Technosols from the Area of Assarel-Medet Mining and Processing Complex in Panagyurishte Municipality, Bulgaria

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Abstract

The paper summarizes the results of Technosols studies related to mining and processing of copper ore. Natural soils and those influenced by anthropogenic activity are identified and briefly indicated. Their distribution at administrative level is visualized, similar to the geographical location of the studied sites. Because of the studies carried out, the substrates included in the composition of built spoils, their supply with nutrients and some unfavourable characteristics requiring ameliorative activities were marked. The results of the discussed studies are combined in several summaries related to the content of heavy metals, pH activity, basic agrochemical characteristics, content of sulphur and its predominant forms in substrates from the different technogenic sites. The established positive influence of the ameliorative measures in relation to the studied Technosols is highlighted. Specific properties of plant species used in biological reclamation of spoils are briefly marked.

Key words: mining activity, copper ore, Technosols, acidity, heavy metals, amelioration

Introduction

Mining activity is one of the main factors having negative impact on soil by disrupting its functions and depositing of waste products accompanying the extraction and processing of minerals (Petrova, 2009). At a later stage, the restoration of fertility and productivity of disturbed lands is carried out through technical reclamation of the built spoils, including formation of suitable relief to limit the erosion processes and implementation of various reclamation measures in connection with subsequent biological reclamation, connected with the development of appropriate vegetation (Dimitrov, 1988).

Mine spoils are known as Technosols, which are artificial soils created by human activity that, in some cases, may contain substances harmful to plant development (IUSS Working Group WRB, 2006). Parts of them are the spoils containing sulphide minerals (Tsolova et al., 2013) or those that are contaminated during mining and processing of ores (Tsolova et al., 2014). In these cases, the biological reclamation becomes difficult to certain

extent due to the presence of limiting factors related to the specific composition and properties of the Technosols (Petrova et al., 2009).

The paper aim is to review the studies of Technosols, created because of mining and processing of copper ore and to summarize the main results of the research conducted regarding reclamation activities and heavy metals content.

Materials and Methods

Object of the study are reclaimed spoils from the area of Assarel-Medet Mining and Processing Complex in Panagyurishte Municipality. Discussions are carried out by comparing results of different authors based on conducted field and laboratory studies.

The natural soils in Panagyurishte Municipality have been established through the digital soil map of Bulgaria at scale of 1:400000 (ISSAPP „Nikola Poushkarov", archive) and are presented according to the World Reference Base for Soil Resources, WRB (IUSS Working Group WRB, 2022) after synchronization of their FAO names (Ivanov et al., in print).

The graphical representation of the soil map is performed using the geographic information system QGIS, 3.22, and the studied sites are visually indicated using OpenStreetMap (OpenStreetMap contributors, https://www.openstreetmap.org/copyright).

Results and Discussion

Soils

Panagyurishte Municipality covers an area of about 598.8 km^2. It is located in the northern part of Pazardzhik District, which is part of South Central Planning Region in Bulgaria.

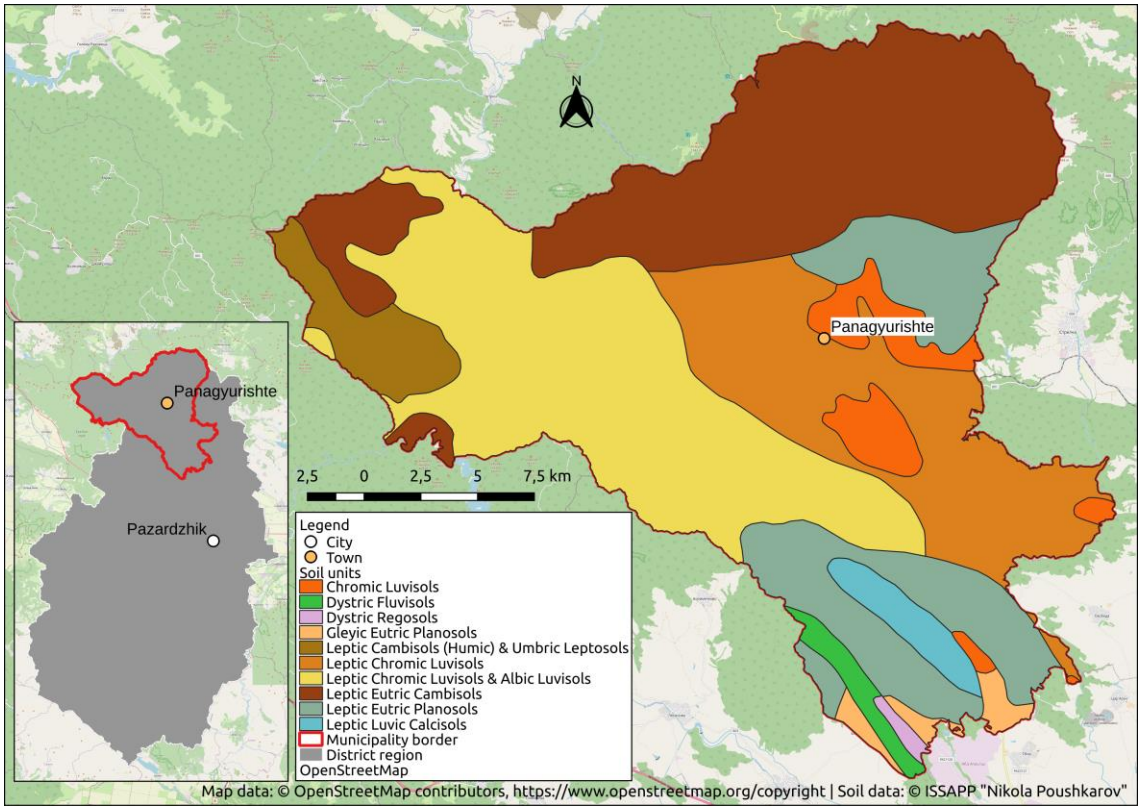


Figure 1. *Soil map of Panagyurishte Municipality, Pazardzhik District*

A large area of the Municipality is located in the Sashtinska Sredna Gora Mountain, which corresponds to the soil cover, represented mainly by Luvisols with their varieties, as well as Cambisols and Planosols. There are also areas with Fluvisols, Calcisols and Regosols in the southern part of the Municipality (figure 1).

Sites

In the northern part of Panagyurishte Municipality, the Cambisols are spread. They are characterized by coarse texture and thickness of the soil profile below 30 cm (figure 1; ISSAPP „Nikola Poushkarov", archive). The soils are formed from different hard rock materials (mainly acid granites, rhyolites, etc), which affects their acid pH values (Gyurov and Artinova, 2015). This area has been affected by anthropogenic activity related to the extraction of copper ore from Assarel-Medet Mining and Processing Complex (figure 2). Medet mine started operations in 1964 and continued until 1994 when Assarel mine is opened. Ore mining is carried out using the open-pit method, accompanied by the construction of spoils of geological materials, which mainly have negative impact on the environment (Nikolov and Borisova, 2009). In the Medet mine area, these materials contain pyrite and are characterized by highly acid pH activity (Tsolova and Banov, 2017).

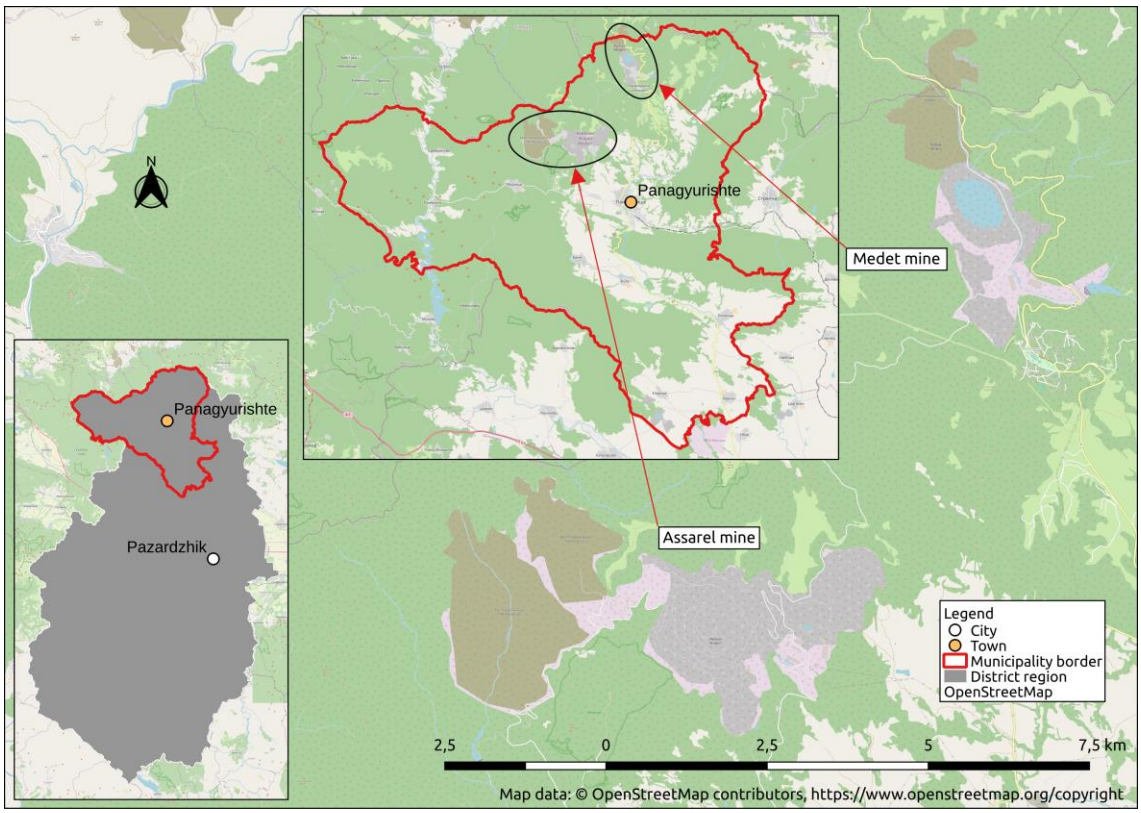


Figure 2. *Assarel-Medet Mining and Processing Complex in Panagyurishte Municipality, Pazardzhik District*

Spoils from Assarel mine include porphyry diorites, granites, gneisses, etc. They also have acid reaction, and this applies to both active (pH H_2O) and exchangeable acidity (pH $CaCl_2$) (Zheleva and Nustorova, 1998). Besides, the materials are very poor in plant nutrients and in conditions of very strong acid reaction of the environment contain higher

concentrations of copper, which is a main argument for carrying out the necessary ameliorative measures (Petrova and Gencheva, 2002).

Their precise implementation requires various preliminary studies to assess the deposited substrates, determine technological reclamation solutions (Zheleva and Nustorova, 1998; Bogdanov and Zheleva-Bogdanova, 2003; Petrova, 2009) and conduct future post-reclamation analysis (Tsolova and Banov, 2017; Atanassova et al., 2023).

Medet mine

Sever spoil from Medet mine area is studied after 20-year post-reclamation period of development in relation to the content and mobility of heavy metals in the Technosol (Tsolova and Banov, 2017). Similar extended studies, including determination of acidity, sulphur content and plant nutrients, are carried out on the substrates of *Small southern spoil* from the same mine (Petrova, 2009), as well as *Large southern spoil*, which is analysed for organic carbon content, physicochemical characteristics and pH activity approximately 20 years after the completion of biological reclamation (Atanassova et al., 2023).

For *Sever spoil*, Tsolova and Banov (2017) specify that it was ameliorated by liming and fertilizing during the technical stage of reclamation for better soil conditions, after which afforestation was carried out with Birch and Acacia. Regarding total copper content, the authors found exceeding of its maximum permissible concentrations (MPC) (Regulation № 3, 2008), ranging up to 668 mg/kg in sampling points from the surface 25 cm horizon, below which rock fragments of different sizes follow. Close maximum concentration of this element (629 mg/kg) characterizes the studied sites in *Small southern spoil* (Petrova, 2009), and the lowest values (Cu from 104.38 mg/kg to 422.77 mg/kg), although exceeding the MPC, are found in some of the sample points from surface 0-20 cm layer of *Large southern spoil*, which has been reclaimed with soil materials from the soils in the area and afforested with Pine and Birch between 1998 and 2006 (Atanassova et al., 2023). Unlike copper, the maximum content of zinc and lead in surface layer of *Sever spoil* does not exceed the MPC (Zn = 132.5 mg/kg; Pb = 22.5 mg/kg) (Tsolova and Banov, 2017). These concentrations are lower for zinc and similar for lead in *Small southern spoil* (Zn = 78 mg/kg; Pb = 25 mg/kg) (Petrova, 2009), and as for *Large southern spoil*, the content of the elements in the sample plots (Zn = 11.68-80.70 mg/kg; Pb = 18.02-37.85 mg/kg) also does not exceed the MPC (Atanassova et al., 2023) (table 1).

Table 1. *Heavy metals, pH and sulphur content in studied Technosols and substrates from Medet mine*

Site	Concentrations of heavy metals (mg/kg)[1]			pH (H_2O)	S (%)[2]
	Cu	Zn	Pb		
Sever spoil[3] (Tsolova and Banov, 2017)	668	132.5	22.5	5.6-8.5	-
Small southern spoil (Petrova, 2009)[4]	629	78	25	~ 5.3	0.30
Large southern spoil[3] (Atanassova et al., 2023)	422.77	80.70	37.85	4.6-7.1	-

[1] Maximum values found among all tested samples.
[2] Average values.
[3] Data refer to surface layer.
[4] Data refer to the studied substrates in general.

The pH activity varies randomly from moderate acid to moderate alkaline (pH (H_2O) 5.6-8.5) among the sample points of *Sever spoil* (Tsolova and Banov, 2017) according to the FAO classification of the pH index (Gyurov and Artinova, 2015). In our opinion, the wide range of active acidity established in the study is possibly due to the ameliorative activities carried out through the technical reclamation of the Technosol. The expressed probability can also be supported by the reduced average value of pH (H_2O) of 4.7, determining highly acid reaction of the environment in the subsurface layer, where the average copper content is also above the permissible concentrations (Tsolova and Banov, 2017). Similar pH index (pH (H_2O) 4.6-4.9) is typical for the surface layer of the Technosol with unfavourable properties and average sorption capacity from *Large southern spoil*, except for one point of the sample plots, which is very weak alkaline (pH (H_2O) 7.1) (Atanassova et al., 2023). In *Small southern spoil* from Medet mine, this analytical parameter is in the mid-acid range (pH (H_2O) ~5.3) with higher sulphur content (0.30 %) (table 1) and its predominant sulphate form (0.28 %) than in natural soils (Petrova, 2009).

Tsolova and Banov (2017) extend the studies of *Sever spoil* with assessment of the role of tree species in extraction of heavy metals from the Technosol and find that Birch is associated with the accumulation of zinc, and Acacia, with the copper.

The increased interest in artificial soils in the area of Medet mine contributes to the expansion of research not only on the spoils from the mining activity, but also on a constructed tailing pond near the mine, containing waste products from the processing of the mined ore (Atanassova et al., 2023). As with the reclaimed areas from *Large southern spoil*, here the authors analyse four sample points, one of which exceeds the MPC for copper, unlike lead and zinc.

Assarel mine

Like Medet mine, the Technosol from Assarel mine are also subject of study for determination of their characteristics from chemical and ecological point of view. Zheleva and Nustorova (1998) direct their scientific interest to study of acidity and physicochemical parameters of materials that built *Eastern spoil* in the area. The authors present research, which is started in 1991, of reclaimed sample plots that differ depending on applied humus (with 50 cm soil layer) and non-humus technical reclamation, and further divide them to establish the effect of ameliorative measures (with or without liming) after five years in 1996. At a later stage, the studies of *Eastern spoil* were expanded in terms of content of humus, nutrients, sulphur and heavy metals (Petrova and Gencheva, 2002; Petrova, 2009).

Zheleva and Nustorova (1998) found the impact of applied amelioration and fertilization in sample plots with humus layer, expressed in change from very strong to highly acid pH activity in unlimed areas (pH (H_2O) 3.70-4.79) to strong to moderate acid reaction in the limed areas (pH (H_2O) 4.25-5.49) (table 2). The authors observe similar effect in exchangeable acidity and point out its negative impact on plants, recommending that the main ameliorative measures should be related to liming and fertilization. Petrova and Gencheva (2002) found similar, very strong to strong acid pH activity in the surface 0-20 cm layer of the sample plots, both for the active (pH (H_2O) 3.17-4.75) and exchangeable (pH ($CaCl_2$) 3.03-4.34) acidity of the substrates, and also found sample areas with extreme acid environment (pH (H_2O) < 3.0). Zheleva and Nustorova (1998) add that at the beginning of research the presence of soil layer has increased the pH values to above 6.0 in the surface 0-20 cm, and

liming affect the acidity for period of up to 3-4 years, with its subsequent increase in the soil layer. Thus, the authors assume that the similarity between the soil-forming rocks and spread materials has impact on the acidity of reclaimed spoils and natural soils, which pH is between 4.75 and 5.18.

Table 2. *Heavy metals, pH and sulphur content in studied Technosols and substrates from Assarel mine (Eastern spoil)*

Source	Concentrations of heavy metals (mg/kg)[1]			pH (H_2O)		S (%)[2]	
	Cu	Zn	Pb	In unlimed areas	In limed areas	In fresh substrates	In reclaimed sites
Zheleva and Nustorova (1998)[3]	-	-	-	3.70-4.79	4.25-5.49	-	-
Petrova and Gencheva (2002)[4]	530	91 (328 in one sample)	62	2.84-4.75		0.27-1.11	0.03-0.7

[1] Maximum values found among all tested samples.
[2] Values are between all tested samples.
[3] pH values refer to samples from the surface and in depth layers.
[4] pH values refer to surface layer among all tested samples.

The Technosol from unlimed site of *Eastern spoil* is characterized by medium sorption capacity (up to 23.70 cmol/kg^{-1} in the surface 0-20 cm layers) due to the light mechanical composition of substrates and the lack of humic substances (Zheleva and Nustorova, 1998). On the other hand, the low content of humus in the substrates, with maximum value of 0.53 % in surface layer, corresponds to their very low supply with total nitrogen (N <0.060 %), similar to the low values of available phosphorus (P_2O_5 ≤4.5 mg/100g soil) and potassium (K_2O), where individual samples reach amount of about 20 mg/100g soil in the surface 20 cm (Petrova and Gencheva, 2002) (table 3).

Table 3. *Basic chemical and physico-chemical characteristics of studied Technosols and substrates from Assarel mine (Eastern spoil)*[1]

Source	Sorption capacity (cmol/kg^{-1})	Humus (%)	N (%)	P_2O_5 (mg/100g)	K_2O (mg/100g)
Zheleva and Nustorova (1998)	23.70	-	-	-	-
Petrova and Gencheva (2002)	-	0.53	0.059	4.5	19.9

[1] Maximum values found in the surface layer among all tested samples.

The sulphur content in fresh substrates from *Eastern spoil* is higher compared to the natural soils (from 0.27 % to 1.11 %) (Petrova and Gencheva, 2002), similar to *Small*

southern spoil from Medet mine (Petrova, 2009), but in reclaimed sites of the studied spoil at Assarel mine, these values are lower (from 0.03 % to 0.7 %) (Petrova and Gencheva, 2002) (table 2). Here, a difference is found in terms of the predominant form of sulphur between the studied spoils from the different copper mines, which is sulphate in *Small southern spoil* from Medet mine and sulphide in *Eastern spoil* from Assarel mine (Petrova and Gencheva, 2002; Petrova, 2009).

The copper content varies widely (from 58 mg/kg to 530 mg/kg) among the 35 analysed soil samples and the very acid ones (at pH (H_2O) ≤3.5) exceed the MPC (Petrova and Gencheva, 2002). The authors add that zinc has lower values (from 23 to 91 mg/kg, except for one sample containing 328 mg/kg) and lead (from 12 mg/kg to 62 mg/kg) does not appear as pollutant of substrates (table 2).

Conclusion

The results of the researches conducted by different authors on soil samples from Technosols in the area of Assarel-Medet Mining and Processing Complex can be combined in several summaries:

The analyses carried out for the content of heavy metals (copper, zinc, lead) found that the amount of copper, in part of the samples, exceeded the maximum permissible concentrations for soils, in contrast to zinc and lead. The pH activity, with the exception of some sample points, varies from very strong acid to moderate acid. Physico-chemical studies found that substrates have medium sorption capacity. Agrochemical analyses define the Technosols as poorly stocked with basic nutrients and low in humus. Studies for sulphur presence found its higher percentage in substrates than in natural soils, with different predominant form in the soil samples at the spoils from the two mines. In *Small southern spoil* from Medet mine it is sulphate, in contrast to the sulphide sulphur, which predominates in *Eastern spoil* from Assarel mine. The amelioration measures applied in the studied Technosols have positive impact on the pH activity, and some plant species used in biological reclamation may show different ability to accumulate certain heavy metals.

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