Assessment of the soil formation process in reclaimed terrains in Bulgarian copper mine

V V Stefanova¹, P G Petrov¹ and E I Zheleva¹
¹Department Ecology, Protection and Remediation of the Environment, University of Forestry, 10 Sv. Kl. Ohridski blvd, 1756 Sofia, Bulgaria

E-mail: venistefanova3@gmail.com

Abstract. One of the most important preconditions of ecosystem rehabilitation in post mining landscapes is the soil formation process. In this context, the soil samples from Ellatzite copper mine are analyzed according to key parameters – the content of heavy metals, alkali and alkaline earth metals, nitrogen, phosphorus and organic matter. The results of the study show that there are soil formation processes in reclaimed terrains whose speed and qualities depend on the soil-forming materials and the type of vegetation.

1. Introduction
Extraction of minerals leads to significant changes in the landscape of large land areas that are partly or wholly disrupted.

Formation of embankments resulting from mining has a significant impact on the environment because it damages much larger areas than the deposits themselves. They change the ground water regime, the natural geochemical migration of the elements, the processes of erosion etc. [1,2].

Embankments from such substrates are unstable and they hide potential problems for human health and the environment - related to the generation of acidic water and pollution of surface and groundwater, dust formation, leaching of heavy metals, soil damage, disturbance of vegetation growth [3,4].

Compared to natural soils, mining soils are characterized by poor structure, lack of characteristic soil horizons and nutrients, high content of toxic elements and poor moisture retention [5].

The environmental risk that mines hide remains even after the end of their work. This necessitates their recultivation [6].

The recultivation of these sites aims at restoring their ecological integrity [7].

The recultivation of disturbed terrains is a complex activity for restoration of damaged lands with the aim of their future rational use and improvement of environmental conditions related to the interests of society.

The reclamation of disturbed terrains is aimed at creating balanced ecological systems representing socio-economic and aesthetic values for humans [8-11].

The success of reclamation of disturbed terrains depends on knowing and reducing the influence of limiting factors such as the content and mobility of heavy metals in soil substrates, regulating acidity, low nutrient content etc. [12].

This article aims to evaluate the physical and chemical indicators of soils taken from recultivated terrains to determine the development of the soil-forming processes in them and the restoration of the ecosystem on them.
2. Materials and methods

2.1 Study area

The two areas, chosen for the study included: the Eastern embankment of Ellatzite mine (Etropole city) and tailing pond „Benkovski 1 “(Benkovski village).

The Ellatzite mine is an open pit deposit for copper and gold located in West Balkan Mountain. Reclaimed lands in Eastern embankment are situated at elevation between 1340 and 1302,5 m with area of 22,042 da. They are steep and they are built of rigid acid rocks and large particle materials [13]. The Eastern embankment was reclaimed in 2011 with trees species – *Pinus sylvestris* L. and *Betula pendula* Roth. The tailing pond „Benkovski 1 “is located entirely in the village of Benkovski. The disturbed land was reclaimed in 1997 with *Robinia pseudoacacia* L.

2.2 Soil sampling

For the purpose of this study were taken three soil profile in June 2018. Every profile had been taken under different tree species: Profile 1 (Eastern embankment) - *Pinus sylvestris* L., Profile 2 (Eastern embankment) - *Betula pendula* Roth., Profile 3 was taken from tailing pond „Benkovski 1 “- *Robinia pseudoacacia* L.

2.3 Soil analysis

The following analyses were conducted. Soil reaction (pH) was measured potentiometrically by ISO 10390. The organic carbon and humus content were measured in all cases by Tyurin titrimetric (Tt) method. The total nitrogen in soil was determined by the Kjeldahl method. The total content of heavy metals, alkaline and alkaline earth metals was determined by dissolving in aqua regia and atomic absorption spectrometry (AAS).

3. Results and discussions

3.1. Acidity of soil-forming materials and basic agrochemical characteristics

The acidity and agrochemical characteristics characterizing the fertility of the substrates are presented in Table 1.

| Soil Profile | Dept cm | pH | Hummus % | C % | N % | P2O5 mg/100g |
|--------------|---------|----|----------|-----|-----|--------------|
| Profil 1     | 5-0     | 4,6 | 4,1      | 4,29 | 2,49 | 0,126 | 7,25 |
|              | 0-18    | 4,3 | 3,8      | 1,76 | 1,03 | 0,136 | 1,5  |
|              | 18-30↓ | 4,4 | 3,87     | 1,69 | 0,98 | 0,112 | 1,5  |
| Profil 2     | 3-0     | 5,3 | 4,8      | 2,06 | 1,19 | 0,127 | 3,75 |
|              | 0-25    | 4,6 | 4,0      | 0,73 | 0,42 | 0,059 | 2,75 |
|              | 25↓     | 4,9 | 4,3      | 0,07 | 0,04 | 0,028 | 2,25 |
| Profil 3     | 5-0     | 6,1 | 5,5      | 1,19 | 0,69 | 0,145 | 6,50 |
|              | 0-25    | 6,1 | 5,6      | 0,96 | 0,56 | 0,099 | 1    |
|              | 25↓     | 7,9 | 7,2      | 0,44 | 0,26 | 0,010 | 0,75 |

3.1.1 Soil acidity. The soil acidity of the studied substrates is very varied and mainly in the acidic range. The soil profiles taken from the Eastern embankment are characterized by a strong acidic and acidic soil reaction (pH). This is mainly due to the geological composition of the substrates. Substrates in Profile 1 are very acidic. This acidity can cause growth inhibition of plants, inhibit the metabolic processes of some microorganisms, reduce the development of nitrogen-fixing bacteria, increase the
bioavailability of heavy metals [13-15]. The litter fall from Profile 1 is higher in comparison with that in Profile 2. The reason for this is that under the pine plantations is formed litter fall with acid reaction, while the birch plantation leads to an increase in pH. However, the substrates in Profile 2 are still highly acidic.

Soil substrates under plantations of *Robinia pseudoacaia L.* are typically characterized by the formation of soils with pH (H2O) in the range 4.6-5.2 [16]. In the studied substrates in Profile 3, the acid reaction ranges from slightly acidic and slightly alkaline to the deepest horizon. The reason for this is the process of enriching ores with calcium-containing materials that give the tailings an alkaline reaction. Reclamation of this terrain uses natural soils from the area, which have a pH of about 5.5. However, there is a rise in pH due to an increase in the calcium content as a result of capillary forces. The profile is also characterized by the highest calcium content (Table 3) as compared to other profiles.

Values of exchangeable acidity can be an indicator of destructive processes and changes in plant nutrition [14]. Their low value in Profiles 1 and 2 is related to the low content of calcium and magnesium. These values may be the reason for uptake of some toxic elements by plants.

3.1.2 Soil organic matter. The humus content follows the natural downward trend in all profiles. Profile 1 that is taken under pine trees is characterized by the highest humus content. The litter fall is determined with a high humus content, and the other two layers are low humus according to the scale of Gurov and Artinova. This is to be expected because the litter fall beneath the pine plantations is difficult to mineralize. The humus content is low in the surface layers, and in depth it can be defined as very low in the other two profiles [17]. The reason for this is that Betula pendula Roht. and Robinia pseudoacacia L. form a smaller amount of litter fall that quickly mineralizes and does not produce humus. The amount of organic matter is extremely low in the deepest layers of Profile 2 and Profile 3. The contained "humus" in them is rather due to the carbon that is contained in some minerals rather than the organic matter in them.

Naturally, the profiles taken from higher altitudes are characterized by a higher humus content as organic matter under these conditions degrades more slowly and accumulates in larger quantities as coarse humus [7].

3.1.3 Essential soil nutrients. Nitrogen content in soils is directly related to the organic matter content. In the studied substrates, nitrogen content varies between 0.010% and 0.216%, following the downward trend. In Profile 1, the nitrogen (total N) stock is defined as the mean in the deeper horizons to the largest in the litter fall. Profile 2 is characterized by a low stocking density in the litter fall and very small in depth. Although Robinia pseudoacaia L. is a nitrogen-fixing species and its litter fall is characterized by a high nitrogen content [16], in Profile 3 the nitrogen stock is very small to small [18].

The phosphorus content varies at different depths, following the downward trend. MGP on Profile 1 and Profile 3 are characterized by the best phosphorous stock. They are classified with average stock. In the rest of the depths, the stock is weak. The data show the need for further introduction of phosphorous fertilizers in reclaimed terrains. This is also due to the fact that the pH varies within the acidic range, which creates a prerequisite for blocking the phosphorus compounds.

3.2. Content of heavy metals, alkaline and alkaline earth elements

3.2.1 Content of heavy metals. The heavy metal content data are presented in Table 2. For the analysis of concentrations of heavy metals are used precaution values and maximum permissible values defined by Ordinance No. 3 of 2008; for the content of iron and manganese are used the indicated concentrations of Gurov and Vinogradov.

Iron is an accompanying element of mining. This suggests higher concentrations of this element in soil samples. According to Gyurov, the average iron content in soil in Bulgaria is 3.8 % or 38 000 mg/kg. In Profile 1 and 2 iron content exceeds the average iron content in soils in Bulgaria almost twice, with a gradual increase of iron in depth which indicates that its excess amounts result from its higher amount in soil-forming materials. The iron content is close to the average iron content in soil in Bulgaria and below these values.
Table 2. Content of heavy metals.

| Soil Profile | Dept cm | Fe mg/kg | Mn mg/kg | Cu mg/kg | Cd mg/kg | Zn mg/kg | Pb mg/kg |
|--------------|---------|----------|----------|----------|----------|----------|----------|
| Profil 1     | 5-0     | 51394    | 735      | 292      | 1,63     | 68,3     | 29,6     |
|              | 0-18    | 56122    | 920      | 264      | 1,33     | 43,9     | 33,7     |
|              | 18-30   | 57522    | 718      | 320      | 1,17     | 40,3     | 31,6     |
|              | 3-0     | 59265    | 488      | 376      | 1,43     | 53,6     | 39,80    |
| Profil 2     | 0-25    | 58252    | 344      | 306      | 0,91     | 34,30    | 40,40    |
|              | 25↓     | 60882    | 266      | 306      | 1,24     | 38,10    | 46,40    |
|              | 5-0     | 19500    | 239      | 350      | 1,67     | 28,80    | 10,60    |
| Profil 3     | 0-25    | 38421    | 404      | 146      | 1,28     | 75,50    | 30,10    |
|              | 25↓     | 16177    | 213      | 398      | 0,82     | 20,90    | 7,10     |
| Precaution values, mg/kg |        |          |          |          |          | 60       | 0.6      | 160      | 45       |
| Maximum permissible values, mg/kg |        |          |          |          |          | 500      | 10       | 600      | 500      |

The manganese content is below the average for Bulgaria (1000 mg / kg) [14] in all three profiles. Only in Profile 1 the manganese content exceeds the mean concentration - 600 mg/kg [19]. All three profiles show the highest manganese content in layer 0-18, due to increased element mobility under these conditions due to the low values of pH.

By analyzing the copper content - the element - the reason for the mining and which can be assumed that naturally is in larger quantities in the soil substrates, it is found that its content exceeds the precaution values in soils regulated by Ordinance № 3/2008 from 2 up to 6 times but does not exceed the maximum permissible values. The trend of increasing content in depth is observed in Profile 1 and Profile 3 due to the presence of the element in soil-forming materials. In Profile 2, the trend is reversed. This profile has a decrease in copper concentrations in depth. The highest content in litter fall is Profile 2 where it exceeds precaution values for this element 6.2 times.

Higher copper content is observed in litter fall compared to the 0-18 cm layer on profile 1, probably because the sampling points are located at the base of a steep slope, and it is possible under specific conditions to form dust deposits carried by the upper parts of the slope or as a result of aerosol deposition from the transfer of particulate matter from the open pit.

Cadmium is one of the most toxic metals. Its increased soil content is considered to be the result of anthropogenic contamination. In the studied profiles it is the other element, which exceeds the precaution values, but it also does not exceed the maximum permissible values. Cadmium content exceeds the precaution values in the litter fall (Profile 1 - 2.7 times, in Profile 2 - 2.45 times, in Profile 3 - 2.7 times). This is due not only to aerosol deposits but also to its accumulation of vegetation deposited on the surface of the embedded surfaces. Cadmium content following the downward trend. However, there is also a tendency to exceed precaution values (Profile 1 - 1.9 times, Profile 2 - 2 times, Profile 3 - 1.3 times).

Lead accumulates in the humus-rich upper soil horizons. The results of the analyzes show that in the studied substrates there are no exceedances of maximum permissible values. There is no pronounced trend for the distribution of zinc in depth. The results of the analyzes indicate that there is no excess of the zinc precaution values.

3.2.2 Content of alkaline and alkaline-earth elements. The data on alkaline and alkaline-earth elements are presented in Table 3. For the analysis of concentrations of alkaline and alkaline-earth elements are used the average values for this elements in soil in Bulgaria.

Calcium is a macro element that improves the structure, general physical, physical-mechanical, water and air properties of the soil. It plays an important role in soil formation. Calcium is involved in buffer systems that regulate the soil acidity, it prevents destruction of the soil absorption complex and
it is an important element for soil fertility. All substrates are classified as poorly stored with respect to their calcium content. Element content is highest in Profile 3 due to tailings treatment with calcium-containing materials during the flotation of copper containing ores. There is no clear trend in the distribution of calcium in depth.

The studied substrates are characterized by a very low magnesium content. Like calcium, there is no clear trend in the distribution of the element in depth of the profile. In all three profiles, the Ca: Mg ratio has opposite values to those in natural soils, which can cause clay dispersion and reducing water infiltration.

Soil substrate analyzes show a very low supply of potassium and sodium. There is no clear trend in the distribution of elements in depth.

4. Conclusion
From the analysis we can conclude that on the recultivated terrains through forest-biological recultivation under the ecological conditions of the Elatsite mine area there are soil-forming processes. The speed and the qualities of soil forming processes depend both on the qualities and properties of the soil-forming materials and the type of vegetation.

5. References
[1] Hou H C, Wang Z, Ding S, Zhang Y, Yang J, Ma F, Chen I D and Li J 2018 Sustainability 10 2286
[2] Kundu N K and Ghose M K 1997 Indian Journal of Soil and Water Conservation 25(1) 28-32
[3] Mendez M R and Maier M 2018 Environmental Health Perspectives 116 278-283
[4] Otte M L and Jacob D L 2008 Applications in Ecological Engineering 90-97
[5] Sheoran V, Sheoran A S and Poonia P 2010 International Journal of Soil Sediment and Water: 3(2) 13
[6] Leia K H and Panb C Lin 2016 Ecological Engineering 90 320-325
[7] Желева Е П Петров П Божинова С Иванова Б Пенчева А Бралтова (2017) Отчет: по тема № 919/2017 г Мониторинг на почвите в района на Елаците Мед АД НИС-ЛТУ
[8] Petrov P, Zheleva E and Ivanova S 2016 Journal of Environmental Protection and Ecology 17(4) 1324-1333
[9] Baker L R, White P M and Pierzynski G M 2011 Soil Ecolology 48 101-110
[10] Tandy S, Healey J R, Nason M A, Williamson J C and Jones D L 2009 Environ Pollution 157 690-697
Acknowledgements
The financial support of the Project BG05M2OP001-2.009-0034 „Support for the Development of Scientific Capacity at the University of Forestry” is greatly acknowledged.