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Physical and chemical properties in reclaimed soils in a stand of *Robinia pseudoacacia* from Mini Maritsa Iztok basin in Southern Bulgaria

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Abstract

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The paper examines physical and chemical properties in reclaimed soils result of restoration practices took place in the surface mining industry in the region of the "Mini Maritsa Iztok", Stara Zagora district in Southern Bulgaria. In brown-coal surface mining, the overburden (the earth and rock sediments lying above the coal seam) is first removed, and the exposed brown-coal (lignite) is then extracted. Priority task for post mining operations is the environmental protection aiming at the sustainable development, restoration and improvement of the environmental conditions. To fulfill this aim, a systematic survey as well sampling was done of overburden terrains including two soil profiles and three additional surface sites in a stand of *Robinia pseudoacacia*. Samples were analyzed for particle size distribution, content and composition of organic substances, cation excange capacity, soil bulk density, soil moisture content at field sampling, soil particle density, porosity and soil moisture content at different matric potentials.

In reclaimed soils the different sized mineral mechanical elements are inherited during the technical activities of excavated materials. The organic matter in the investigated reclaimed soils was not directly dependent on the local environmental conditions but was result of technology of reclamation of landscape. The studied reclaimed soils under Robinia pseudoacacia contain an amount of ancient organic substances that cannot be decomposed, due to the nature of stable carbon. Despite the high content of organic substances, soil particle density was identified also as high particularly in the profile 1 at the depth 68-97 cm. This specific feature related to the physical properties of reclaimed soils is probably due to the presence of brown-coal particles involved in the mixed mineral materials have deposited in the East Dump Site. The manifold relationship of bulk density and organic matter, total porosity, gravimetric water content and hygroscopic water content was faint and irregular.

The intrinsic peculiarity of high mobility of organic substances was identified and the specific relationship within different fractions of extractable organic carbon. Probably the relationship with bulk density is not clearly expressed in case of labile organic matter not bound to the soil mineral part where content of extractable carbon was extremely very high. Humic acids by their molecular weight and structure are very similar to those of fulvic acids being low molecular and with predominance of aliphatic over aromatic moieties in their molecules.

Soil pH (H_2O) was diverse from acidic to neutral. Soil adsorbent was affected by acidification so there was evidence of initial destructive processes of the soil adsorption complex. Reclaimed soils were characterized by relatively high degree of saturation with bases (67-82%) in profile 1 and very high saturation (81-95%) in profile 2.

Keywords: physical and chemical properties; reclaimed soils; sustainability; lignite; surface mining; Mini Maritsa Iztok

Introduction

The environmental effects of coal surface mining are clearly regional in nature. Drastic morphological changes in the exploited areas resulting at earth surface environmental hazard are produced by mining operations. In brown-coal surface mining, the overburden (the earth and rock sediments lying above the coal seam) is first removed, and the exposed brown-coal is then extracted. The major problem with opencast mining is the disruption of large areas of productive land and the reclamation activities aiming at restoring the land to its previous state and at creating new landforms with newly soil functions (Uzarowicza, 2017).

In new geological epoch (Anthropocene) the mining industry has shown interest in environmental issues and integration of sustainability into practices (Hilson & Murck, 2000). Specific regulations for the mining sector have been enacted to deal with the environmental effects of mining operations. Environmental management includes a variety of mandatory practices rehabilitation of mining sites and payment of taxes (Nikolaou & Evangelinos, 2010). In terms of soil sustainability ISO 14001:2015 specifies the requirements for an environmental management system that an "organization" can use to enhance its environmental performance.

The paper examines physical and chemical properties in reclaimed soils from restoration practices took place in the surface mining industry in the region of the "Mini Maritsa Iztok", Stara Zagora district and is continuation of our previous studies in the area (Atanassova et al., 2018; 2019; 2020).The primary data for this study was collected during fieldwork in 2019-2020 and deals with interpretation in ecological aspect of physical and chemical characteristics of reclaimed soils in the area of a stand of *Robinia pseudoacacia* result of applied biological reclamation.

The study site was on opencast lignite field some fifty years old in the eastern area of the Maritsa Coal Basin. This object was located in the East Dump Site of the Troyanovo-3 Mine, at the "Mini Maritsa Iztok" the largest coal mining complex in Bulgaria, located in the Southern part of the Upper Thracian Lowland. The mine was regularly operated since 1961 and the reclamation has been commenced in 1974.

Priority task for post mining operations is the environmental protection aiming at the sustainable development, restoration and improvement of the environmental conditions. Mining industry has to comply with the law currently in force and have to satisfy the external demands. The reclamation of the areas disrupted by mining operations strictly complies with the effective environmental legislation and comprises storage and usage of the humus layer at the dump sites. Three years after completing the mining and backfilling activities, technical reclamation should be done – a series of landscaping and leveling operations and covering the area with a compact humus layer 40 cm thick, determined by Ordinance № 26 (promulgated, SG No. 89/1996; amended, No. 30 of 2002) for reclamation of disturbed terrains converted into agricultural lands.

Area for forestry over 1500 ha has been reclaimed at the "Mini Maritsa Iztok" since then. The lignite is extracted from the huge, open-pit mines, resulting in large areas of disturbed land. Overburden removal in the mines is deposited into the dumps, and there is a tendency to increase the volume of overburden dumped at the internal sites (Figure 1).

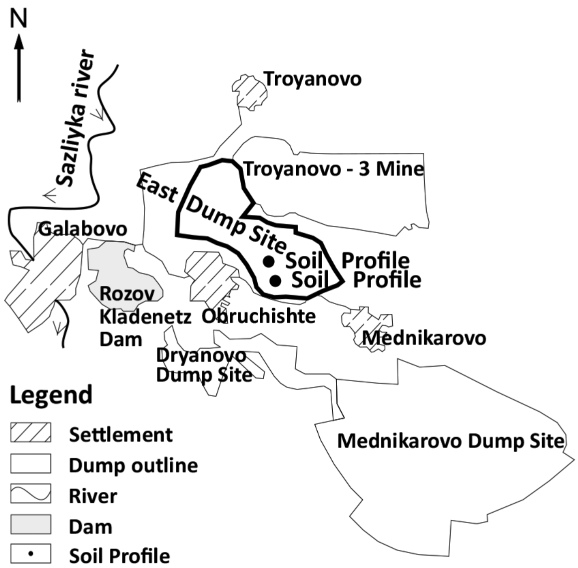

Fig. 1. Scheme for outline of localization of studied object in Maritsa Iztok basin

Materials and Methods

The Stara Zagora district is referred to the transitional region of the European moderate-continental climate zone. The annual air temperature is over 12°C, and humidity is about 70%. Mean air temperature is 0.9°C in January and is 22.9°C in July. The mean annual precipitation is 537 mm. Cold snap occurs much earlier than in other parts of Stara Zagora district. However, the Maritsa River enhances the Mediterranean climatic influence, manifested mainly on the seasonal precipitation regime. The amount of precipitation in May and June, as well November and December is with the highest rates. In winter, the Balkan Mountains stop the cold continental air masses invading from the north and northeast. Summer is hot, and winter is mostly mild and short. The months with drought are August and September, and the second precipitation minimum occurs in February and March. Snowfall is relatively rare and snow cover lasts too short. The fog regime is with normal trend (number of foggy days during the year) and depends primarily on the overall synoptic situation – the heat balance, air temperature and relative humidity.

The Sokolitsa River (left tributary of the Sazliyka River) is the main water artery of the region, which flows through the territory of the Obruchiste municipality from east to west. Water from the constructed dams „Mednikorovo", „Chervena Reka" and „Madrets" is used mainly for irrigation of agricultural land in the regions.

The processes during the Neogene led to the formation of a large brown-coal (lignite) field, the brown-coal seams in the Maritsa Iztok basin are located relatively shallow at 6-10 meter to 110-120 meter below the surface and spreads on the area of about 240 km². General geological section of substrata sequential order in the East Maritsa coal basin is a soil layer and yellowish-brown clay, grayish-green clay, mixed grain-size sand, limestone, black chalk clay, brown-coal, stratified clay, marl, conglomerate, Laramide dikes, limestone, marble, granite, gneiss. The lignite is supplied to the thermal power plants. The lignite coal has disadvantageous quality characteristics: soft, with low organic matter coalification level, high moisture content (50-60%), low calorific value 1550 kcal/kg, combustible sulfur contents 2.4%, characterized with high ash content (25-45%).

Laboratory methods. Soil organic carbon content was determined by modified Turin's method (Filcheva & Tsadilas, 2002; Filcheva, 2015) (dichromate digestion at 125°C, 45 min, in presence of Ag_2SO_4 and $(NH_4)_2SO_4$ $FeSO_4$ $6H_2O$ titration, phenyl anthranilic acid as indicator). According to the method of Ganev & Arsova (1980) the total acidity is determined by the solutions of 1.0 N sodium acetate and 0.2 N potassium malate at pH 8.25, the value with maximum saturation of soil colloids with strong alkaline bases.

Particle size distribution was determined by sieving and the pipette method after chemical dispersion of air- dry gridded soil sample (< 2 mm) with 25 cm³ 0.4N sodium pyrophosphate ($Na_4P_2O_7$) without preliminary removal of the organic matter and carbonates from the soil sample. By means of sieving four fractions of sand (2.0-1.0; 1.0-0.5; 0.5-0.25; 0.25-0.1 mm) was determined, and was estimated the fifth sand fraction (0.1-0.05 mm). By means of conventional pipette method the fractions smaller than 0.005 mm, 0.02 mm and 0.002 mm were determined. Particle-size distribution and textural classes were determined according to USDA (Soil Survey Division Staff, 1993).

Vertically oriented undisturbed cores were sampled in 100 cm³ metal cylinders for determination of bulk density (ISO11272, 1998) and water retention at low suctions (ISO11274, 1998).

Aiming to characterize soil pores distribution in the United States the recommended value for laboratory measurements of water retention is at 33 kPa (WpF 2.5) for loams and clays (Kirkham, 2005). This is widely accepted as a field soil water capacity and the water retention measured at suction 1500 kPa pressure ($WpF_{4.2}$) respond to wilting point determined using pressure-membrane in the Richards Extractor. Diameter of pore size 10 µm and 0.2 µm correspond to 33 kPa and 1500 kPa. Soil water retention is according to ISO 11274:1998. The hygroscopic water content ($WpF_{5.6}$) was determined using the vapour pressure method with controlled 75% relative humidity of air in desiccators containing saturated solution of NaCl. Particle density analysis was carried out in water with 100 cm³ pycnometers. Total porosity (Pt) was calculated using the measured bulk density (Db) and particle density (Ds).

Results and Discussion

In Stara Zagora district the relief is hilly rolling (Figure 2). The investigated area in the East Dump Site of the Troyanovo-3 Mine, is localized nearby the village of Obruchishte, the Galabovo municipality, at the "Mini Maritsa Iztok" with coordinates of profile 1 (42.145535 N, 25.951663 E) and coordinates of profile 2 (42.12692 N, 25.953082 E), altitude 540 m.

Soil classification is as follows: Anthroportic Ustortents (Human-Transported Soils, Reclaimed land (landform), Surface mines) (Soil Survey Staff, 2014), Spolic Technosols (Clayic, Eutric, Laxic, Ochric, Pantotransportic) (IUSS WORKING GROUP, 2015).

The morphological diagnostic of mixed stratified layers of reclaimed soil (profile 1) in a stand of *Robinia pseudoacacia* (Figure 3) was, as follows:

A 0-14 cm Color grayish brown, (10YR 5/2 dry) and dark brown, (10YR 4/3 sub wet); clay loamy texture, presence abundance of coarse sand; weakly compacted, friable, weakly shaped granular structure with an average aggregate of fine size (1-2 mm diameter); and moderately developed, firm, subangular-blocky structure with medium size (of 10-20 mm); many roots with a diameter of 1-2 mm, and pebbles of different size up to 3 cm, no effervescence by HCl, wavy boundary and clear transition to;

1B 14-42 cm Color light brownish gray (10YR 6/2 dry) and dark grayish brown (10YR 4/2 subwet); clayey texture, abundance of grains of coarse sand; compacted; firm, moderate shaped subangular structure with very fine size (<5 mm about 60%) and of fine size (5-10 mm near 40%), many quartz grains, and single roots and small pebbles, no effervescence by HCl, clear wavy boundary, sharp transition to;

2A 42-68 cm Homogeneous, color dark brown (7.5YR 3/2 dry) and dark reddish brown (5YR 3/2 subwet); sandy clay loamy texture; weak shaped, granular structure with an average aggregate of coarse size (5-10 mm diameter); no effervescence by HCl, clear wavy boundary, sharp transition to;

3B 68-97 cm Color dark grayish brown (10YR 4/2 dry) and very dark grayish brown (10YR 3/2 subwet); clayey texture, with abundance of coarse sand grains; firm, subangular blocky structure with medium size (10-20 mm), no effervescence by HCl, clear wavy boundary, and transition to;

BC 97-150 cm Color brown (10YR 5/3 dry) and dark brown (10YR 3/3 subwet); sandy loamy texture; with abundance of coarse sand grains; very firm; subangular blocky structure with sharp sides and fine size (5-10 mm about 40%), and with medium size (10-20 mm about 60%); quartz grains included, no effervescence by HCl.

Fig. 2. Rolling landscape in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine, nearby the village of Obruchishte, Galabovo municipality

The morphological diagnostic of mixed stratified layers of reclaimed soil (profile 2) in a stand of *Robinia pseudoacacia* (Figure 4) is, as follows:

Ah 0-18 cm Color dark gray (10YR 4/1 dry) and very dark gray (10YR 3/1 subwet); clayey texture; weakly compacted, firm, well shaped granular structure with an average aggregate medium size of 2-5 mm diameter; a few roots up

Fig. 3. Reclaimed soil (profile 1) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine

to 1mm in diameter, single pebbles 1-2 cm in size, no effervescence by HCl, transition noticeable to;

A1 18-37 cm Color: dark grayish brown (10YR 4/2 dry) and very dark grayish brown (10YR 3/2 subwet); clayey texture; firm; moderately shaped subangular blocky structure with an average aggregate size 5-10 mm; many fine roots, no effervescence by HCl, transition noticeable to;

1B 37-52 cm Color dark grayish brown (10YR 4/2 dry) and very dark grayish brown (10YR 3/2 subwet); compacted, firm, moderately shaped subangular blocky structure with an average aggregate fine size 5-10 mm, and about 10% few subangular blocky peds of corse size 20-50 mm, few small size pebbles, no effervescence by HCl, transition noticeable to;

2B 52-120 cm Homogeneous, color light brownish gray (2.5Y 6/2 dry) and grayish brown (2.5Y 5/2 subwet), clayey texture; compacted; firm, strongly shaped subangular blocky structure with an average aggregate of fine size 5-10 mm,

Fig. 4. Reclaimed soil (profile 2) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine

and about 10% of corse size 20-50 mm subangular blocky structure.

Soil physical properties influence nearly the all processes occurring in the soil. The data obtained on the particle size distribution in the reclaimed soils was described by using seven particle size classes according to method (Kachynsky, 1958), which are a diagnostic feature and determined many soil properties. Generally particles of similar size are grouped into groups (Table 1), called mechanical fractions. The particles with size < 0.001 mm is a clay fraction, which actively binds organic substances, cations, anions and water molecules in soil aggregates.

In the USDA soil classification system (2011), soil texture refers to the relative proportions of clay, silt, and sand mineral particles less than 2 mm. Total sand is 2.0-0.05 mm fraction; silt is 0.05-0.002 mm fraction; clay particles have an effective diameter less than 0.002 mm (less than 2 micrometer).

Soil texture depends on organic matter content and exchangeable cations, which effect physical characteristics of soils, infiltration rate, etc (Bayat et al., 2017). In reclaimed soils the different sized mineral mechanical elements are inherited during the technical activities of overburden deposition. Studied reclaimed soil (profile 1) was characterized by silty clay loam texture (physical clay 43.9%) in the surface layer (Table 1) according to classification of Kachinsky (1958), deeper it was altered to clay loam texture (physical clay 50.8%), and physical clay 58.1% at the depth 68-97 cm.

Table 1. Particle size distribution (%), according to the method of Kachinsky (revised) and the USDA texture classes USDA (2011)

Layers and depth, cm	Higros moisture, %	Size of textural fractions (mm) and their content, (%) of oven dry soil weight, method of (Kachynski, 1958)							Texture Class (USDA, 2011)
		1.0-0.25	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	< 0.001	∑ < 0.01*	
Reclaimed soil (profile 1) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine									
A 0-14	4.90	37.3	9.6	9.2	6.3	4.3	33.3	43.9	Clay Loam
1B 14-42	5.88	33.2	8.6	7.4	7.1	3.7	40.0	50.8	Clay
2A 42-68	5.90	35.5	22.4	11.3	4.3	4,4	22.1	30.8	Sandy Clay Loam
3B 68-97	7.97	25.0	6.9	10.0	5.8	5.8	46.5	58.1	Clay
BC 97-150	2.56	72.0	3.3	1.9	6.7	4.3	11.8	22.8	Sandy Loam
Reclaimed soil (profile 2) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine									
Ah 0-18	5.30	35.5	7.9	5.1	5.4	8.0	38.1	51.5	Clay
A1 18-37	6.33	33.9	8.4	2.6	9.3	3.0	42.8	55.1	Clay
1B 37-52	9.40	37.0	4.0	5.3	6.0	3.2	44.5	53.7	Clay
2B 52-120	4.68	23.2	21.0	2.1	7.9	3.0	42.8	53.7	Clay

Abbreviation: *Physical clay, the parameter characterized sum of the particle-size distribution, according to Kachinsky method (mm) ∑ < 0.01 = < 0.001+ (0.005 – 0.001) + (0.01 – 0.005)

Predominant was the coarse sand fraction with size (1.0-0.25 mm), which was 35.5-37.3%, downward sharply decreasing to 25% in (3B) layer at the depth (68-97cm) and altering to 72.0% in (BC) layer 97-150 cm depth. It was followed by the clay fraction, which was 33.3% in the surface horizon, varying in the layers downward, increasing to 40.0% in the subsurface layer and changed to 46.5% in the BC layer (97-150 cm). Such increase cannot be explained by the ongoing process of weathering in situ in deposited materials in the East Dump Site probably it could be due to technical stratification. In the middle part of profile 1 in the buried layer (2A) at a depth 42-68 cm a sharp decrease in the clay content up to 22.1% was observed together with a significant change to very high organic carbon content (Tables 1 – 4).

The distribution of sand, silt and clay fractions, according to the USDA Manual (2011), showed a similar trend in profile 1 (Table 2). Predominant fraction of medium sand (2.0-0.05 mm) was followed by the fraction of clay (<0.002 mm). In the profile 2 the predominant fraction was clay (<0.002 mm) followed by medium sand (2.0-0.05 mm).

Particle density (Ds), g/cm^{-3} is the average density of soil particles (mass of solid phase excludes pore space), which are characterized by different size and specific surface of soil particles. Generally in mineral soils the main density of the particles is close to the density of quartz as well as alumino-silicate clay minerals, which have a similar density, whereas the presence of organic matter lowers it. This relationship is clearly showed only in the buried layer (2A) at the depth (42-68 cm) in profile 1 (Table 3). Such close relationship of particle density with content of soil organic matter was not evident in the surface and subsurface layers in reclaimed soils where organic matter content is low to average 1.13-2.29% and particle density was average 2.45-2.55 g/cm^{-3}. In the (3B) layer at the depth 68-97 cm despite the high content of organic substances, soil particle density was also high. This specific feature related to the physical properties of reclaimed soils is probably due to the presence of brown-coal particles (Sapko et al., 2007) involved in the mixed mineral materials.

Soil bulk density is the volume of both solid and pore space, rock fragments more >2 mm are excluded. Bulk density indicates aeration and water movement and is used to estimate saturated hydraulic conductivity and to identify compaction. Bulk density is highly dependent on water content as well as, on the content of soil organic carbon, clay, gravimetric water content, basic cations, and sesquioxides (Nemes et al., 2010). The manifold relationship of bulk density and organic matter, total porosity, gravimetric water content and hygroscopic water content was faint and irregular in reclaimed soil (profile 1). The exception was manifested only in the layer (2A) at depth (42-68 cm).

Due to the enhanced adhesion capacity of organic substances (Rawlset et al., 2003) in the buried (2A) layer at depth (42-68 cm) in profile 1 (Table 3), characterized with sandy clay loam texture class, the high content 36.3% of gravimetric soil moisture was measured as well as, the highest 17.9% hygroscopic water content at 75% relative air humidity. Total porosity 66.4% was also well pronounced in the buried layer (2A) at the depth (42-68 cm) as well in the surface layer where total porosity was 64.3% but with the lowest content of organic carbon 1.13%. Generally the aeration conditions were poor. The relationship of high content of organic matter with lesser measurement of bulk density was only in the surface layer and in the layer (2A) at depth (42-68 cm).

Table 2. Particle size distribution and texture classes according to USDA and texture classification after Kachinsky N. A.

Layers and depth, cm	Particle size distribution <2 mm and fractions (%) after USDA			Texture class (USDA, 2011)	Particle size, mm, after Kachinsky, %		Texture class (Kachinsky, 1958)
	Sand 2.0-0.05	Silt 0.05-0.002	Clay < 0.002		Clay < 0.001	Physical clay ∑< 0.01*	
Reclaimed soil (profile1) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine							
A 0-14	43.2	19.2	37.6	Clay Loam	33.3	43.9	Silty clay loam
1B 14-42	38.3	17.5	44.2	Clay	40.0	50.8	Clay loam
2A 42-68	53.7	20.1	26.2	Sandy Clay Loam	22.1	30.8	Silty clay loam
3B 68-97	28.8	19.4	51.7	Clay	46.5	58.1	Clay loam
BC 97-150	70.4	14.0	15.6	Sandy Loam	11.8	22.8	Silty loam
Reclaimed soil (profile2) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine							
Ah 0-18	39.8	16.1	44.1	Clay	38.1	51.5	Clay loam
A1 18-37	38.8	14.5	46.7	Clay	42.8	55.1	Clay loam
1B 37-52	37.5	13.9	48.5	Clay	44.5	53.7	Clay loam
2B 52-120	40.6	12.7	46.7	Clay	42.8	53.7	Clay loam

Table 3. Main physical properties and organic carbon content measured in reclaimed soil (profile 1) in a stand of Robinia pseudoacacia in the East Dump Site of the Troyanovo-3 Mine

Layers and depth, cm	Core sampling depth, cm	Org.C, %	Bulk density (Db), $g.cm^{-3}$	Particle density (Ds), $g.cm^{-3}$	Total porosity (Pt), % vol.	Water cont. (W), %	$W_{pF\ 5.6}$, % (75 % rel.air humidity)
A 0-14	5-10	1.13	0.88	2.45	64.3	19.8	12.3
1B 14-42	25-30	2.29	1.20	2.55	52.9	19.8	13.6
2A 42-68	50-55	10.05	0.78	2.32	66.4	36.3	17.9
3B 68-97	80-85	3.89	1.57	2.65	40.6	10.4	7.7
BC 97-150	–	1.45	–	–	–	–	3.8

Notes: ($W_{pF\ 5.6}$) – hygroscopic water content at 75% relative air humidity

Three additional representative sites were selected in the area of a stand of *Robinia pseudoacacia* and sampling campaign took place in 2019-2020 respectively on site 1.1 with coordinates (42,14462 N, 25,95237 E), site 1.2 (42,14343 N, 25,95383 E) and site 1.3 (42,14218 N, 25,95319 E). Most of the undisturbed soil cores (100 cm^3) have been taken from the topsoil 0-5 cm and 5-15 cm layers.

Stratified distribution of organic substances in the studied sites was observed (Table 4). Obviously reclaimed soils are characterized by high variability of physical and chemical properties especially in rolling landscape. In the first site (1.1) slight decrease of humus content took place at the depth (5-15 cm) compared to the surface but the reverse trend was observed in the second (1.2) and the third (1.3) site, where humus content was significantly increased almost by one fourth. Extractable organic carbon showed very high content, which is evidence of the lesser bound with soil mineral particles. Sharp increase of extractable organic carbon occurred in the first (1.1) site 68.90% as well in the third (1.3) site 52.53% at the depth (5-15 cm) both. Based on the ratio of humic and fulvic acids content the type of humus was determined as humic and only in the third site it was of fulvic-humic type according to Kononova (1966).

The variation of particle density (Ds) and bulk density (Db) in the investigated sites showed the robust relationship with variation of obtained values on humus content on the surface 0-5 cm (Table 4). Respectively, the lowest value of bulk density (Db) corresponds to the highest content of humus in first (1.1) site and reverse trend was in the second (1.2) site, where high content of extractable organic carbon was identified (61.36%). Probably the relationship with bulk density is not clearly expressed in cases of labile (Haynes, 2005) or easy extractable organic matter not binding to the soil mineral part as in the layer 5-15 cm, where content of extractable carbon was very high (52.53-68.90%). Robust relationship was of bulk density (Db) with particle density (Ds), and reverse relationship with gravimetric soil moisture content (W), hygroscopic water content at 75% relative air humidity (Wh_{75}), and with water to field capacity. Due to a high variability within the soil texture the relationship of bulk density (Db) and particle density (Ds) with clay content was faint.

Soil properties depend on water storage and movement. Despite its dynamic character, field capacity is usually obtained with tension value of 33 kPa (0.33 atm) in clay soils (Nemes , 2011). The suction that defines field capacity varies from soil to soil but is generally 33kPa used in United States (Kirkham, 2005). Diameters of pore size 10 μm correspond to water retention at 33kPa pressure. Water retention, obtained with the tension of 1500 kPa pressure (15 atm), identified the permanent wilting point and this respond to the maximum pore size filled with water >0.2 μm diameter. The wilting point like field capacity is depending on the soil texture, compaction, stratification, temperature. To draw the retention curve, soil moisture values are obtained after submitting samples to different tensions in the Richards Extractor.

The difference in the water content of soil between field capacity and permanent wilting point is the amount of soil water available for uptake by plant roots. The highest value for soil water field capacity was obtained in the first (1.1) site 38.6%, that related to diameter of pore distribution 10 μm and in the second and third sites it was 28.3%. Usually the ability of fine texture to absorb and retain higher amount of water is recognized but not in case of reclaimed soils (Table 4).

The organic matter in the investigated reclaimed soils was not directly dependent on the local environmental conditions but was a result of technology of reclamation of landscape. Balance of processes of humification and mineralization or the processes related to the microbiological and enzymatic activity provoked formation of organic matter only at the topsoil. This fact was not valid for the organic substances distribution at the depth of reclaimed soils where they have been inherited (Table 5).

The evaluation of the total organic carbon content was according to Filcheva (2015), thus was very high >3%, high 1.8-3%, mean 1.2-1.7%, low 0.6-1.2%, very low < 0.6%.

Table 4. Content and composition of organic matter and the main physical properties in reclaimed soils in the area of stand of *Robinia pseudoacacia*

Site and depth, cm		Humus, %	C extr. %, of total Org.C	Texture <2 mm and fractions (%) after USDA			Bulk density (Db), g/cm^{-3}	Particle density (Ds), g/cm^{-3}	Total porosity (Pt), %	Water cont. (W), %	kPa 33, % $W_{pF2.5}$	kPa 1500, % $W_{pF4.2}$	$W_{pF 5.6}$, % 75 % rel.air humidity
				Sand 2.0-0.05	Silt 0.05-0.002	Clay <0.002							
1.1	0-5	12.51	48.61	50.2	22.9	26.9	0.67	2.33	71.1	22.4	38.6	22.4	11.8
	5-15	11.90	68.90	42.3	28.5	29.2	1.31	2.55	48.6	24.7	36.5	24.2	13.2
1.2	0-5	6.58	61.36	48.1	32.1	19.8	1.07	2.52	57.6	17.6	28.3	21.3	11.4
	5-15	8.09	45.81	33.9	31.1	35.0	1.13	2.50	54.8	20.5	28.9	20.2	11.5
1.3	0-5	7.52	40.35	26.2	31.3	42.4	0.89	2.49	64.2	19.2	28.3	24.4	13.6
	5-15	9.65	52.53	31.4	29.1	39.5	1.22	2.66	54.1	19.4	43.6	25.2	14.1

Notes: (Cextr.) of total carbon extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH; (kPa_{33}) soil water retentions in weight percent at potential 33 kPa ($pF_{2.5}$) saturation with water to field capacity; (kPa_{1500}) soil water retention in weight percent at potential 1500 kPa ($pF_{4.2}$) a Wilting Point; ($W_{pF 5.6}$) – hygroscopic water content at 75 % relative air humidity

Table 5. Content and composition of organic substances in reclaimed soils

Layers and depth, cm	Org.C, %	Extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH			C_{ha}/C_{fa}	Org. C, % Humic acids fractions		Unextr. Org.C, %	Cfa extracted with 0.1N H_2SO_4, %	Optic characteristic (E_4/E_6)		Org. C NaOH, %
		C extr.%	Cha, %	Cfa, %		Free or R_2O_3 complexed	Ca complexed			Total Cha, %	Free Cha, %	
Reclaimed soil (profile1) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine												
A 0-14	1.13	0.43[a] / 38.05[b]	0.25 / 22.12	0.18 / 25.93	1.39	0.16 / 64.00[c]	0.09 / 36.00	0.70 / 61.95	0.07 / 6.19	3.43	5.36	0.42 / 37.17
1B 14-42	2.29	0.74 / 32.31	0.48 / 20.96	0.26 / 11.35	1.84	0.26 / 54.17	0.22 / 45.83	1.55 / 67.69	0.08 / 3.49	6.69	6.19	0.47 / 20.52
2A 42-68	10.05	6.76 / 67.26	4.86 / 48.36	1.90 / 18.90	2.56	100.00	0.00	3.29 / 32.74	0.22 / 2.19	7.75	7.75	6.76 / 67.26
3B 68-97	3.89	1.24 / 31.88	0.96 / 24.68	0.28 / 7.20	3.43	0.69 / 71.87	0.27 / 28.13	2.65 / 68.12	0.10 / 2.57	6.19	7.23	1.12 / 28.79
BC 97-150	1.45	0.42 / 28.96	0.25 / 17.24	0.17 / 11.72	1.47	0.16 / 64.00	0.09 / 36.00	1.03 / 71.03	0.05 / 3.45	5.79	6.35	0.41 / 28.28
Reclaimed soil (profile2) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine												
Ah 0-18	2.79	0.68[a] / 24.37[б]	0.53 / 18.99	0.15 / 5.38	3.53	0.20 / 37.74	0.33 / 62.26	2.11 / 75.63	0.09 / 3.23	5.89	5.76	0.33 / 11.83
A1 18-37	2.59	0.75 / 28.96	0.75 / 28.96	0.00	–	0.15 / 20.00	0.60 / 80.00	1.84 / 71.04	0.09 / 3.47	6.52	4.82	0.38 / 14.67
1B 37-52	5.15	0.43 / 38.05	0.25 / 22.12	0.18 / 15.93	1.39	0.16 / 64.00	0.09 / 36.00	0.70 / 61.95	0.07 / 6.19	3.43	5.36	0.42 / 37.17
2B 52-120	0.29	–	–	–	–	–	–	–	–	–	–	–

Notes: (a) % of dry mass; (b) % of total carbon; (c) of total humic acids; (Cha) humic acids; (Cfa) fulvic acids; (E4/E6) optic characteristic; (Cha total) of pyrophosphate extract; (Cha free) of alkali extract

Profile 1 was characterized by irregular distribution of organic carbon (Table 5). In the surface mineral layers the content of organic carbon can be defined as low 1.13% and downwards it was stratified. In the buried (2A) layer located at the depth of 42-68 cm the amount of carbon sharply increased to 10.05%. Deeper a sharp decrease of organic carbon content 1.45% was identified at the most lower part, respectively in (BC) layer at the depth 97-150 cm. The content of organic carbon in profile 2 was relatively higher 2.79% in the surface layer, increasing to 5.15% at the depth of 37-52 cm. In the lower (2B) layer at the depth 52-120 cm it was negligible low 0.29%.

The amount of organic carbon, that was extractable with 0.1M $Na_4P_2O_7$ + 0.1M NaOH, was highly variable in the layers in profile 1 and gradually increased at the depth in profile 2. It was especially with the anomalous maximum values of 67.26% of total organic carbon in (2A) layer at the depth of 42-68 cm (profile 1). The content of extractable carbon was almost corresponded to the data of amount of extractable organic carbon in alkali extract with NaOH particularly in the layers (A), (2A) and (BC) in profile 1 and (1B) layer in profile 2. That means, that fraction of humic acids was composed almost of "free" humic acids not complexed with sesquioxides. Otherwise, sesquioxides should be identified within fraction extracted with NaOH.

Humic acids extractable with 0.1M $Na_4P_2O_7$ + 0.1M NaOH were characterized by low degree of humification. Free humic acids predominate in profile 1 which was a prerequisite for unfavorable physical properties and soil water movement. The maximum content 48.36% of extractable humic acids in profile 1 were 100% "free" humic acids identified in the layer (2A) at depth 42-68 cm, respectively the highest content of fulvic acids 18.90% was found there also. The content of humic acids complexed with calcium predominated to the 37 cm depth in profile 2, but sharply altered downwards. The content of fraction of aggressive fulvic acids (extracted with 0.1N H_2SO_4) was low 2.57-6.19%.

In the above-mentioned layers the intrinsic peculiarity of high mobility of organic substances was identified and the specific relationship within different fractions of extractable organic carbon stated. Inclusion of mixed micro particles or dispersed coal particles (Atanassova et al., 2018), could provoke variability on organic substances content and diverse distribution within stratification of soil profiles.

The ratio C_{ha}/C_{fa} defined humic humus type according to Kononova (1966). However, ratio of 3.53 is too high, which indicates contribution of mixed micro brown-coal particles. The amount of unextractable organic carbon from the total organic carbon was comparatively high 61.95-75.63% due to the nature of stable carbon. Lower content of unextractable organic carbon 32.74% was found in the layer (2A) at a depth 42-68 cm in profile 1, which indicated easily extractable organic carbon occurrence.

Studies have shown that there is a good correlation between the composition of humic and fulvic acids and their optical spectral characteristics consideration (Eshwar et al., 2017). Absorbance on wavelength 465 nm reflects the organic material at the beginning of humification, while absorbance on wavelength 665 nm shows a higher degree of condensation of aromatic constituents of the carbon structure and molecular

Table 6. Cation exchange capacity and degree of saturation with bases (%) in reclaimed soils, according to Ganev & Arsova (1980)

Layer and depth, cm	pH (H_2O)	Exchange cations, (cmol/kg^{-1} of soil) Note: (meq/100 g soil = cmol/kg)							Exchange cations, of $T_{8.2}$, %						Base saturation, %
		$T_{8.2}$	T_{SA}	T_A	$H_{8.2}$	Al+H	Ca	Mg	T_{SA}	T_A	$H_{8.2}$	Al+H	Ca	Mg	
Reclaimed soil (profile1) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine															
A 0-14	4.80	29.2	24.2	5.0	7.9	2.8	18.0	3.2	82.88	17.12	27.05	9.59	61.64	10.96	72.95
1B 14-42	5.20	29.5	25.0	4.5	5.2	0.9	21.0	3.4	84.75	15.25	17.63	3.05	71.19	11.53	82.37
2A 42-68	4.60	36.2	26.8	9.4	11.8	2.3	21.6	3.3	74.03	25.97	32.60	6.35	59.67	9.12	67.40
3B 68-97	5.35	35.5	30.0	5.5	6.2	0.8	26.0	3.5	84.51	15.49	17.46	2.25	73.24	9.86	82.54
BC 97-150	4.40	24.2	19.9	4.3	6.5	2.0	24.5	2.9	82.23	17.77	26.86	8.26	59.92	11.98	73.14
Reclaimed soil (profile 2) in a stand of *Robinia pseudoacacia* in the East Dump Site of the Troyanovo-3 Mine															
A1 0-18	7.00	41.3	37.5	3.8	2.0	0.0	35.6	3.7	90.80	9.20	4.84	0.00	86.20	8.96	95.16
A2 18-37	6.20	39.5	35.5	4.0	2.5	0.0	33.	3.7	89.87	10.13	6.33	0.00	83.54	9.37	90.63
1B 37-52	5.50	41.2	34.2	7.0	7.7	0.8	30.0	3.5	83.01	16.99	18.69	1.94	72.82	8.50	81.31
2B 52-120	6.85	30.4	27.2	3.2	1.4	0.0	25.5	3.5	89.47	10.53	4.61	0.00	83.88	11.51	95.39

weight (Albrecht et al., 2011). Optic characteristic of the ratio (E_4/E_6) of the total and "free" humic acids showed almost similar values (Table 5), which proves that humic acids are very similar in their molecular weight and structure to those of fulvic acids being with low molecular weight and with predominance of aliphatic over aromatic moieties in their molecules. Comparatively more mature humic substances were identified only in the surface layer 0-14 cm in profile 1 and in profile 2 in (1B) layer at the depth 37-52 cm.

Based on analysis of the specific physicochemical (ion exchange) values of the studied reclaimed soils, a physicochemical characterisation and diagnostics was made according to the method of Ganev & Arsova (1980). The quantity and quality of soil colloids is used as an important feature in soil characterisation. The sorption capacity of the soil is expressed by the total amount of ions that soil can retain in exchange under certain conditions. The hydrolytic acidity was determined by extraction with potassium or sodium acetate (pH 8.2), and treating of soil mass until complete extraction of the exchenge acidity. The saturation of the soil mass with neutral calcium dichloride in sufficient concentration has the task of displacing in the filtrate the cationic components of acidity at the strongly acidic positions (exchanged hydrogen, exchanged aluminum and other ions). (Table 6).

The cation exchange capacity measures the colloidal formation of the soils. Colloidal structures in the soil have negative charges on their surface, resulting from isomorphic substitutions in the crystalline lattices of clay minerals and from the acidic ionization of the functional groups of humic substances. These negative charges are compensated by positive charges of cations adsorbed on the colloidal surfaces (calcium, magnesium, potassium, hydrogen, aluminum, etc.). These can be exchanged with other cations of solutions, or called exchange cations. The substitution of weakly acidic hydrogen with basic cations is pH-dependent.

Reclaimed soils are characterized by well developed soil adsorbent in the surface layers in profile 1 ($T_{8.2}$ = 29.2 cmol/kg soil) and very well developed ($T_{8.2}$ = 41.3 cmol/kg soil) in profile 2. In profile 1 the constant cation-exchange capacity in the soils was without relationship with the clay fraction (<0.002 mm) distribution, probably because of the contribution of organic colloids which were concentrated in the sand fraction (Atanassova et al., 2018). In terms of adsorption structures quality, the relative share of strongly acidic ion exchange positions (T_{CA}) was about 74.03-90.80% with minimal differences in different parts.

The exchange hydrogen ($H_{8.2}$) showed initial soil acidification (17.46-27.05% of $T_{8.2}$) with higher identified value (32.60% of $T_{8.2}$) in the (2A) layer at a depth of 42-68 cm. Content of exchangeable (Al + H) varied in profile 1 and was negligible low (1.94%) in profile 2. Data on soil acidification (exchangeable $H_{8.2}$) was about 27.05-32.60% of $T_{8.2}$ in profile 1 and together with the appearance of exchange aluminum (Al + H) about 9.59% of $T_{8.2}$ in the surface (A) layer (0-14 cm), 6.35% of $T_{8.2}$ in (2A) layer (42-68 cm) and 8.26% of $T_{8.2}$ in (BC) layer were sufficient to affect not only the weakly acidic exchange positions (T_A) of the adsorbent, but also the strongly acidic adsorbent positions (T_{CA}).

Soil pH (H_2O) was diverse from 4.8 in (A) layer and 4.4 in (BC) layer to 5.2-5.35 in (B) layers in profile 1, respectively from 5.5 to 7.0 in profile 2. Weakly acidic positions (T_A) and strongly acidic positions (T_{SA}) of the soil adsorbent were affected by acidification so there were initial destructive processes identified in the soil adsorption complex. Reclaimed soils were characterized by relatively high degree of saturation with bases (67-82%) in profile 1, probably due to the high saturation with Ca and Mg by organic colloids and very high saturation 81-95% in profile 2.

Conclusion

The studied reclaimed soils under *Robinia pseudoacacia* contain an amount of ancient organic substances that cannot be decomposed, due to the nature of stable carbon leading to water repellency. Carbon stabilization mechanisms are based on the concept of biochemical return, in which organic molecular structures are inherently resistant to degradation by the activity of microorganisms. The precise determination of changes in organic carbon stocks in reclaimed soils can only be assessed with limited accuracy.

The different sized mineral textural elements are inherited during the technical activities of excavated materials. Despite the high content of organic substances, soil particle density was identified also as high. This specific feature related to the physical properties of reclaimed soils is probably due to the presence of brown-coal particles.

The intrinsic peculiarity of high mobility of organic substances was identified and the specific relationship with different fractions of extractable organic carbon was established. Humic acids by their molecular weight and structure are very similar to those of fulvic acids being low molecular and with predominance of aliphatic over aromatic moieties of their molecules. Probably the relationship with bulk density is not clearly expressed in cases of labile organic matter not bound to the soil mineral part.

Soil pH (H_2O) was diverse from acidic to neutral. Soil adsorbent was affected by acidification so there was evidence of initial destructive processes of the soil adsorption complex. Reclaimed soils were characterized by relatively high degree of saturation with bases.

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