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Assessment of physical and chemical characteristics of water repellent soil profiles of Technosols from Maritsa-Iztok open-cast coal mine in Bulgaria

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Abstract

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The paper compares physical and chemical characteristics of technogenic soil profiles at coal mine spoil from Maritsa-Iztok Mines. Sites with coniferous vegetation and without vegetation were selected. Brief comparison was made between physico-chemical characteristics of studied soil profiles and those from other mine spoils. Relations with previous studies are also provided. The technogenic soil profiles have high cation exchange capacity and organic carbon content. Soil water repellency was measured and its correlation with studied soil characteristics of the Technosols was established. The water drop penetration time (WDPT) decreases sharply after heating of extremely hydrophobic soil samples. Before heating it correlates significantly with exchangeable cations of aluminium ($R^*_{WDPT\text{-}Al} = 0.863$) in the soil profile under pine and less with hydrogen in the profile without vegetation ($R_{WDPT\text{-}H8.2} = 0.409$). In the pine site, significant correlation was also found between the WDPT and the total organic carbon ($R^*_{WDPT\text{-}TOC} = 0.711$) as well as with fulvic organic carbon ($R^*_{WDPT\text{-}FOC} = 0.824$). In the non-vegetated soil profile, the correlation is significant with the fraction of unextracted organic carbon ($R^*_{WDPT\text{-}Cunextr.} = 0.644$).

Keywords: Technosols; soil physical characteristics; soil chemical characteristics; soil hydrophobicity

Introduction

Mine spoils, known as Technosols (IUSS Working Group WRB, 2006), occupy large areas of land and are characterized by diversity in terms of substrates, which built them (Penkov et al., 1992). Their increasing prevalence provokes recent research to establish their specific features, properties and characteristics (Zheleva et al., 2016; Petrov, 2019; Banov et al., 2020; Banov, 2021; Tsolova et al., 2021). Soil water repellency (SWR) is similar soil property, which is found both in the surface and subsurface soil layers (Ivanov et al., 2019), and at the Technosol's profile depth (Atanassova et al., 2020a). In most cases, SWR in these soils is related to various chemical, physical and microbiological soil characteristics such as total carbon content, soil organic matter fractions (Atanassova et al., 2018a), sand fraction (Ivanov et al., 2021) and the amount of bacteria (Nedyalkova et al., 2018). Despite the recent increase in scientific research on horizontal spatial variability of SWR in the Technosols (Atanassova et al., 2018b, c; 2019; 2020b; Simeonova et al., 2018; 2020), the information on its presence in depth of soil profiles is still insufficient in terms of plant species and specific features of the composition of the soil profiles.

The present paper aims to present comparative characteristics of physical and chemical properties of technogenic soil profiles with coniferous vegetation and without vegetation and their relationship with soil water repellency.

Materials and Methods

The study site is a mine spoil from the region of Obruchishte village near Maritsa-Iztok Mines. The spoil is built from Pliocene clays because of open-cast coal mining, with impurities of black clays and coal ash, which is a waste product from coal combustion in nearby thermal power plants. For the purpose of the study, at the end of July 2017, soil samples were taken from the layers of two soil profiles. One of them is under pine plantation (*Pinus nigra*) and the other is without vegetation. The soil samples were collected in 10 cm layers to a depth of 100 cm. Thus, 20 soil samples were provided. During the field trial, another soil profile was dug under tussock grass vegetation using the same methodology, which was analyzed and discussed independently in another study (Atanassova et al., 2020a). At a later stage, in October 2019, another bare soil profile without vegetation (stubble site) (Ivanov et al., 2021) was studied at a depth 0-85 cm.

The collected samples were analyzed for SWR by the method of measuring the water drop penetration time (WDPT) (Dekker & Ritsema, 1996; Doerr et al., 2002). The analysis was identical to our previous measurements (Ivanov et al., 2019; 2021) by drying of soil samples in the laboratory to room temperature (25–27°C, 67–82% air humidity) and sieving to 2 mm. WDPT was established with three drops of distilled water with a volume of 80 µl on the surface of the individual samples and measurement of the time for complete droplet absorption in the soil. Then, the soil samples were heated in an incubator NUVE EN500 at 65°C for 24 h and WDPT was measured again in the same way. In the last stage, the median values were determined between the three water drops, which distributed the soil samples into five classes, similar to the research of Bisdom et al. (1993), Dekker & Ritsema (1996; 2000): 0 – wettable or nonwater repellent (< 5 s); 1 – slightly (5 – 60 s); 2 – strongly (60 – 600 s); 3 – severely (600 – 3600 s); 4 – extremely water repellent (> 3600 s).

Beside WDPT measurements, the soil samples from the different profile layers were analyzed for the following soil characteristics:

– Texture – by the method of Kachinski (1965). Additionally, the texture fractions of sand, silt and clay were calculated in accordance with Soil Taxonomy (USDA Soil Survey Staff, 1975) and FAO (2006).

– pH – potentiometrically (Arinushkina, 1970).

– Cation exchange capacity (CEC) – by the method of Ganev & Arsova (1980).

– Total carbon content (TOC) – by the method of Tyurin (Kononova, 1966).

– Composition of soil organic carbon with 0.1M $Na_4P_2O_7$+0.1M NaOH extraction (as % of the soil sample) – extracted (EOC), humic (HOC), fulvic (FOC) and unextracted organic carbon (C_{unextr}) – by the method of Kononova-Belchikova (Kononova, 1966).

Previously, Simeonova et al. (2020) presented partial data for minimum and maximum values of sorption capacity and exchangeable cations in the soil profiles.

Statistical correlations were established by SPSS 22 for MS Windows.

Results and Discussions

WDPT measurements before heating the soil samples show clear differentiation between the two soil profiles. The pine site stands out with extreme hydrophobicity to a depth of 60 cm. An exception is the surface layer, which is still severely water repellent according to the scale used (Bisdom et al., 1993; Dekker & Ritsema, 1996; 2000). Iovino et al. (2018) also determine severe SWR under *Pinus sylvestris* trees. In our study, the other soil layers at a depth below 60 cm contrast with their water permeability (Table 1). The established extreme SWR to some extent resembles the one measured in a soil profile with tussock grass vegetation, with the difference that the extreme water repellent class is typical for a greater depth up to 80 cm (Atanassova et al., 2020a). On the other hand, in our study, the soil profile without vegetation is characterized by variation in the measured time intervals in all layers. In this case, the individual samples possess slight, strong and extreme water repellency, but here we will emphasize that the measured WDPT is characterized by variability, even if the soil layers fall into the same class (Table 1).

Table 1. WDPT (s, medians) in soil profile layers

Depth, cm	Profile under pine		Profile without vegetation	
	Before heating	After heating	Before heating	After heating
0–10	870	7	8	254
10–20	9820	75	34	36
20–30	12315	11	93	13
30–40	12100	21	26	8
40–50	2870	2	144	7
50–60	10820	8	10845	17
60–70	1	1	8920	24
70–80	0	0	302	15
80–90	0	0	7	2
90–100	1	0	6	17

Laboratory heating of the samples from the profile under pine leads to changes of SWR from extreme to slight. The same feature is observed in the layers with the longest measured WDPT in the soil profile without vegetation (Table 1). The reduction of WDPT after heating of the soil samples has been established in our previous studies of technogenic soil profiles (Atanassova et al., 2020a; Ivanov et al., 2021). However, the observed trend makes an exception in the surface 0–10 cm layer of the profile without vegetation, where the SWR increases from slight to strong (Table 1). Dekker et al. (1998) also found similar contrast in changes of WDPT after heating at 65°C of samples from three dune sands and suggest that this could be connected with some differences of organic matter orientation on soil particles.

The pH in the soil profile under pine vegetation is very strongly acidic in all layers except in the surface one, where it is strongly acidic depending on the accepted classification (Koynov et al., 1980) (Table 2). The values are slightly higher than those of the profile with tussock grass vegetation (Atanassova et al., 2020a) with average pH (H_2O) 3.12. The same value characterizes the soil profile without vegetation in the present study (Table 3).

As it is found in many studies in the area (Atanassova et al., 2018a, d; 2020a; Nedyalkova et al., 2018; Simeonova et al., 2018), we consider that such strongly acidic pH is result of the presence of black clays and coal impurities in the soil profiles. Under these conditions, in both studied soil profiles, pH correlates positively with CEC ($R^*_{pH\text{-}CEC}$ = 0.688 under pine; 0.874 without vegetation) and base saturation ($R^*_{pH\text{-}Bases}$ = 0.967 under pine; 0.873 without vegetation) as well as with calcium ($R^*_{pH\text{-}Ca}$ = 0.975 under pine; 0.931 without vegetation) and magnesium cations ($R^*_{pH\text{-}Mg}$ = 0.984 under pine; 0.892 without vegetation) of the soil adsorbent. The correlations are significant at * $p \leq 0.05$.

The physicochemical characteristics of the reclaimed soils show that they have high sorption capacity, which is higher in

Table 2. CEC and composition of soil organic carbon in soil profile under pine

Depth, cm	pH H_2O	CEC	$H_{8.2}$	Al	Ca	Mg	Base saturation, %	TOC	EOC	HOC	FOC	C unextr.
		cmol.kg^{-1}						% of soil sample				
0–10	4.10	55.3	22.6	6.6	27.0	5.9	59.13	5.71	2.36	1.96	0.40	3.35
10–20	3.20	52.4	30.1	8.6	16.5	5.5	42.56	5.38	2.26	1.80	0.46	3.12
20–30	3.30	53.0	28.9	8.2	18.0	5.5	45.47	5.88	2.15	1.80	1.35	2.73
30–40	3.30	53.2	29.6	8.5	18.2	5.5	44.36	6.50	3.13	2.21	0.92	3.37
40–50	3.40	54.0	28.6	7.9	20.1	5.6	47.05	5.57	3.13	2.27	0.86	2.44
50–60	3.46	55.0	28.6	7.9	21.1	5.6	48.00	5.74	3.69	2.50	1.17	2.07
60–70	3.70	57.7	27.9	7.1	24.2	5.7	51.65	5.04	2.36	2.01	0.35	2.68
70–80	3.75	55.2	28.2	7.4	24.5	5.7	48.91	4.49	1.72	1.72	0.00	2.77
80–90	3.75	58.5	27.8	7.1	24.8	5.7	52.48	3.19	1.28	1.04	0.24	1.91
90–100	3.75	58.5	27.8	7.0	25.2	5.7	52.48	3.65	1.20	1.20	0.00	2.45
Average	3.57	55.3	28.0	7.6	22.0	5.6	49.21	5.12	2.33	1.85	0.58	2.69

Table 3. CEC and composition of soil organic carbon in soil profile without vegetation

Depth, cm	pH H_2O	CEC	$H_{8.2}$	Al	Ca	Mg	Base saturation, %	TOC	EOC	HOC	FOC	C unextr.
		cmol.kg^{-1}						% of soil sample				
0–10	3.30	78.4	34.0	18.2	38.6	5.8	56.63	3.37	1.47	0.85	0.62	1.70
10–20	3.10	73.5	38.2	19.0	29.5	5.4	48.03	4.73	2.45	1.07	1.38	2.28
20–30	3.06	73.2	38.5	23.1	29.1	5.4	47.40	4.53	2.00	1.07	0.93	2.53
30–40	3.10	74.2	38.1	20.0	30.2	5.6	48.65	5.68	2.87	1.07	1.80	2.81
40–50	3.10	74.3	38.1	20.1	30.4	5.6	48.72	7.37	2.77	1.07	1.70	4.60
50–60	3.00	72.0	38.6	19.8	28.0	5.3	46.39	9.05	3.37	1.74	1.63	5.68
60–70	3.10	74.0	38.0	18.0	30.2	5.5	48.65	8.63	3.25	1.78	1.47	5.38
70–80	3.13	72.0	33.1	16.0	33.1	5.6	54.03	8.63	4.52	2.68	1.84	4.11
80–90	3.13	75.2	35.1	16.8	34.4	5.6	53.32	7.68	3.37	1.56	1.81	4.31
90–100	3.17	76.0	34.5	17.2	35.6	5.7	54.61	8.32	3.37	1.65	1.72	4.95
Average	3.12	74.3	36.6	18.8	31.9	5.6	50.64	6.80	2.94	1.45	1.49	3.84

the profile without vegetation. For each of the profiles, the values are relatively close between the individual layers (Tables 2 and 3). This feature is no exception to the profile with tussock grass vegetation and extreme SWR in the region (CEC 50.0–61.5 cmol.kg^{-1}) (Atanassova et al., 2020a). However, the established physicochemical characteristics are not typical for all technogenic soils in Maritsa-Iztok coal mine complex because in afforested area of mine spoil “Iztok” the sorption capacity is lower (CEC 32.6-40.3 cmol.kg^{-1}) (Hristova, 2013), and in mine spoil “Mednikarovo” it varies between 23.2-30.0 cmol.kg^{-1} (Ivanov, 2007). In contrast, the average value of base saturation in the studied profiles (Tables 2 and 3) has lower percentage (around 50%) than in other afforested areas in the region: 96.7% for spoil “Iztok” soil profile (Hristova, 2013) and 92.3% for profile in spoil “Mednikarovo” (Ivanov, 2007). This is due to the dominance of hydrogen and aluminium ions over basic calcium and magnesium ions (Ganev, 1990) in almost all the layers of the studied soil profiles (Tables 2 and 3). In the established physicochemical characteristics of the studied soils, WDPT before heating correlates positively with hydrogen ($R^*_{WDPT-H8.2}$ = 0.524) and aluminium ($R^*_{WDPT-Al}$ = 0.863) in the soil profile under pine and negatively with calcium ($R^*_{WDPT-Ca}$ = -0.862) and magnesium ($R_{WDPT-Mg}$ = -0.802). In the profile without vegetation, the correlation between WDPT and hydrogen is slightly weaker, but positive ($R_{WDPT-H8.2}$ = 0.409) and also negative with calcium ($R^*_{WDPT-Ca}$ = -0.456) and magnesium ($R^*_{WDPT-Mg}$ = -0.557).

The organic carbon content in the studied Technosols is high in all the layers of the soil profiles under pine and without vegetation, and organic carbon has no accumulative distribution in the soil surface layers (Tables 2 and 3). We think that this is due to coal impurities, which are also presented in the studied profile with tussock grass vegetation (Atanassova et al., 2020a), rather than to the soil-forming processes. However, the ratio between fractions of EOC (HOC and FOC) determines its type as humic in all depth of the soil profile under pine (except for the layer 20–30 cm). As for the profile without vegetation, the individual soil layers are distributed randomly between fulvic-humic and humic-fulvic type according to the classification of Grishina and Orlov (Orlov, 1985). In almost all the layers of both soil profiles, the EOC has lower percentage than the unextracted one (Tables 2 and 3). As SWR is related to organic matter content (Bisdom et al., 1993), we found that WDPT before heating of the soil samples correlates positively, but to varying degrees, with TOC content and its fractions (EOC, HOC, FOC, $C_{unextr.}$). In this case, in the profile under pine this correlation is significant with TOC EOC HOC and FOC (Figure 1). Regarding profile without vegetation the correlation is significant between WDPT and fraction of the unextracted carbon (Figure 2).

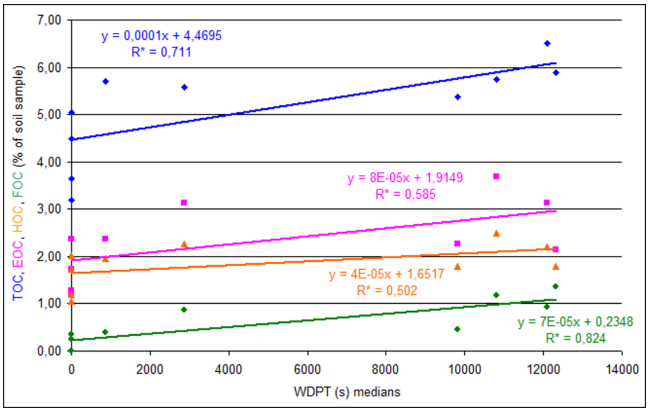

Fig. 1. Correlation between WDPT before heating and the fractions of soil organic carbon in the soil profile under pine

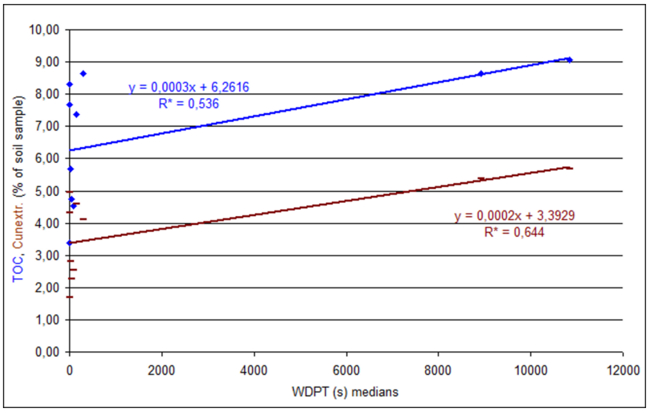

Fig. 2. Correlation between WDPT before heating and the fractions of soil organic carbon in the soil profile without vegetation

The data on the textural composition of the studied Technosols, presented as fractions depending on the texture classes (USDA Soil Survey Staff, 1975; FAO, 2006), show a clear differentiation between the two soil profiles. The main difference is the predominance of clay in the profile under pine, in contrast to the sand fraction, which has the highest percentage in the layers of the profile without vegetation (Figure 3). Therefore, the texture of the soil layers in the area with pine is *clay,* except for the depth 80–90 cm, which is *heavy clay* due to the highest content of the fraction <0.001 mm. Regarding the profile without vegetation, its lighter mechanical composition determines the texture of soil layers as *clay loam*. Here we also found an exception in the layers 10–20 cm and 30–40 cm, which have *sandy loam* texture, because of the highest sand (1–0.05 mm) content in them (Figure 3).

In general, the amount of the sand fraction has randomly distributed values in the profile without vegetation, similarly to that with tussock grass vegetation (Atanassova et al., 2020a), and is lowest in the soil profile under pine. In this profile (under pine) we found a positive and significant correlation between the percentage of the sand fraction (1-0.05 mm) and WDPT before heating ($R^*_{SAND\text{-}WDPT} = 0.865$), exchangeable aluminium ($R^*_{SAND\text{-}Al} = 0.763$), TOC ($R^*_{SAND\text{-}TOC} = 0.821$) and FOC ($R^*_{SAND\text{-}FOC} = 846$).

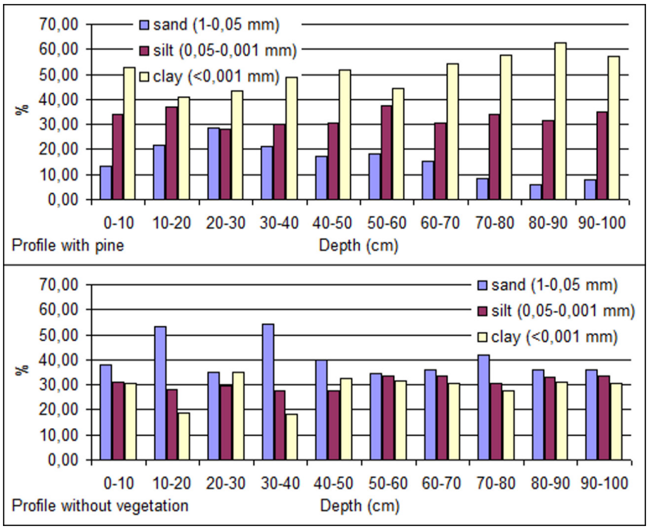

Fig. 3. Texture fractions ratio in studied soil profiles

Conclusions

The studied technogenic soil profiles are characterized by heterogeneity in terms of the presence of SWR. The soil profile under pine is severely and extremely water repellent from the very surface, and in this without vegetation, the extremely hydrophobic layers are located between 50-70 cm. Similarly to previous studies in the region, laboratory heating of the soil samples decrease the extreme SWR to slight. The pH in the profile under pine is very strongly acidic under the influence of the materials that built it up. The reclaimed soils have high CEC and relatively close values among the soil layers. A positive correlation was established in the profile under pine between WDPT before heating of soil samples and exchangeable hydrogen and aluminium cations. The technogenic soil profiles have high organic carbon content with a predominance of the fraction of the non-extractable organic carbon. Significant positive correlation was found in the profile under pine between WDPT and TOC and in the profile without vegetation, with non-extractable organic carbon. According to the texture classes (USDA Soil Survey Staff, 1975; FAO, 2006) the textural composition of the studied soils determines a *clay* texture in almost all the layers of the profile under pine, and *clay loam* in the profile without vegetation. The *sand* fraction in the profile under pine correlates significantly and positively with WDPT, exchangeable Al, TOC and FOC.

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