraporosity was used in the Wright and Fawty work [5]. Energy and geometric heterogeneity of soil surface is characterized by the value of the specific surface. Studied soils were largely differentiated by this indicator. On the one hand it is explained by their clayey parent material, as well as the imposition of soil-forming processes, associated with both humus-formation and the severity of the gley processes, that is, the degree of their hydromorphism, on the other hand. The absolute maximum value of the total specific surface area was in the upper organogenic horizon of Mollic Gleyic Umbrisols Loamic. In mineral horizons of the studied soils, the total specific surface area varies from 89 to 227 m\(^2\)/g, with the highest values noted in the gleyed horizons (table1).

Table 1. Characteristics of the surface of the studied soils.

| Soil                  | Horizon, depth, cm | Full specific surface, m\(^2\)/g | External specific surface, m\(^2\)/g | Cos \(\phi\) | Contact angle \(\phi\), degree |
|-----------------------|--------------------|----------------------------------|-------------------------------------|-------------|------------------------------|
| Mollic Gleyic Umbrisols Loamic | Ah 10-25           | 298                              | 88                                  | 0.30        | 73                           |
|                       | C 50-70            | 161                              | 61                                  | 0.38        | 67                           |
|                       | Cg 70-110          | 178                              | 74                                  | 0.42        | 65                           |
| Mollic Gleyic Umbrisols Aric Loamic (1) | AP 20-25          | 113                              | 62                                  | 0.61        | 52                           |
|                       | C 50-60            | 89                               | 61                                  | 0.69        | 46                           |
|                       | Cg 80-90           | 130                              | 68                                  | 0.52        | 59                           |
| Mollic Gleyic Umbrisols Aric Loamic (2) | AP 15-20          | 152                              | 83                                  | 0.54        | 57                           |
|                       | C 40-50            | 181                              | 54                                  | 0.29        | 73                           |
|                       | Cg 70-80           | 227                              | 74                                  | 0.33        | 71                           |
Genetic features of the studied soils were also reflected in the surface quality indicators – on the values of the contact angle. The investigated Mollic Gleyic Umbrisols Loamic soils were characterized by high values of contact angle, which have varied from 73° to 65° with the maximum in the upper humus-accumulative horizon, and down the profile was gradually decreased. In Mollic Gleyic Umbrisols Aric Loamic the contact angle was changed from 52° to 71° and was the minimal in the upper humus horizon, and gradually increase down the profile.

5. Conclusions
The upper organogenic horizon of Mollic Gleyic Umbrisols Loamic soil was characterized by the highest value of the total specific surface area (S total = 298 m²/g). In mineral horizons of the studied soils the value of the total specific surface area varied from 89 to 227 m²/g, with the highest values in the gley horizons. Differences in sorption capacity in the genetic horizons of the studied soils can be related with the content of organic matter and with the processes of hydromorphism.

The shape of water vapor desorption isotherms of almost all soils samples indicated the transition type of ultraprosity from non-porous to mixed, inhomogeneous-porous. And only the desorption isotherm of the horizon Ah of Mollic Gleyic Umbrisols Loamic (Figure 1A) have indicated pure mixed type of ultraprosity.

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Hydrophobicity of the studied soils have in creased as the result of humus formation and hydromorphism processes.

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