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Monitoring of Heavy Metals Migration into Edaphic Horizons of Coal Mine Dumps

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Abstract. Mining of minerals is accompanied by direct irreversible changes in the biosphere. An analysis of the latest researches on the technogenic hazard of rock dumps at coal mines, as well as specifics of their reclamation and phytomelioration in a global context, necessiates the study of the ecological state and natural phytomelioration of the Nadiya mine waste heap in the Lviv-Volyn coal basin (Ukraine). This scientific work presents the results of research on heavy metals migration into the genetic horizons of the rock dump, as well as their influence on forming the phytomeliorative cover on its surface. It has been revealed that the studied site of the No.4 rock dump in the 0-15 cm horizon, which is located from the eastern side near the foot, is the most contaminated with heavy metals. The indicators of heavy metal content at the background site, which is located within a radius of 3 km from the rock dump, are the lowest in the 0-15 cm horizon. The uneven distribution of heavy metals in the genetic horizons of the rock dump substrate is caused by frequent landslides, changing rock acidity, heterogeneity of natural overgrowth, and existing combustion sources. In the event of precipitation, toxic compounds, heavy metals and other harmful substances are washed out from the rock dump surface, and in our case, these substances also enter the natural water body.

Key words: rock dump, coal mine, ecological hazard, natural overgrowth, technogenic reservoir, heavy metals.

Introduction

The Lviv-Volyn coal basin functioning has led to numerous negative changes in flora and fauna, atmosphere, hydrosphere, biosphere, and also had a significant impact on the life and health of people of Ukraine and Poland, on the border with which it is located (Bosak et al., 2020). The basin includes three mining districts – Chervonohrad, Novovolynsk and Southwest districts, mining in which began in the 60s of the twentieth century.

In the global context, a lot of scientific papers have been devoted to the environmental and technogenic hazard of rock dumps. Among such works, it is worth noting the scientific research of Polish scientists (Abramowicz et al., 2021; Nadudvari et al., 2021). In particular, changes in organic and mineral substances caused by thermal effects have been revealed in coal waste. Irregular fractures and fissures appear inside and at the edges of the organic substance particles, which oxidize, volatilize and plasticize. Mineral phases have undergone oxidation, dehydration, structure restoration and recrystallization (Nadudvari et al., 2021). The vegetation area distribution due to changes in soil thermals has been studied for three periods within the selected transect, on which three types of surfaces with different soil thermals and spontaneous combustion directions have been distinguished. The temperature ranges from +9.9°C to +139°C at a depth of 20 cm and at the same time from +3.1°C to +69.0°C on the surface. The total organic carbon content in all samples ranges from 1.7% to 7.6% and at the same time from 3.1% to 4.5% in places of active fire. The total nitrogen concentration ranges from 0.023% to 0.29%. The soil (pH) reaction ranges from 5.8 to 8.0 (in H_2O). The vegetation area variability in time and space indicates the directions of displacement of the fire spots. The analysis has shown that underground temperature has a significant impact on the distribution and species composition of plants growing on coal dumps (Abramowicz et al., 2021).

Studies conducted at coal mines in North Africa (Onifade & Genc, 2018) have revealed that coal has a higher reactivity to spontaneous combustion than shale. Both materials show that an increase in the content of carbon, moisture, hydrogen, volatile substances, nitrogen and a decrease in the ash content can add to the tendency to spontaneous combustion. An approximate and final analysis of the tested samples indicates that these properties can be used as a tool to measure the tendency to spontaneous combustion.

Further research on petrographic analysis and detailed geotechnical study of coal and coal shale has been conducted to assess their impact on predicting and minimizing spontaneous heating events (Wu et al., 2019; Petlovanyi et al., 2020; Vo et al., 2022). In addition to the impact of rock dumps, significant damage to the environment is caused by oil pollution of soils resulting from emergency situations (Karabyn et al., 2019; Popovych et al., 2019).

The distribution of heavy metals depending on the places of burning rock dumps and the influence of these phenomena on natural phytoremediation processes within the limits of the Lviv-Volyn coal basin has not been fully investigated. The development of vegetation on waste dumps of coal mines depends on the temperature of the substrate, microclimate, climate, radiation background and other landscape-transforming factors. We did not find a combination of this kind of research in the process of analyzing scientific sources. For the most part, researchers limit themselves to the analysis of one direction of research on rock dumps of coal mines.

Materials and Methods

The geographical location of the Lviv-Volyn coal basin corresponds to the zone of Male Polissia, the climate of which is influenced by the air masses of the Atlantic. Since the Chervonohrad Mining District was the first to be mined, the largest rock volume is concentrated on its waste heaps. Nadiya mine, with a waste heap volume of 2869.4 thousand m^3, is one of the largest mines in the district (Fig. 1).

To determine the technogenic-ecological situation and take substrate samples for composition analysis in stationary laboratories, 7 sites are selected in the zone of the Nadiya mine rock dump influence for rock sampling from depths of 0-15 cm and 0-20 cm. In addition, water samples are taken from the centre of a technogenic reservoir, formed as a result of anthropogenic activities, which accumulates effluents from the dump. Coordinates of the rock dump location are 50.296540, 24.271369.

The edaphotopes from rock dumps are sampled according to the standard (DSTU ISO 10381-1:2004). The analysis of the micronutrient content in the selected rock substrates is performed using the ICP-MS device in the chemical laboratory of the Freiberg University of Mining and Technology (Saxony, Germany). The method for performing analyses is microwave induced combustion with subsequent measurement by the method of inductive-plasma mass spectrometry. The maximum permissible concentrations (MPC) of heavy metal content in the rock are compared with the data given in the works (Miedviediev & Laktionova, 1998; Kuraeva et al., 2012).

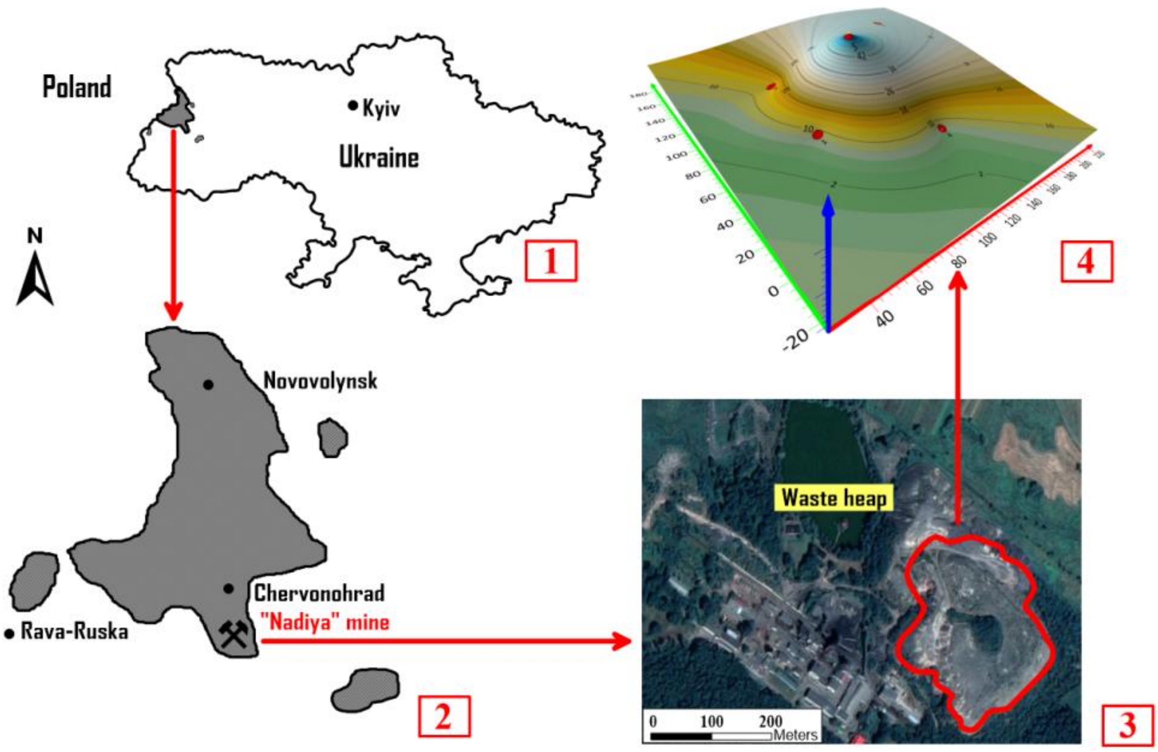
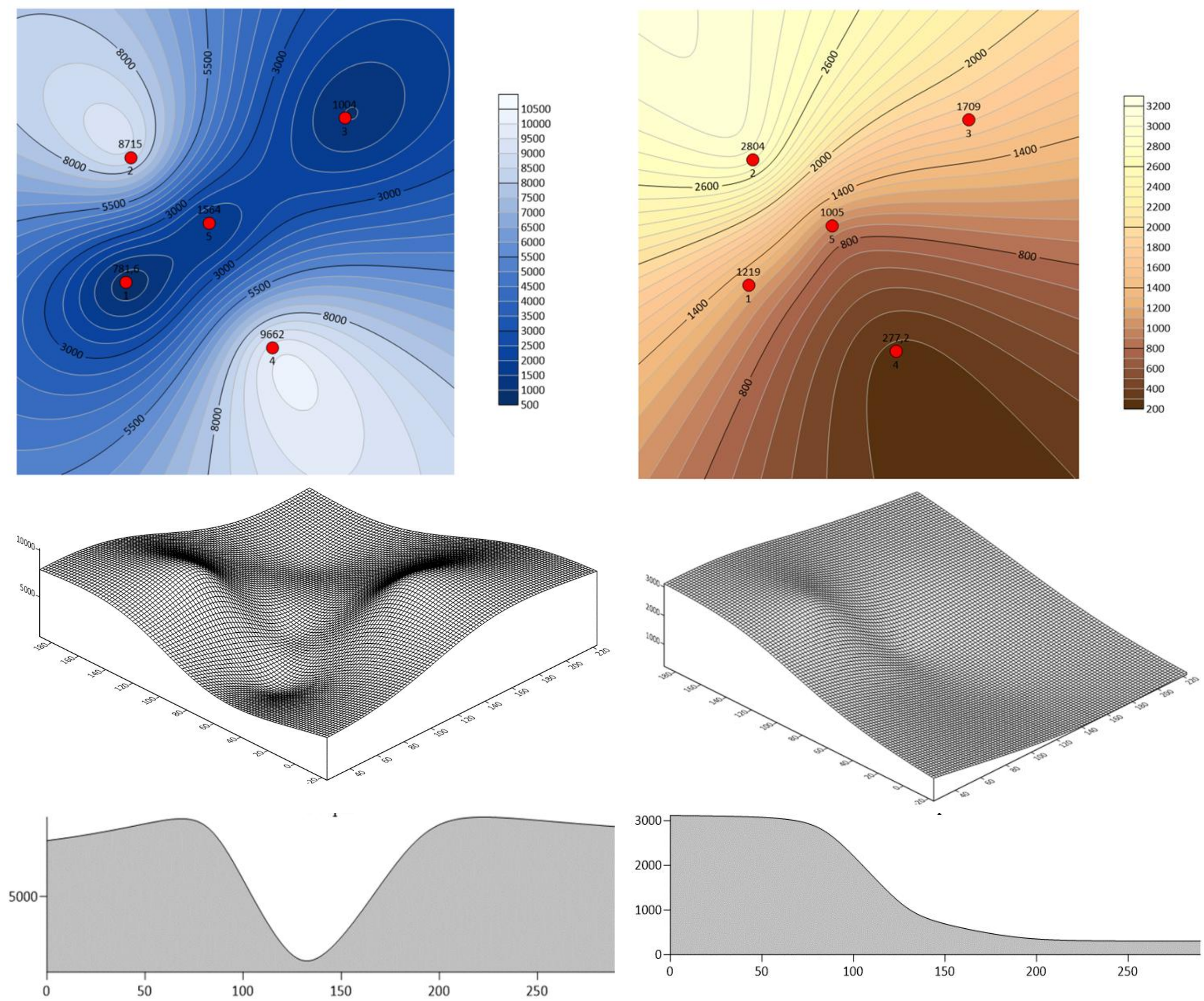


Fig. 1. Layout of the studied object: 1 – a map of Ukraine with the designation of the Lviv-Volyn coal basin; 2 – the Lviv-Volyn coal basin scheme with the designation of the Nadiya mine; 3 – the Nadiya mine map with the designation of a rock dump, made using GoogleMaps; 4 – 3-D rock dump model.

Results and Discussion

Analysis of the gross content of heavy metals Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb in the 0-15 cm and 0-20 cm horizons of the Nadiya mine rock dump in the Chervonohrad Mining District indicates that their values do not exceed the maximum permissible concentrations for soils. The only value exceeding the maximum permissible concentrations is set for Cu (studied site No.4) near the rock dump foot from the east. However, the indicators of heavy metal content in comparison with the background values (studied site No.6) exceed for individual elements by dozens of times.

The highest Mn content (894.6 mg/kg) is observed at the studied site No.4 in the 0-15 cm horizon on the eastern side near the rock dump foot. The lowest Mn content (19 mg/kg) is observed at the studied site No.6 in the 0-15 cm horizon, which is the background and is located 3 km south of the rock dump. In the 0-20 cm horizon, the highest Mn content (259.6 mg/kg) is observed at the studied site No.2 on the western side of the rock dump slope. The lowest Mn content in the 0-20 cm horizon (25.6 mg/kg) is observed at the studied site No.4 on the eastern side near the rock dump foot. Modeling of Mn (mg/kg) distribution in the edaphic horizons of the Nadiya mine rock dump in the 0-15 cm and 0-20 cm horizons is given in Fig. 2.



a) b)

Fig. 2. Distribution of Mn (mg/kg) in the edaphic horizons of the Nadiya mine rock dump: a) 0-15 cm; b) 0-20 cm.

The highest Fe content (44157.4 mg/kg) is observed at the studied site No.4 in the 0-15 cm horizon on the eastern side near the rock dump foot. The lowest Fe content (1128.7 mg/kg) is observed at the studied site No.6 in the 0-15 cm horizon, which is the background and is located 3 km south of the rock dump.

In the 0-20 cm horizon, the highest Fe content (21444.4 mg/kg) is observed at the studied site No.1 on the southern side near the rock dump foot. The lowest Fe content in the 0-20 cm horizon (1392.5 mg/kg) is observed at the studied site No.4 on the eastern side near the rock dump foot. Modeling of Fe (mg/kg) distribution in the edaphic horizons of the Nadiya mine rock dump in the 0-15 cm and 0-20 cm horizons is given in Fig. 3.

The highest Co content (23.8 mg/kg) is observed at the studied site No.4 in the 0-15 cm horizon on the eastern side near the rock dump foot. The lowest Co content (0.3 mg/kg) is observed at the studied site No.6 in the 0-15 cm horizon, which is the background and is located 3 km south of the rock dump.

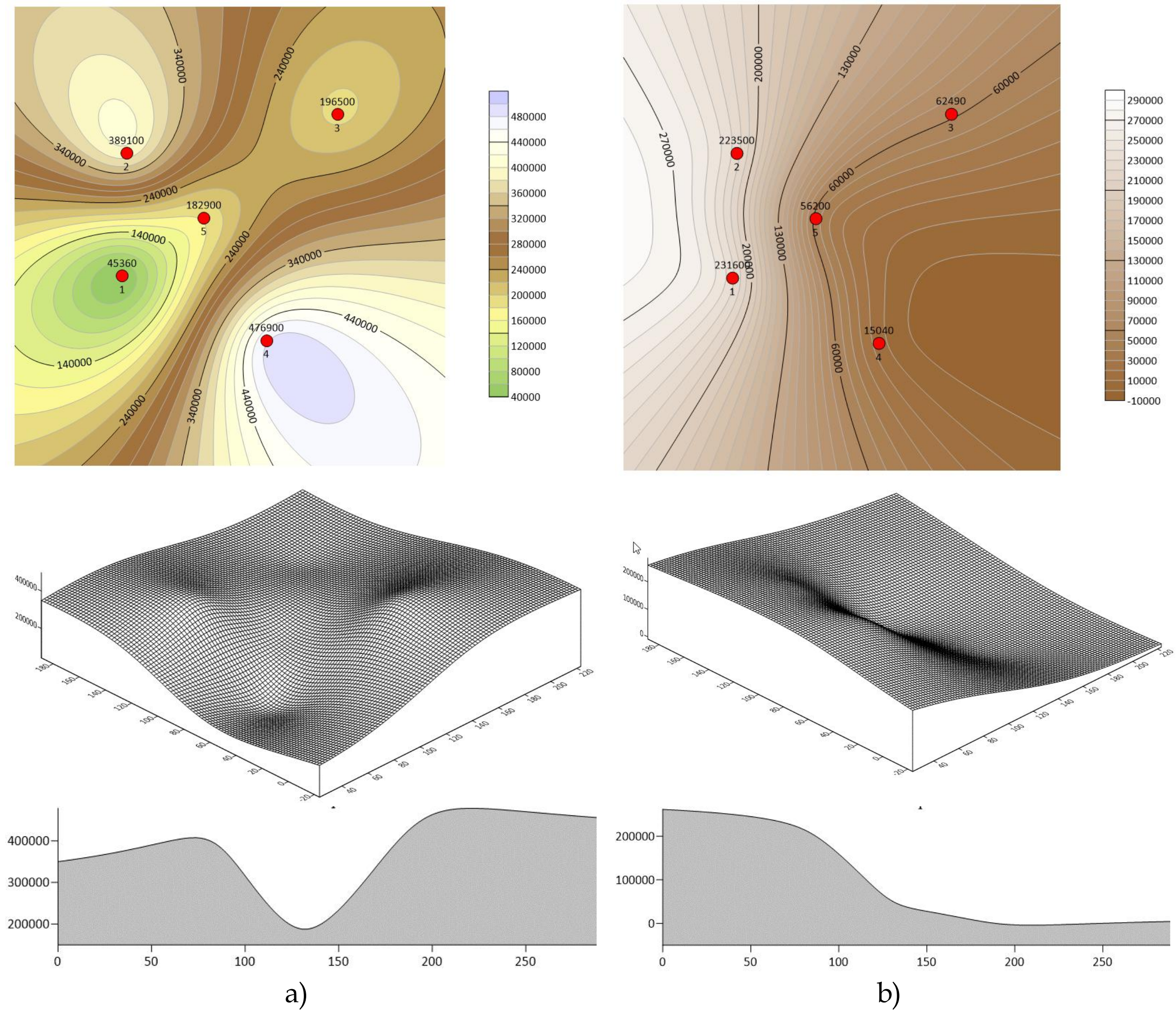
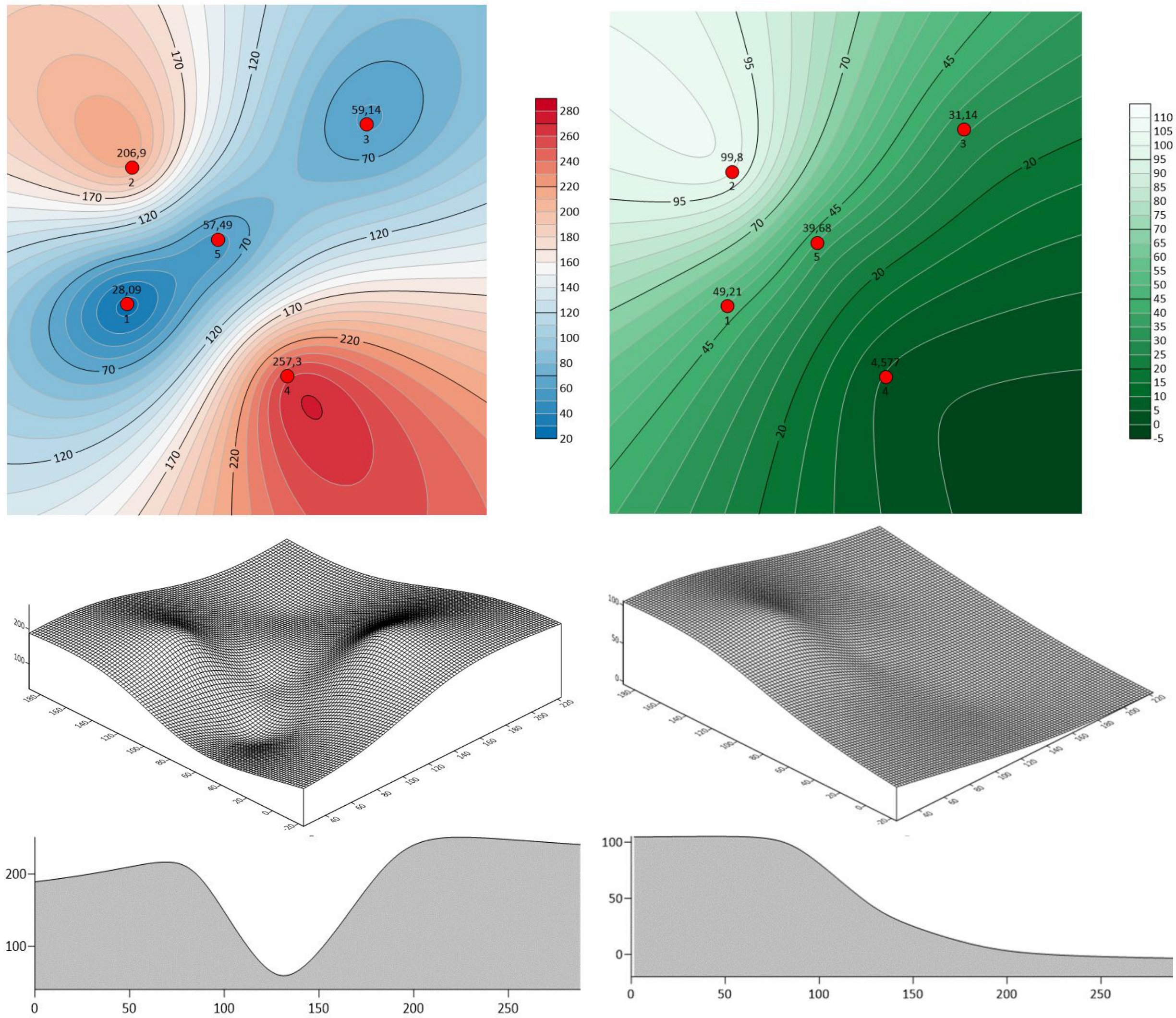


Fig. 3. Distribution of Fe (mg/kg) in the edaphic horizons of the Nadiya mine rock dump: a) 0-15 cm; b) 0-20 cm.

In the 0-20 cm horizon, the highest Co content (9.2 mg/kg) is observed at the studied site No.2 on the western side of the rock dump slope. The lowest Co content in the 0-20 cm horizon (0.4 mg/kg) is observed at the studied site No.4 on the eastern side near the rock dump foot. Modeling of Co (mg/kg) distribution in the edaphic horizons of the Nadiya mine rock dump in the 0-15 cm and 0-20 cm horizons is given in Fig. 4.

The highest Ni content (67.6 mg/kg) is observed at the studied site No.4 in the 0-15 cm horizon on the eastern side near the rock dump foot. The lowest Ni content (10.9 mg/kg) is observed at the studied site No.6 in the 0-15 cm horizon, which is the background and is located 3 km south of the rock dump.

In the 0-20 cm horizon, the highest Ni content (36.1 mg/kg) is observed at the studied site No.6 (area with a background value). The lowest Ni content in the 0-20 cm horizon (11.8 mg/kg) is observed at the studied site No.4 on the eastern side near the rock dump foot. Modeling of Ni (mg/kg) distribution in the edaphic horizons of the Nadiya mine rock dump in the 0-15 cm and 0-20 cm horizons is given in Fig. 5.



a) b)

Fig. 4. Distribution of Co (mg/kg) in the edaphic horizons of the Nadiya mine rock dump: a) 0-15 cm; b) 0-20 cm

The highest Cu content (55.7 mg/kg) is observed at the studied site No.4 in the 0-15 cm horizon on the eastern side near the rock dump foot. The lowest Cu content (1.3 mg/kg) is observed at the studied site No.6 in the 0-15 cm horizon, which is the background and is located 3 km south of the rock dump.

In the 0-20 cm horizon, the highest Cu content (34.6 mg/kg) is observed at the studied site No.6 (area with a background value). The lowest Cu content in the 0-20 cm horizon (1.8 mg/kg) is observed at the studied site No.4 on the eastern side near the rock dump foot. Modeling of Cu (mg/kg) distribution in the edaphic horizons of the Nadiya mine rock dump in the 0-15 cm and 0-20 cm horizons is given in Fig. 6.

The highest Zn content (67.9 mg/kg) is observed at the studied site No.4 in the 0-15 cm horizon on the eastern side near the rock dump foot. The lowest Zn content (2.4 mg/kg) is observed at the studied site No.6 in the 0-15 cm horizon, which is the background and is located 3 km south of the rock dump.

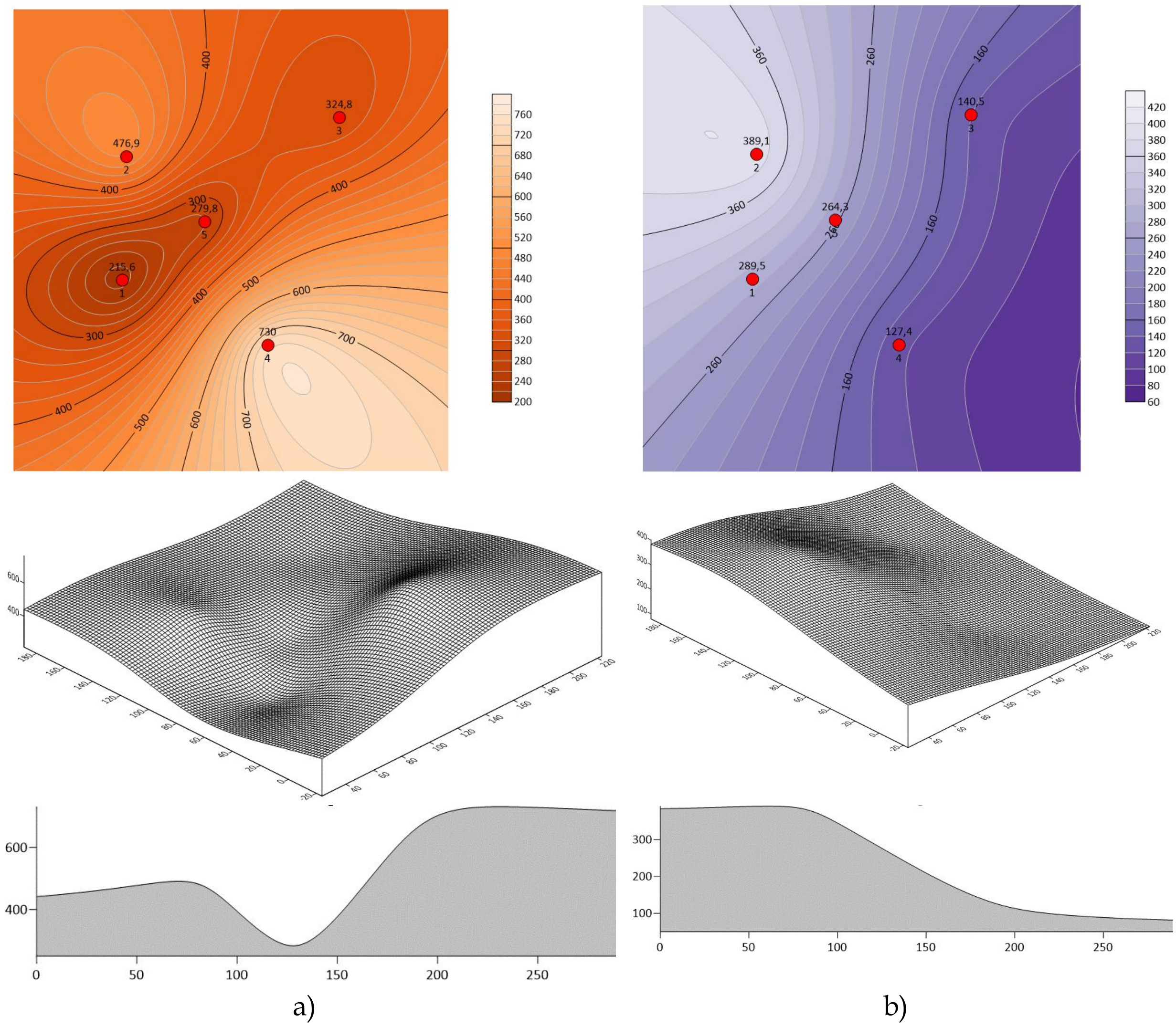
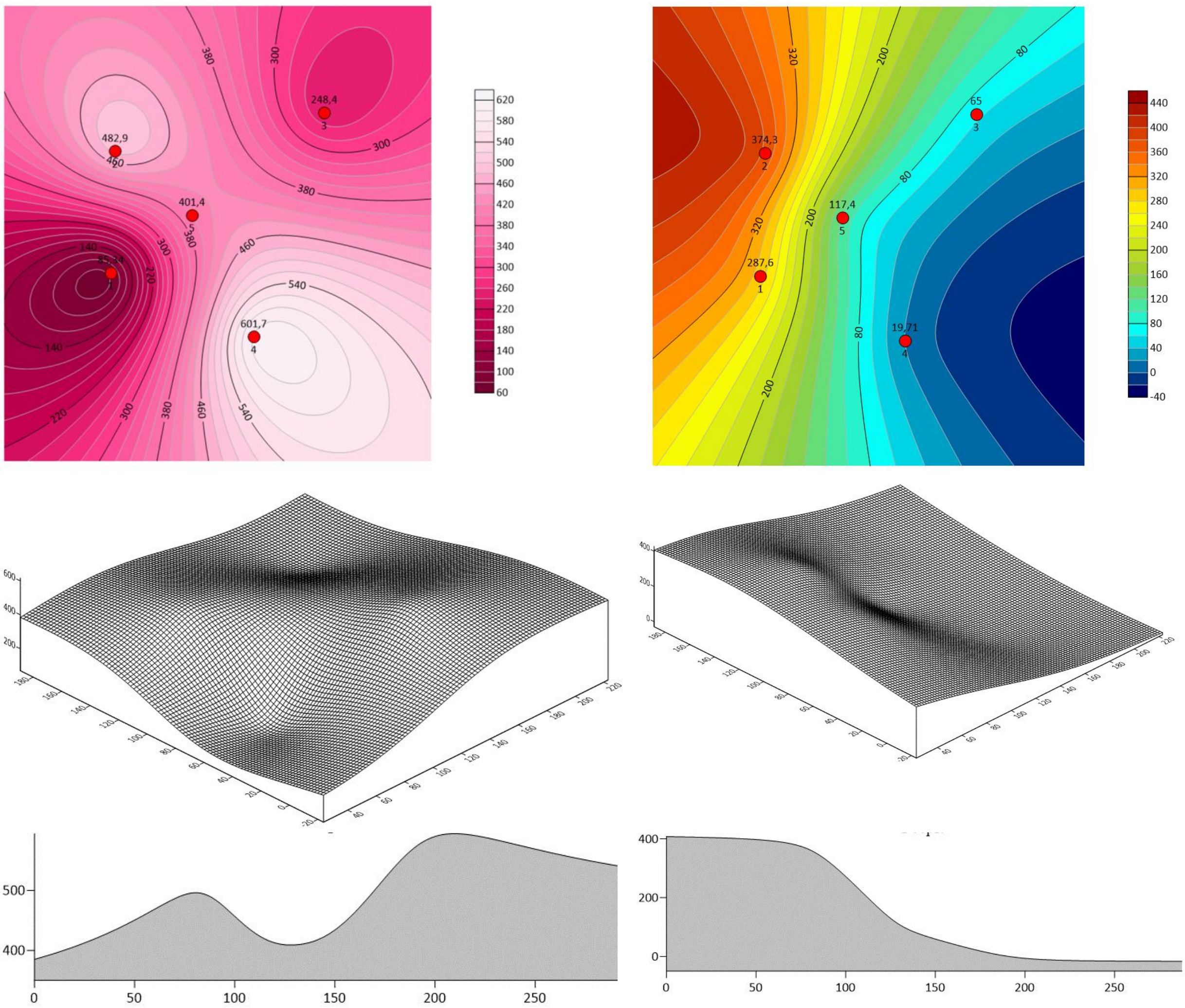


Fig. 5. Distribution of Ni (mg/kg) in the edaphic horizons of the Nadiya mine rock dump: a) 0-15 cm; b) 0-20 cm.

In the 0-20 cm horizon, the highest Zn content (32.3 mg/kg) is observed at the studied site No.2 on the western side of the rock dump slope. The lowest Zn content in the 0-20 cm horizon (6.7 mg/kg) is observed at the studied site No.4 on the eastern side near the rock dump foot. Modeling of Zn (mg/kg) distribution in the edaphic horizons of the Nadiya mine rock dump in the 0-15 cm and 0-20 cm horizons is given in Fig. 7.

The highest Cd content (0.3 mg/kg) is observed at the studied site No.6 (background site) in the 0-20 cm horizon. The lowest Cd content in the 0-20 cm horizon (0.15 mg/kg) is observed at the studied site No.4 on the eastern side near the rock dump foot.

The lowest Cd content (0.14 mg/kg) is observed at the studied site No.6 in the 0-15 cm horizon, which is the background and is located 3 km south of the rock dump. The highest Cd content (0.26 mg/kg) in the 0-15 cm horizon is observed at the studied site No.5 on the rock dump top. Modeling of Cd (mg/kg) distribution in the edaphic horizons of the Nadiya mine rock dump in the 0-15 cm and 0-20 cm horizons is given in Fig. 8.



a) b)

Fig. 6. Distribution of Cu (mg/kg) in the edaphic horizons of the Nadiya mine rock dump: a) 0-15 cm; b) 0-20 cm.

The uneven distribution of heavy metals in the genetic horizons of the rock dump substrate is caused by frequent landslides, changing rock acidity, heterogeneity of natural overgrowth, and existing combustion sources. In the event of precipitation, toxic compounds, heavy metals and other harmful substances are washed out from the rock dump surface, and in our case, these substances also enter a natural water body.

To study the pollution of the reservoir, located on the north-western side of the Nadiya mine rock dump foot, a water sample has been taken and the physical-chemical properties have been tested. The obtained data are compared with the maximum permissible concentrations. It has been determined that the maximum permissible concentrations exceed NH_4 and are 2.1 mg/dm^3. In general, the water is characterized by a high degree of salinity, since chlorides and sulphates reach values of 47.9 mg/dm^3 and 120 mg/dm^3, respectively. Physical-chemical properties of water in the studied pond are presented in Table 3.

Table 3. Results of studying the physical-chemical parameters of the reservoir in the zone of the Nadiya mine rock dump influence.

Seq. No.	Indicator name	Result	MPC
1.	Odor threshold at 20 °C, points	0	to 2
2.	Transparency, cm	25	more than 20
3.	Hydrogen indicator (pH)	7.8	6.5-8.5
4.	Suspended substances, mg/dm3	25.1	not normal
5.	Total dry matter, mg/dm^3	109.7	to 1000
6.	Total hardness, $mg\text{-}eq/dm^3$	1.0	to 7.0
7.	Carbonate hardness, $mg\text{-}eq/dm^3$	0.9	to 6.5
8.	Hydrocarbons (HCO_3^-), mg/dm^3	54.6	to 300
9.	Chlorides (Cl^-), mg/dm^3	47.9	to 250
10.	Sulphates (SO_4^{2-}), mg/dm^3	120	to 500
11.	Nitrites (NO_2^-), mg/dm^3	0.74	to 3.3
12.	Nitrates (NO_3^-), mg/dm^3	5.6	to 45
13.	Phosphates (PO_4^{3-}), mg/dm^3	0	not normal
14.	Calcium (Ca^{2+}), mg/dm^3	17.3	not normal
15.	Magnesium (Mg^{2+}), mg/dm^3	5.0	to 80
16.	Total Ferrum (Fe_{tot}), mg/dm^3	0.2	to 0.3
17.	Salt ammonium (NH_4^+), mg/dm^3	2.1	to 2.0
18.	Sum of $Na^+ + K^+$, mg/dm^3	25.6	to 300

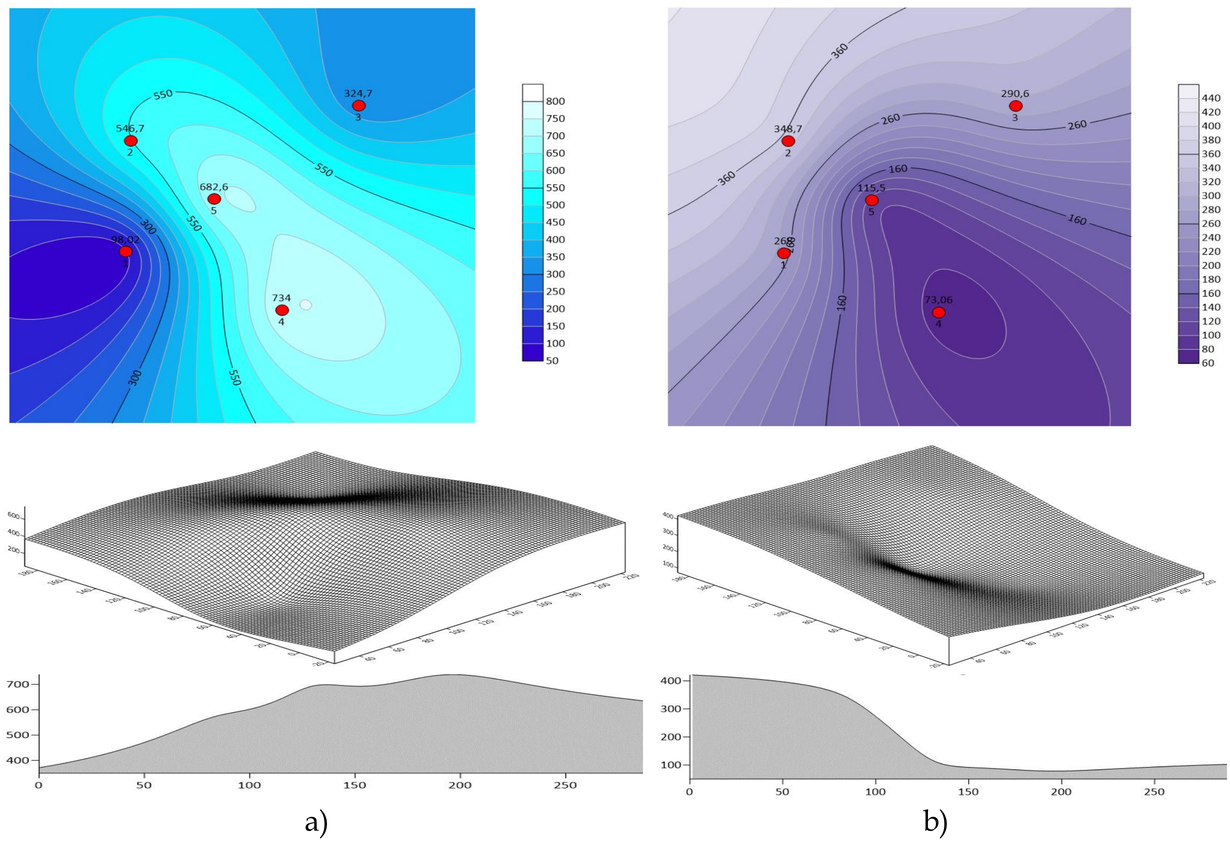


Fig. 7. Distribution of Zn (mg/kg) in the edaphic horizons of the Nadiya mine rock dump: a) 0-15 cm; b) 0-20 cm.

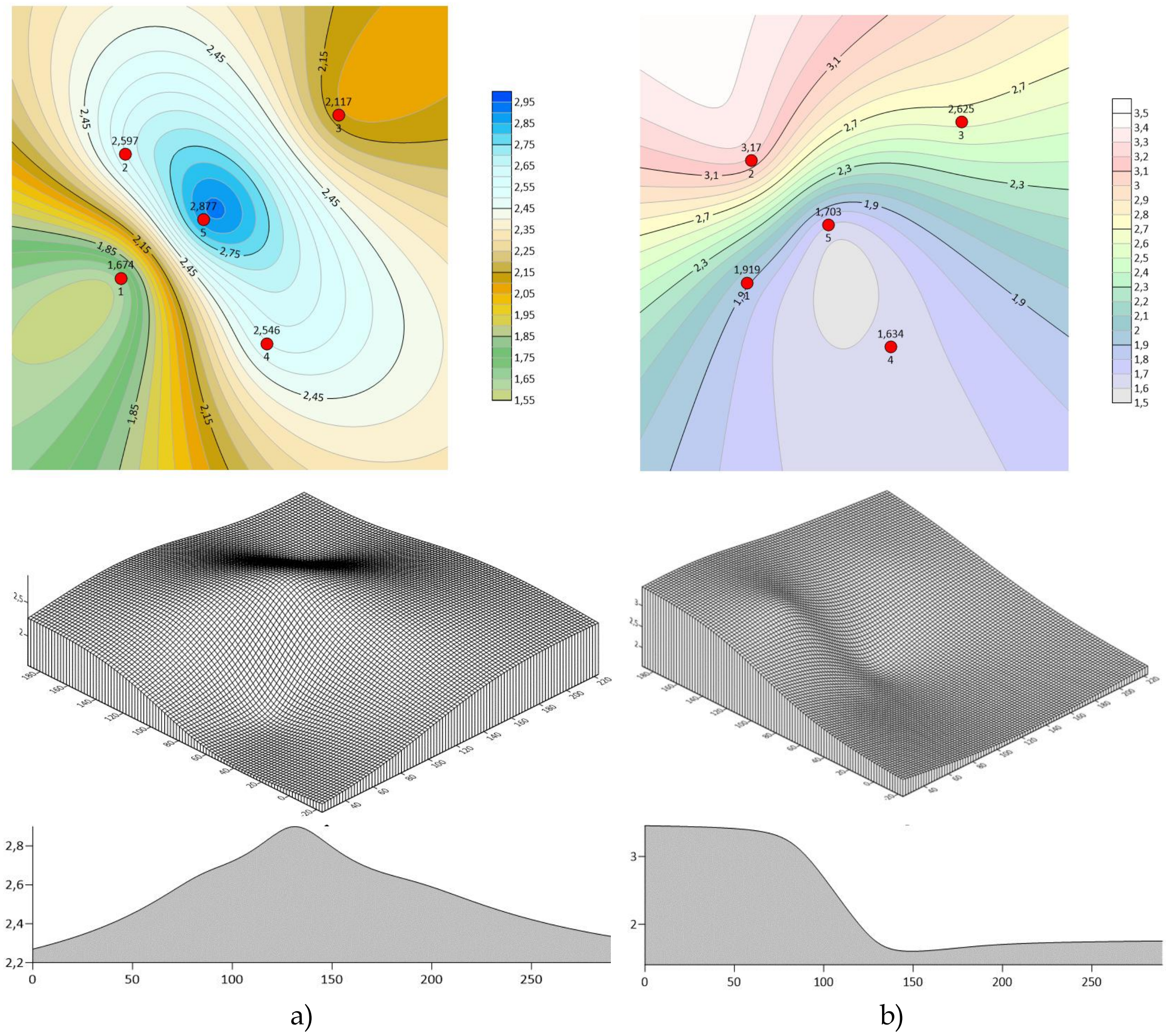


Fig. 8. Distribution of Cd (mg/kg) in the edaphic horizons of the Nadiya mine rock dump: a) 0-15 cm; b) 0-20 cm.

Thus, in order to reduce the reservoir salinity in the zone of the rock dump influence, it is recommended to set the geochemical barriers near the foot, as well as to plant salt-resistant species and violents in the coastal zone. Since wastewater from the rock dump enters the studied reservoir almost without restriction.

Conclusions

Rock dumps of coal mines entail a significant technogenic burden on the environment due to landscape-transforming, chemical, and physical factors. The physical-chemical, ecological and phytocenotic properties of the Nadiya mine rock dump of the Chervonohrad Mining District, which belongs to the Lviv-Volyn Coal Basin (Ukraine), have been studied in the paper.

The study of the gross content of heavy metals Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb in the 0-15 cm and 0-20 cm horizons of the rock dump indicates that their values do not exceed the maximum permissible concentrations set for soils by state standards of Ukraine. The value of Cu (studied site No.4) near the rock dump foot from the east has been determined as exceeding the maximum permissible concentrations. However, the indicators of heavy metal content in comparison with the background values (studied site No.6) exceed for individual elements by dozens of times. It has been revealed that the studied site No.4 in the 0-15 cm horizon, which is located on the eastern side near the rock dump foot, is the most contaminated with heavy metals. The indicators of heavy metal content at the background site, which is located within a radius of 3 km from the rock dump, are the lowest in the 0-15 cm horizon.

In the event of precipitation, toxic compounds, heavy metals and other harmful substances are washed out from the rock dump surface and enter the natural water body. Thus, in order to reduce the reservoir salinity in the zone of the Nadiya mine rock dump influence, it is recommended to set the geochemical barriers near the foot, as well as to plant salt-resistant species and violents in the coastal zone.

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