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Soil profile distribution of water repellency and relationships with properties and characteristics of Technosols from open-cast mining

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Abstract

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The present paper presents a study of soil water repellency in Technosols, formed on spoils with Pliocene clays after open-cast mining in the area of Maritsa-Iztok Mines, Bulgaria. At present, different soil properties and characteristics have been studied in areas of the mine spoils from Obruchishte village to establish their relationships with soil hydrophobicity and its spatial distribution in the surface and subsurface soil layers. To obtain complete information, the present study characterizes soil water repellency in vertical direction by assessing the similarity and differences in its appearance in depth of the soil profile. The effect of laboratory heating on hydrophobicity in the individual soil layers has been assessed. Extreme water repellency (water drop penetration time (WDPT) 10160 – 13391 s) is found in the 10–80 cm depth of the soil profile, which decreases abruptly after laboratory heating of the soil samples. Extreme acidity pH and high carbon content are reported. Assumptions for the presence of impurities of coal particles in the substrates were checked. Humic organic carbon correlates positively with water drop penetration time ($R_{WDPT\text{-}HOC}$ = 0.440*), which confirms its determination so far, as one of the main factors influencing the soil water repellency in the studied technogenic soil profile. A significant correlation between residual fraction of soil organic matter and clay (< 0.001 mm) in soil layers ($R_{clay\text{-}C\ res.}$ = 0.579**), as well as regarding cation exchange capacity ($R_{CEC\text{-}C\ res.}$ = 0.433*) was found.

Keywords: Technosols; soil profile; soil water repellency; water drop penetration time; soil organic matter
Abbreviations: SWR – soil water repellency; WR – water repellency; WDPT – water drop penetration time; SOM – soil organic matter; HOC – humic organic carbon; FOC – fulvic organic carbon; CEC – cation exchange capacity; SE – standard error

Introduction

Soil water repellency (SWR) is a topic whose research is growing and attracting great scientific interest (DeBano, 2000). Despite the availability of research on this issue, the cause of hydrophobicity in soil sometimes remains unclear (Hurraß & Schaumann, 2006). Recently, some of the factors influencing SWR have become more apparent, regardless of its still not wide recognition (Jordán et al., 2013). Soils with similar properties can be found not only in natural but also in arable land (DeBano, 1981). Therefore, a number of scientists have carried out a variety of studies on SWR related to the effect of fires (Zavala et al., 2009; Bodí et al., 2013; Jiménez-Pinilla et al., 2016; etc.), changes in forest species (Wahl et al., 2003), impacts on crop development (Li et al., 2019), effects of fertilization with manure (Jiménez-de-

Santiago et al., 2019), etc. Various plant species and factors, such as organic matter and acidity, are also subject of studies for establishment of relationships with SWR (Martínez-Zavala & Jordán-López, 2009). In this respect, Technosols are not isolated in terms of appearance of SWR to a certain extent. Since the information on these issues is still insufficient, a series of studies have been carried out in recent years (Atanassova et al., 2018a, b; Nedyalkova et al., 2018a, b; Simeonova et al., 2018; Ivanov et al., 2019). Peculiarity of these studies of Technosols is the discussion of data on SWR covering its horizontal direction by studies on surface and subsurface layers of the areas. Obtaining of further information on the occurrence of hydrophobicity in these soils can be accomplished through its in-depth evaluation of the soil profile.

Present paper aims at assessing the vertical distribution of SWR in Technosols formed on open-cast mine spoils and evaluating its interrelations with some physical, chemical and physicochemical soil characteristics.

Material and Methods

The study site is a mine spoil built up with geological materials from open-cast coal mining in the region of Obruchishte village, Maritsa-Iztok Mines, Bulgaria. The spoil is reclaimed with coal ash and has tussock grass vegetation. The geographical location of the mine soil profile is 42.14416 N, 25.95357 E. At this stage, the mine spoil has been studied for different soil properties and characteristics, including soil water repellency (SWR) (Atanassova et al., 2018a,b; Nedyalkova et al., 2018a,b; Simeonova et al., 2018). In these studies, soil samples from the surface (0–5 cm, 0–10 cm) and subsurface (10–20 cm) layers were collected for laboratory analyses from two test plots (each ~ 40 m^2) in a pine site with *Pinus nigra* and other non-vegetated site. The sampling was done in grids (Δ 2 m). Preparation of the surface and subsurface samples for the laboratory analyses and their implementation were realized using the specific methods for each study. In this way, the spatial distribution of water repellency (WR) in the surface of studied areas was established and its possible interactions with some soil properties and characteristics were presented. A special feature of these studies is that they present data on soil hydrophobicity without laboratory heating of soil samples.

Recently, an assessment of WR of the test plots has been carried out by comparing soil samples from the grids at different annual seasons, different vegetation and different soil depths (surface and subsurface layers) before and after controlled heating (Ivanov et al., 2019).

For the purpose of the present study, additional samples from the soil profile were collected to a depth of 100 cm. Samples were taken from profile layers at 10 cm at the end of July 2017. Their preparation for determining SWR was carried out identically with the samples from the surface and subsurface layers of the sites by drying of soil at room temperature and sieving to a fraction of 2 mm. The WR measurement was carried out by the water drop penetration time (WDPT) test (Dekker & Ritsema, 1996; Doerr et al., 2002) with three water drops of distilled water with a volume of 80 µl. Two measurements of WDPT were carried out, immediately after the soil samples were dried at room temperature and after subsequent heating of the samples in an incubator (NUVE EN500) at temperature of 65°C for 24 hours. WDPT tests before and after heating of soil samples were carried out at temperature 25 ± 1°C and humidity 75 ± 5%. Following heating analysis, soil samples were grouped according to the WDPT in a five-class scale: 1 – wettable or non-water repellent (< 5 s); 2 – slightly (5 – 60 s); 3 – strongly (60 – 600 s); 4 – severely (600 – 3600 s); 5 – extremely water repellent (> 3600 s) (Dekker & Ritsema, 1996). For all soil samples, medians of WDPT were determined, on which the discussions in the present study were based.

The data for carbon content and fractional composition of soil organic matter (SOM) were obtained by the method of Kononova-Belchikova (Kononova, 1963), modified by Filcheva & Tsadilas (2002). pH was measured potentiometrically. Cation exchange capacity was determined by the method of Ganev & Arsova (1980). The textural composition of the soil profile layers was obtained by the method of Kachinski (1965). All correlations of SWR with studied soil properties are presented through the medians of WDPT test, before heating of the soil samples. Correlations were assessed by using SPSS 21 for MS Windows.

Results and Discussion

The researched mine spoil contains heterogeneous mixture of yellow-green Pliocene clays intermixed with black clays in 1970s of 20th century (Atanassova et al., 2018a, b; Nedyalkova et al., 2018a; Simeonova et al., 2018; Ivanov et al., 2019). These are the main geological materials in the stratigraphic strata above the coal seams in Maritsa-Iztok coal basin (Garbuchev et al., 1975). Because the mine spoil is a result of man's industrial activity (open-cast coal mining), the studied reclaimed soil is classified as *Spolic Technosol (Dystric, Hyperhumic, Loamic, Tephric, Pantotransportic)* according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014). The Technosol has the following morphological characteristics of the individual layers at a depth of 100 cm from the soil surface:

0–10 cm	Colour of 7,5 YR 4/2 (dry) and 7,5 YR 3/2 (moist), structureless single grains, not porous, many coal particles of 10 YR 3/2;
10–20 cm	Colour of 5 YR 3/3 (dry) and 5 YR 3/2 (moist), structure subangular blocky fine 5–10 mm diameter firm moderately developed, many large coal particles of 5 YR 2/2;
20–30 cm	Colour of 10 YR 3/3 (dry) and 10 YR 3/2 (moist), structure subangular blocky very fine < 5 mm very friable and fine 5-10 mm diameter firm moderately developed, few coal particles of 5 YR 2/2;
30–40 cm	Colour of 7,5 YR 3/2 (dry) and 10 YR 3/2 (moist), structure subangular blocky very fine < 5 mm very friable weakly developed, few coal particles of 5 YR 2/2;
40–50 cm	Colour of 5 YR 2/2 (dry) and 5 YR 1/2 (moist), structure subangular blocky fine 5–10 mm firm moderately developed;
50–60 cm	Colour of 7,5 YR 3/2 (dry) and 10 YR 3/2 (moist), structure subangular blocky very fine < 5 mm very friable weakly developed and few peds of fine 5-10 mm weakly developed;
60–70 cm	Colour of 5 YR 2/2 (dry) and 5 YR 1/2 (moist), structure subangular blocky medium 10–20 mm firm moderately developed;
70–80 cm	Colour of 5 YR 2/2 (dry) and 5 YR 1/2 (moist), structure subangular blocky medium 10–20 mm firm moderately developed;
80–90 cm	Colour of 5 YR 2/2 (dry) and 10 YR 1/2 (moist), structure subangular blocky coarse 20–50 mm firm moderately developed;
90–100 cm	Black clays of colour 10 YR 2/1, structureless massive.

The overall view of data on WDPT measurements after drying of soil samples at room temperature shows relative similarities in most parts of the soil profile. The soil layers with prevailing extreme WR and WDPT over 3 hours predominate (Figure 1a). An exception is the surface 0 – 10 cm layer, where WR is significantly weaker (470 s). Nevertheless, this layer is still classified as strongly water repellent (class 3) according to the used scale (Dekker & Ritsema, 1996) (Figure 2a). The differentiation of the soil profile is also emphasized in its deepest part, where in the 80 – 90 cm layer WDPT slightly above 40 minutes is measured, which reaches its minimum in 90 – 100 cm depth (Figure 1a). Compared to the horizontal test grids, the established median for WDPT in the surface layer of the profile is close to the one at the non-vegetated site studied in spring (Ivanov et al., 2019).

After the laboratory heating of soil samples, the WDPT sharply decreases in all layers of the profile with a range of 5 seconds to 2 minutes (Figure 1b). These variations divide most of the samples into class 2 (slightly water repellent), according to the scale of Dekker & Ritsema (1996), but there are layers in class 3 (strongly water repellent), which changes the WR ratio in soil profile (Figure 2a, b). Here we will note that the deepest soil layer again has the shortest measured WDPT, which makes it wettable (Figure 1b). Compared to the horizontal test grids, the surface layer of the profile is characterized by almost equal WDPTs with one sample from non-vegetated site studied in summer (18 s). There is also close value of WDPT with another soil sample from the pine-vegetated site (10 s) from the same season (Ivanov et al., 2019).

The total carbon content also fluctuates widely. Despite its high values, no significant accumulation of organic matter is found in the surface of the soil profile (Table 1). Atanassova et al. (2018a, b) assume that such amounts of

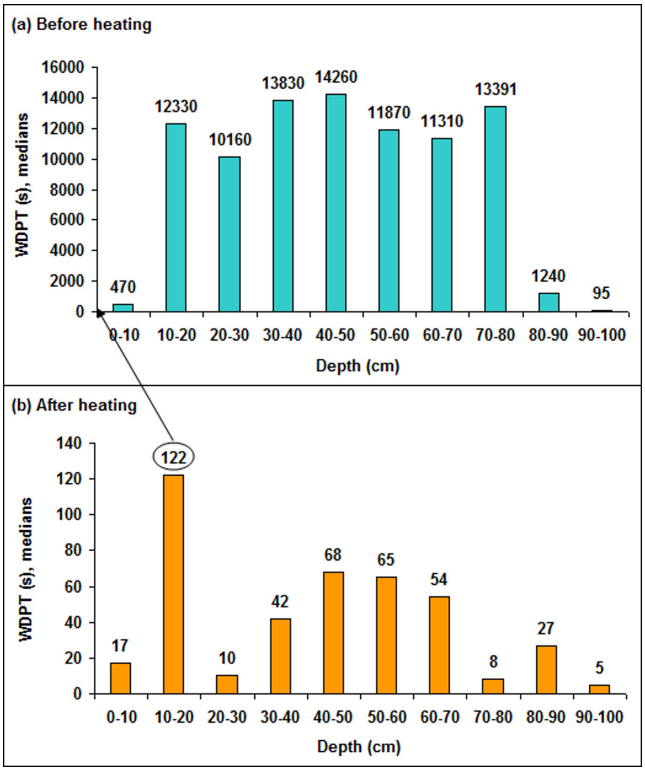

Fig. 1. Water drop penetration time in the soil profile layers (medians)

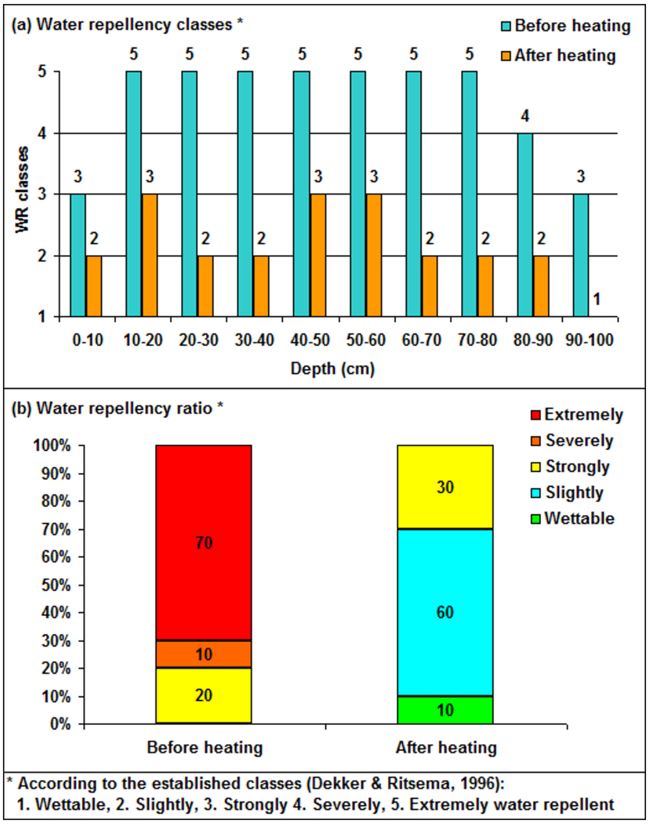

Fig. 2. Classes and ratio distribution of water repellency in the soil profile

carbon are result of the presence of coal particles and coal and ash dust in geological materials indiscriminately introduced during the deposition of spoils in the opencast mining of the 1970s of the last century. These impurities affect the total amount of carbon in Technosols (Hristova, 2013) and in some cases may influence locally the content and type of humus in the surface horizon of natural soils (Hristov et al., 2013). However, in an early study of areas from mine spoil Iztok in Maritsa-Iztok Mines, with forest biological reclamation and different rates of fertilization, Zheleva & Bozhinova (2011) did not find coal particles and present accumulative distribution of humus only in the surface 5 – 7 cm layers. We found positive correlation between the total carbon content and residual fraction of SOM ($R_{C\ total-\ C\ res.}$ = 0.940***) and less with the extracted one ($R_{C\ total-\ C\ ext.}$ = 0.638**). Positive and significant is also the correlation between extracted fraction of SOM and cation exchange capacity (CEC) ($R_{C\ ext.\ -\ CEC}$ = 0.538*) (Table 2).

The state of SOM fractions (humic organic carbon (HOC) and fulvic organic carbon (FOC) shows varying tendencies in their quantity along the depth of the soil profile with random values between soil layers (Figure 3a). Their ratio (C_{HOC}/C_{FOC}) determines the humic to fulvic-humic type of organic matter according to the classification of Grishina and Orlov for soil humus status (Orlov, 1985) (Table 1). HOC predominate over FOC throughout the profile but in uncomplexed state. Similar is the HOC fraction in non-humus reclaimed mine spoil from the region of mine Chukurovo, which makes it highly mobile and bound with sesquioxides

Table 1. Content and composition of soil organic matter in the studied Technosol (% in soil)

Depth, cm	Total carbon, (C_{total}) %	Organic carbon, extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH, %			C_h/C_f	Residual organic Carbon, ($C_{res.}$), %	Extracted carbon with 0,1N H_2SO_4, %	Optical characteristics (E_4/E_6)	
		$C_{ext.}$	HOC	FOC				Total HOC	Free HOC
0–10	7.38	4.80	2.67	2.13	1.25	2.58	0.16	6.11	6.58
10–20	11.07	7.79	5.19	2.60	1.99	3.28	0.17	7.27	7.02
20–30	5.35	3.48	2.39	1.09	2.19	1.87	0.18	6.57	5.87
30–40	7.10	5.20	3.20	2.00	1.60	1.90	0.16	6.93	6.50
40–50	11.53	5.60	3.86	1.74	2.22	5.93	0.16	6.96	6.16
50–60	9.41	5.68	3.99	1.69	2.36	3.73	0.17	7.33	6.71
60–70	13.38	6.92	5.33	1.59	3.35	6.46	0.18	8.08	7.11
70–80	13.60	6.08	5.33	0.75	7.10	7.52	0.19	7.66	7.57
80–90	16.00	6.40	4.26	2.14	1.99	9.60	0.19	7.41	7.19
90–100	12.46	4.68	2.79	1.89	1.48	7.78	0.16	6.54	5.76
Average	9.92	5.66	3.90	1.76	1.37	5.07	0.17	6.33	6.17

Table 2. Correlation matrix between the measured parameters

		WDPT	SAND	CLAY	CEC	C_{total}	C_{ext}	C_{res}	HOC	FOC
Correlation	WDPT	1.000	.052	-.246	-.347	-.179	.267	-.338	.440*	-.318
	SAND	.052	1.000	-.938***	-.096	-.366	.202	-.537**	.097	.268
	CLAY	-.246	-.938***	1.000	.293	.410	-.176	.579**	-.109	-.180
	CEC	-.347	-.096	.293	1.000	.549**	.538**	.433*	.410	.386
	C_{total}	-.179	-.366	.410	.549**	1.000	.638**	.940***	.677**	.046
	C_{ext}	.267	.202	-.176	.538**	.638**	1.000	.335	.906***	.408*
	$C_{res.}$	-.338	-.537**	.579**	.433*	.940***	.335	1.000	.426*	-.125
	HOC	.440*	.097	-.109	.410	.677**	.906***	.426*	1.000	-.017
	FOC	-.318	.268	-.180	.386	.046	.408*	-.125	-.017	1.000

* $p \leq 0.05$; ** $p \leq 0.01$; *** $p \leq 0.001$

R_2O_3 (Hristova, 2013). In our case, the free HOC correlate positively with the WDPT ($R_{WDPT\text{-}HOC}$ = 0.440*), similarly to surface soil samples from other experimental sites (Atanassova et al., 2018a). Higher is the correlation of HOC in the soil profile regarding extracted form of SOM ($R_{C\ ext.\text{-}\ HOC}$ = 0.906***) and total carbon content ($R_{C\ total\text{-}\ HOC}$ = 0.677**) (Table 2). Therefore, they are defined as one of the drivers for SWR in the Technosol (Atanassova et al., 2018a, b). In this aspect, Sepehrnia et al. (2017) compare the organic matter between soil profiles with thickness 0–60 cm in water repellent and water permeable natural soils and find that it is higher in the water repellent soil. In our study, we found a weaker positive but insignificant correlation between WDPT and extracted organic carbon ($R_{WDPT\text{-}C\ ext.}$ = 0.267) (Table 2). In general, the extracted organic carbon varies within the soil layers, but maintains a relatively uniform trend along the depth of the soil profile. On the other hand, the values of residual carbon fraction also fluctuate, but increase in deepest soil layers. Under these conditions, a partial equilibrium of extracted and residual carbon in soil layers 40–50 cm and 60–70 cm is established (Figure 3b).

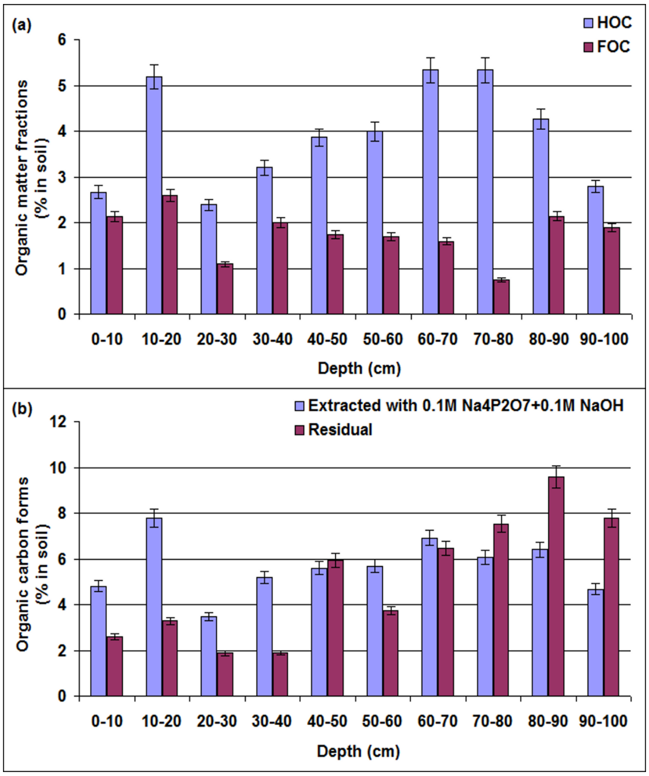

Fig. 3. Variation of soil organic matter fractions and organic carbon forms in the soil profile (SE = ± 5%)

The aggressive and most mobile fraction of FOC (Filcheva et al., 2018) occupies small percentage of the composition of SOM in the studied profile (Table 1). Another feature of SOM is its very high humification degree in all soil layers according to the Bulgarian classification of Artinova et al. for humus state of soils (Filcheva, 2007). However, the average values of the optical characteristics of HOC (Table 1) are slightly higher than those in mine spoil Iztok from Maritsa-Iztok region determined by Hristova (2013) who describe the HOC as low molecular and mobile.

The studied mine soil profile has very strong to extremely acidic pH (Table 3). Some surface and subsurface soil samples from other experimental sites nearby (Project DN06/1, National Science Fund) are characterized by similar pH values due to the presence of black clays in the substrates (Atanassova et al., 2018a, b; Nedyalkova et al., 2018a; Simeonova et al., 2018).

The content of sand (1–0.05 mm) and clay (< 0.001 mm) fractions vary randomly in the layers of the soil profile (Table 3). On the soil surface (0–30 cm), the % of sand is higher, but there is a tendency for increasing the % of clay along the depth of the profile below 40 cm. There is a lack of correlation between the % of sand and clay fractions in the Technosol and WDPTs before heating of soil samples. However, clay content correlates significantly with residual fraction of SOM ($R_{clay\text{-}\ C\ res.}$ = 0.579**) (Table 2).

Table 3. Physical and physicochemical characteristics of the studied Technosol

Depth, cm	Sand 1–0.05 mm %	Clay < 0.001 mm %	pH (H_2O)	CEC $cmol.kg^{-1}$	Base saturation V %
0–10	45.1	37.5	3.02	61.4	35.51
10–20	47.7	33.9	3.10	59.8	36.29
20–30	44.2	34.2	3.60	50.0	41.00
30–40	37.4	39.8	3.16	59.8	37.46
40–50	22.8	47.9	2.96	55.2	27.18
50–60	35.4	46.6	3.15	60.3	37.00
60–70	40.5	36.4	3.03	61.2	35.00
70–80	30.2	47.6	3.05	61.0	36.07
80–90	38.6	42.9	3.06	61.5	37.40
90–100	18.6	57.6	3.06	61.5	37.40

The CEC ranges from 50.0 to 61.5 $cmol.kg^{-1}$ (Table 3). In the surface layer of the soil profile, it reaches the values established at some points from the horizontal experimental plot, at depth of 20 cm from the soil surface at non-vegetated area in the region of Obruchishte village (Simeonova et al., 2018). The base saturation (V) is less than 50% and has the lowest % in depth of 40–50 cm. This quantity fully corresponds to the lowest pH value (2.96) (Table 3). Similarly to the horizontal grids surveys (Atanassova et al., 2018a, b), the CEC in the soil profile correlates positively with the total carbon content ($R_{CEC\text{-}C\ total}$ = 0.549**). Less, but also significant, is the correlation of CEC with residual fraction of carbon in SOM ($R_{CEC\text{-}\ C\ res.}$ = 0.433*) (Table 2).

Conclusions

The larger part of the soil profile is characterized by extreme water repellency with ~ 3 hours of water drop penetration time. It decreases sharply in the surface and in the deepest soil layers. After laboratory heating of soil samples, the established water repellency declines in all layers to a degree with maximum water drop penetration time of 2 min. The high content of total carbon and its random values between soil layers is due to the presence of coal particles and coal and ash dust in the deposited geological materials, which leads to indiscriminate accumulation of organic matter in the surface soil layers. The positive correlation between humic organic carbon and water drop penetration time ($R_{WDPT\text{-}HOC}$ = 0.440*) confirms that humic acids are the main factor influencing soil water repellency in the technogenic soil profile. The significant correlation of the residual fraction of soil organic matter with clay confirms the intimate association of stable carbon in organo-mineral complexes of soil colloids.

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