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ECOLOGICAL TESTING OF OVERBURDEN ROCKS AFTER A LONG PHYTOMELIORATION PROCESS

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Abstract: All technosols belong to slightly alkaline substrates, with the exception of dark gray shale clay (pH 6.6). The concentration of soluble salts and manganese was the highest in the dark gray schist clay. The humus content does not exceed 1.4% in the phytomeliorated rocks. It was established that phytomelioration led to change intensity of reflectance of loess like loam from 0.6 to 0.53. The presence of fossil carbon was reflected in the spectrum of dark gray schist clay. The interpretation of VIS–NIR spectra of overburdened rocks should be done taking into account their geological age, formation and the stage of phytomelioration.

Keywords: technosols, chemical and physical properties, phytomelioration

1. INTRODUCTION

Rocks brought to the earth's surface enter into active interaction with the environment (lithosphere, atmosphere, hydrosphere, and biosphere) and find themselves under the impact of intense weathering (*Menéndez and Loredo, 2018*). The duration of their geochemical activity existence depends on their composition (*Borůvka et al., 2005; Navarro et al., 2008*). There are technical and biological kinds of mineland reclamation (*Kuter, 2013*). Technical reclamation is the most mass-intensive and energy-intensive stage. This is due to the movement and stacking of large masses of rocks and the humus layer of soil removed before development in a certain order.

The work related to increasing the fertility of the top layer of dumps is the most difficult (*Legwaila et al., 2015; Vondráčková et al., 2017*). The possibility of acid migration to the surface of the dump is not excluded, if the lower layers of man-made substrate consist of particularly toxic rocks. This risk is increased in arid conditions when evaporation exceeds precipitation. Creation of an underlying layer of the necessary capacity and application of potentially fertile rocks suitable for biological reclamation to its surface is the ultimate step of the technical stage of landscape restoration. It is most expedient to carry out the technical stage of reclamation in one cycle with the development of minerals to include it in the technological process of production.

The biological stage of land reclamation involves restoration and formation of soil cover, accumulation of humus and nutrients. crops of perennial legumes and grasses or their mixtures (*Tarika and Zabaluev, 2001; Wong, 2003, Le et al., 2017*). The implementation of the stage of biological reclamation leads to an increase in the organic carbon content of the soil (*Sheoran et al., 2010*). Man-made soils (technosols) differ significantly from zonal soils in the level of fertility, physical and physico-chemical indicators, despite the fact that reclamation processes last several decades. Therefore, the assessment of the properties and composition of rocks brought to the surface provides a certain perspective for assessing the effectiveness of land reclamation.

Last years the hyperspectral imaging technology has been widely used in quality classification, component detection, and other related studies of soils (*Nawar et al., 2016*). Visible–near infrared diffuse reflectance (vis–NIR) spectroscopy nondestructive and repeatable analytical technique well suited for analyses of SOM. (*Ba et al., 2020*). Meantime the accuracy of Vis–NIR needs to compare new data with obtained by conventional laboratory methods for estimating SOM. The potential of vis–NIR spectroscopy and PLSR for prediction of chemical and physical properties (silt, clay, organic carbon, total nitrogen etc) of soils representative of three Mediterranean agro–ecosystems from the Campania region, southern Italy was evaluated (*Leone et al. 2012*). It was demonstrated that VIS–NIR spectra can provide a viable alternative for the rapid determination of SOM content, mainly owing to the various chemical bonds,

such as C–H, O–H, N–H (Stenberg *et al.*, 2010). The near infrared (NIR) and the short-wave infrared (SWIR) spectrums were more accurate to prediction of soil organic carbon in the red Mediterranean soils from Croatia (Miloš and Bensa, 2017). The wavelengths contributing most to the prediction of SOC were at: 1925, 1915, 2170, 2315, 1875, 2260, 1910, 2380, 435, 1960, 2200, 1050, 1420, 1425 and 500 nm.

The main objective of our study was to see the prospect to use hyperspectral imaging technology as approach to compare spectra for technosols with different geological age and stage of phytomelioration.

2. MATERIALS AND METHODS

Overburden rocks of the Nikopol manganese ore basin are represented by Holocene, Pliocene, Miocene, and Paleocene deposits (Figure 1, Table 1).



Figure 1 – Quarry pit quarry board panorama

Table 1. Stratigraphy of mining rocks of the Nikopol manganese ore deposit

Substrata	Rock age, period (era)	Depth, [m]
Black soil, loess like loam	Quaternary (Holocene)	0–7
Red brown clay	Neogene (Pliocene)	7–12
Grey green clay	Neogene (Miocene)	12–47
Darc grey schist clay	Paleogene (Paleocene)	63–71

Hydrosilicates of aluminum, magnesium and iron (clay minerals) with the addition of feldspar, calcite and chlorites are the main minerals of the investigated technosols (Kharytonov, 2007; Kharytonov & Resio Espejo, 2013).

The total share of clay minerals varies from 23.5% to 63.5% depending on the type of substrate. The clay fraction of dark gray schist and red-brown clay is represented mainly by hydromicas. Montmorillonite is the main component of gray-green clay. The distribution of all clay minerals in loess loam and black soil is more or less the same.

The objects of research in the pot and field experiments were overburden and phytomeliorated rocks of the open pit of the Nikopol manganese ore deposit, represented by loess like loam (LLL), red-brown clay (RBC), gray-green clay (GGC), dark-gray schist clay (DGSC), as well as two layers of black soil from an artificial reclamation profile: a bulk layer of black soil on a sand substrate (BS+Sand) and a bulk layer of black soil on loess-like loam (BS+LLL).

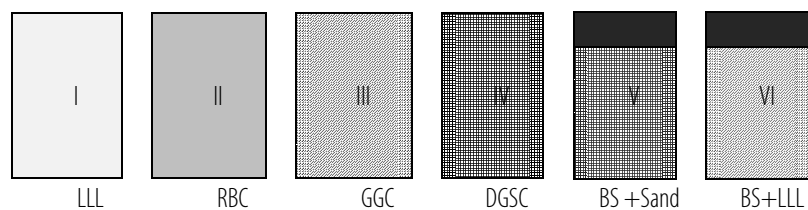


Figure 2 – Soil profiles in pot experiments

In the first pot experiment, rocks (LLL, RBC, GGC and DGSC) and black soil were under successive rotation of leguminous (alfalfa and peas) and cereal (barley and corn) crops for 20 years.

Part of the scheme for conducting the second pot experiment with overburden rocks is shown in Figure 2. For the last 8 years, testing of the fertility of "young" soils took place by growing miscanthus. As usual the soil mass is taken off, piled up and heaped onto the land after the rock has been replaced (Figure 3).



Figure 3 – Land reclamation process and soil storage in the day surface

The mass of black soil removed as a result of the development of manganese ore is stored in heaps without the usual interaction with the ecotope. This leads to rapid degradation of black soil fertility.



Figure 4 – Field experiment on several phytomeliorated rocks

The four types of rocks brought to the surface are in a state of biological weathering under the action of phytomelioration for about 50 years (Figure 4).

Determination of pH, mineralization of techno-zems was carried out by ordinary methods. The content of manganese, as the element that is found in the studied techno-zems in the largest quantity, was determined using atomic absorption analysis on a S-115 spectrophotometer.

The soil texture and particles size were determined with “Mastersizer” 3000E analyzer. FieldSpec Pro 30 with a spectral range of 350–2500 nm was applied to detect spectra for samples with different duration of their plant melioration.

3. RESULTS

The data of particle size distribution in the four technosols are shown in the table 2.

Table 2. Technosols soil texture, [µm]

Rock	Medium sand (200–630µm)	Fine sand (125–200µm)	Very fine sand (63–125µm)	Sand (63–2000µm)	Coarse silt (20–63µm)	Fine silt (2–20µm)	Silt (2–63µm)	Clay (<2µm)
LLL	0	0	0	1.45	33.24	60.2	93.45	5.1
RBC	0	0.1	1.53	1.64	7.22	70.72	77.94	20.42
GGC	2.52	2.96	5.29	10.77	24.83	56.77	81.6	7.63
DGSC	0.55	4.94	14.14	19.63	34.31	42.78	77.09	3.28

The red brown and dark grey schist clay soil texture characterize as silt loam, loess like loam and grey green clay – as silt.

The pH values of the soil and phytomeliorated rocks varied from 6.6 (dark gray clay) to 7.9 in other samples. It is known that the best conditions for plant growth are created with a neutral reaction of the soil solution (Gould *et al.*, 1996). Leguminous plants begin to react negatively when the pH drops to 5.5. This is due to increased levels of iron, manganese and nickel (Maiti, S.K., Ghose M.K., 2005). This growth blocks the growth of the plant root system and many other metabolic processes (Gitt and Dollhopf, 1991). Increased soil mineralization is one of the limiting factors for crops cultivation. The determination of the general mineralization of technozems showed the presence of weak salinity of the sulfate–chloride type in some rocks (Figure 5). Thus, in the gray–green clay, an increased concentration of soluble salts was found both in the arable (0.214%) and in the subsoil (0.202%) layer. In dark gray schist clay, salinization was observed only in the subsoil layer, but it was stronger than in gray–green clay (0.281%).

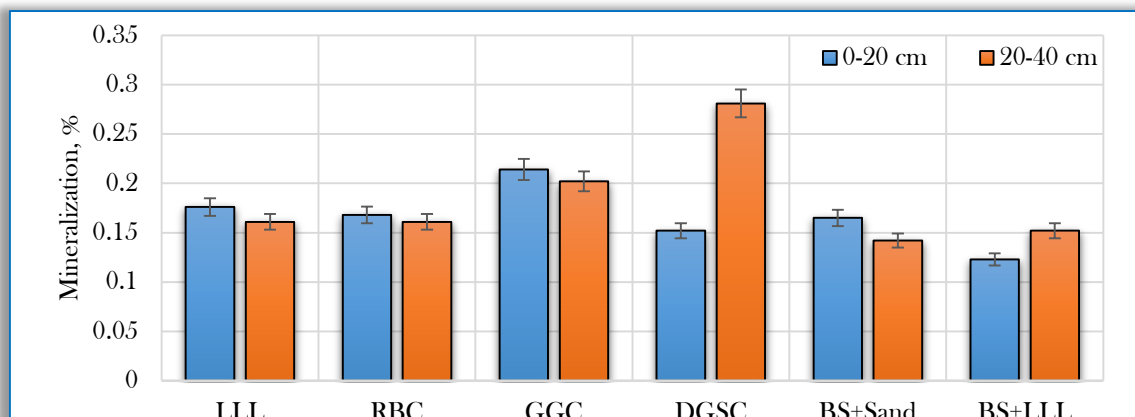


Figure 5 –The value of the total mineralization of the water extract of the soil and phyto–reclaimed rocks

The content of manganese in the investigated technics is in the range of 70.3–297.4 mg/kg (Figure 6).

The lowest concentration of the element was observed in red–brown clay, and the highest in dark gray shale clay.

The long term pot experiment data obtained allow us to estimate the growth rate of the amount of humus in the plant meliorated substrates of rocks and soil (Figure 7). The 20–year presence of rocks

under the influence of plants contributed to an increase in the amount of humus (5–8 times) in loess like loam, red brown and grey green clays.

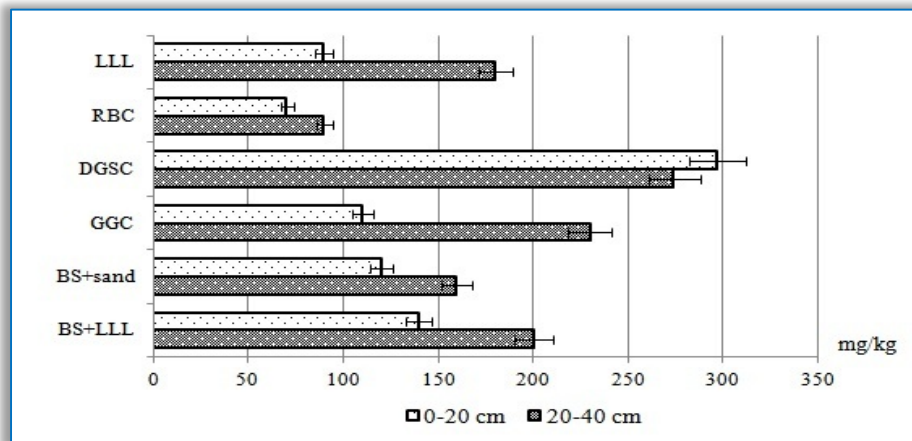


Figure 6 – Manganese content in different types of techno-zems, mg/kg.

It is known that the rocks of the Nikopol manganese ore deposit are of sedimentary origin. Dark grey schist clay takes a special place due to the significant content of the organic carbon (1.4%) and pyrite traces.

In the USDA system black soils (chernozems) fall into the broad grouping of mollisols. They generally have a high cation exchange capacity (CEC). The CEC of the upper profile is derived from humus with pH-dependent charge and clay-sized phyllosilicates having permanent charge (Liu *et al.*, 2012).

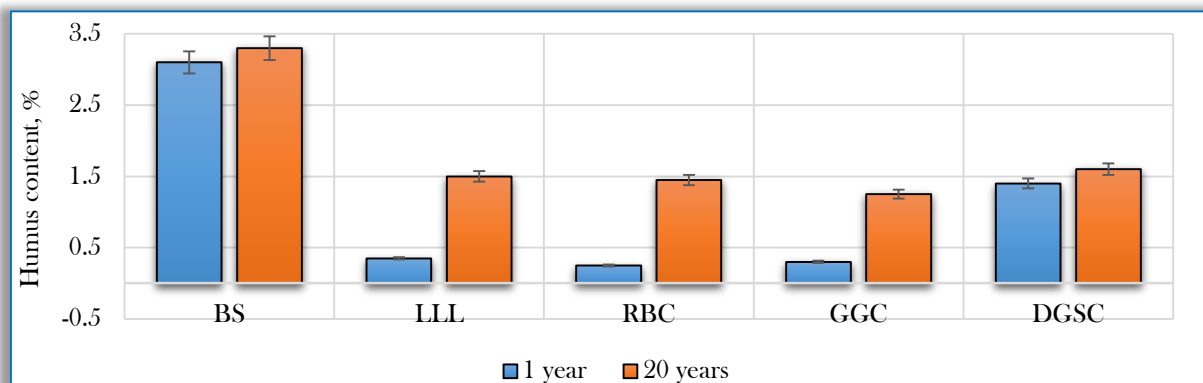


Figure 7 – Changes in humus content in soil and rocks after 20 years of plant melioration

Both black soil and loess like loam are riched with carbonates (Kharytonov *et al.*, 2004). The data on spectra of degraded black soil and overburden rocks after 8 years of plant melioration are shown in the figure 8.

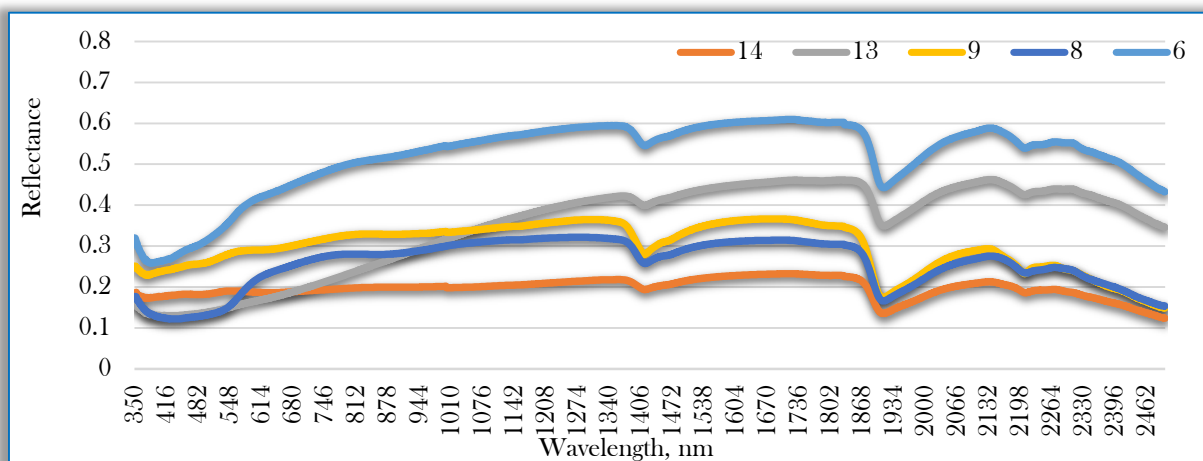


Figure 8 – Spectra of overburden rocks and black soil

Legend: 6–loess like loam; 8–red–brown clay; 9–grey–green clay; 13–degraded black soil; 14–dark–grey schist clay

Loess like loam had a highest reflectance 0.6. Dark grey schist clay had spectral curve with low reflectance in the range between 500 and 800. It is known that the presence of a linear shape of the spectral line with a low slope of the curve is typical for soils with high SOC content (Latz *et al*, 1984). In our case, it must be taken into account that the dark gray clay is a shale deposit. However, later it turned out to be difficult to use it as an organic soil amendment (Kharytonov *et al*, 2019). The data on spectra of black soil and technosols after 50 years of phytomelioration are shown in the figure 9.

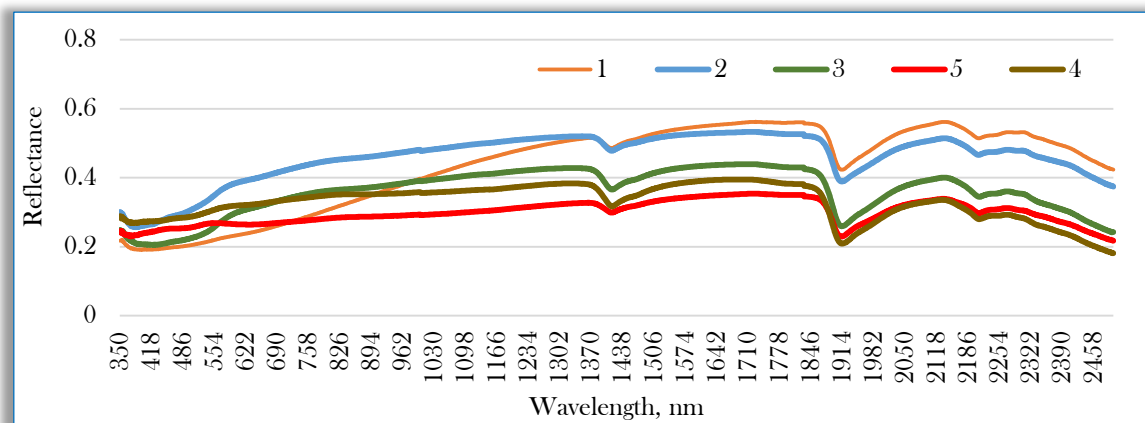


Figure 9 – Spectra of black soil and technosols under 50 years phytomelioration

Legend: 1–degraded black soil; 2– loess like loam; 3 – red brown clay; 4–grey–green clay; 5– dark–grey schist clay

The long term phytomelioration led to decreasing of the intensity of reflectance for all studied soil substrata. It has also been established that the absorption band in the wavelength region of 2342 nm indicates the presence of CaCO_3 in the soil (Hunt and Salisbury, 1971; Conforti and Buttafuoco, 2014). Obviously, the increase in the reflection coefficient of black soil and loess–like loam within the same limits is associated with the presence of carbonates.

4. CONCLUSION

Overburden rocks of the Nikopol manganese ore basin are represented by Holocene, Pliocene, Miocene and Paleocene sediments brought to the earth's surface in the process of manganese ore mining. The studied rocks belong to slightly alkaline substrates, with the exception of dark gray schist clay (pH 6.6). The concentration of soluble salts and the content of manganese were highest in the subsoil layer of dark gray schist clay. Phytomeliorated rocks are weakly humus – rich.

It was established that phytomelioration led to change intensity of reflectance of loess like loam from 0.6 to 0.53. Dark grey schist clay had spectral curve with low reflectance in the range between 500 and 800. The presence of fossil carbon was reflected in the spectrum of dark gray schist clay.

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