

Heavy Metals in Soil and Plants During Revegetation of Coal Mine Spoil Tips and Surrounded Territories

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ABSTRACT

Coal mining in Donbas is a global problem as it causes the destabilization of ecological landscapes. Spoil tips, covering almost 52% of the territory, alter the topography of the land, affect the ecosystem, and decrease soil fertility. The soils become degraded and are unsuitable for agricultural use. The occupation of the Donetsk region by the Russian Federation has suspended the observation and research of man-made influence on this territory, which is a major concern for the scientific community. To reduce the negative impact of spoil tips, it is necessary to slow down the process of pyrite oxidation and the formation of toxic substances, as well as the migration of heavy metals due to erosion. Biological reclamation with grass and woody plants can help in achieving this goal. Another urgent issue is the constant supervision and assessment of the suitability of the bedrock of coal mines for agricultural use. The study investigated the total and mobile content of heavy metals in the rock samples from the “South Donbaska-1” mine, ordinary chernozem (background soil), and vegetation growing on the spoil tip. The results showed that the content of Co, Cr, Cu, and Fe in the rock of the spoil tip is higher than in the background soils. The content of heavy metals gradually decreases as the distance from the spoil tip increases. The content of Pb in ordinary chernozem and rock is practically the same, indicating its active migration. An analysis of the biomass of plant samples growing on the spoil tip showed that the content of Co, Cu, and Zn was within the limits of the threshold limiting values. However, the content of other studied elements exceeded the permissible norms. The research results provide information on the ecological state of the spoil tip and can be used for recreational as well as reclamation works in these areas.

Keywords: spoil tip, rock waste, heavy metals, threshold limiting values, soil, pH, ordinary chernozem, plant biomass.

INTRODUCTION

The increase in heavy metal concentrations in the soils of industrial regions has become a global concern. In many regions, including Donbass, spoil tips - rock dumps resulting from coal mining - are a hallmark feature. These spoil tips contain all the elements of the periodic table and are considered by many scientists to be a potential source of minerals or raw materials for immediate use

or future deposits. Despite the potential value of these spoil tips, their impact on the environment and public health remains a concern [Kachmar et al., 2018; Tubis et al., 2022; Islam et al., 2022; Vaziri et al., 2022]. Located in the southeast of Ukraine, the Donbas region is heavily influenced by both the Atlantic Ocean and the expansive Asian continent. For nearly 300 years, the coal mining industry has been the primary driver of the region's economic and social development.

Unfortunately, the process of coal mining and beneficiation has resulted in the intensive formation of large spoil tips, which have had negative effects on the environment. Mining is conducted through an open method that completely collapses the cover of the coal-bearing rock, which causes the rock to loosen and expand in volume. As a result, for every 1,000 tons of coal produced, there are approximately 150 tons of rock waste generated, and in some cases, up to 800 tons [Landa et al., 2016]. The formation of a large amount of coal mining waste is attributed to the fact that the majority of the industrial reserves in the mines of Donbas (84.8%) are located in thin layers, with a thickness of no more than 1.2 meters. The remaining industrial reserves of the basin are distributed among medium-thickness layers, making up 15.2% of the total. The coal reserves in the Donbas region are stored in reservoirs with a capacity exceeding 108.5 billion tons. The region has up to 300 coal-bearing layers, with an average working layer thickness ranging from 0.6 to 1.2 meters.

Currently, there are 97 active mines in the Donbas region, which is a decrease from the more than 150 mines that were in operation before the Russian Federation occupied the territory in 2014. Unfortunately, over 70 of these mines are located in non-controlled territory that is now occupied by Russia. As a result, the information about these mines can only be obtained from open sources or thematic groups on social networks due to the lack of direct access to the assessment. In addition to the active mines, there are a total of 1.185 stockpiles in the Donbas region, with 381 currently active and 804 inactive. It is concerning that approximately 397 of these inactive dumps are burning, contributing to the already significant environmental issues in the area [Artemov et al., 2022; Zhenqi Huand & Qing Xia, 2017]. The volume of rocks in the stockpiles is more than 1,050 million m³, occupying an area of more than 7,190 hectares of agricultural land [Kucher et al., 2022].

Moreover, long-term self-heating of stockpiles caused the formation of sulfuric acid that interacts with calcium carbonate and accelerates the hydrolysis of feldspars with the formation of kaolinite at such high temperatures – $Al^2[Si_2O_5](OH)_4$. Also, hot acid oxidizes coal and carbon compounds ($C+2H_2SO_4=2SO_2+CO_2+H_2O$), as well as interacts with elemental sulfur ($S+2H_2SO_4=3SO_2+2H_2O$) and pyrite ($FeS_2+6H_2SO_4=FeSO_4+7SO_2+6H_2O$). All these reactions lead to the release of SO_2 and CO_2 , and

the formation of sulfurous fog near the surface, which falls together with precipitation in the form of “acid rain” [Doulati et al., 2010; Shi-Lei Yu & Xin Liu, 2022]. Non-concentrated solutions of sulfuric acid contribute to more active dissolution and extraction of Fe, Al, Mg, Na, K, Co, Ni, Zn, Cu and other elements from the rock of the dumps, which are located around the mines [Goncharova, 2015; Opara et al., 2023; Sidkina et al., 2022; Dold, 2017]

Oxidative processes on the surface of spoil tips result in the formation of sulfuric acid, leading to severe acidification of the environment. This process causes the acidic components to spread over considerable distances beyond the mining area, contributing to the pollution of both surface and underground waters with sulfate and hydrogen ions [Reshetnyak et al., 2022; Linetal., 2022]. The sulfate content in the rock and at the base of the spoil tip is in the range of 0.2–0.4%, significantly exceeds the natural content in steppe soils equal to 0.006%, but on the territory surrounded spoil tip, it amounts to – 0.06–0.43 % [Mianovski et al., 2005; Křibek et al., 2021; Jamieson et al., 2015].

Uranium is present in the coal and rocks of Donbas, with the amount varying depending on the lithological composition of the rock, typically ranging from 2 to $2.6 \cdot 10^{-4}\%$. The coal that contains sulfide minerals, particularly pyrite, has the highest amount of uranium. Due to this fact, further detailed research is required [Artemov et al., 2022]. Burning and spreading of mine rock dust particles is the main source of pollution of atmospheric air and surrounding territories. Self-ignition affects 60–75% of conical and 17–37% of flat spoil tips, emitting more than 500,000 tons of gaseous substances annually into the atmosphere. In addition, waste burning and coal processing factories in Donbas emit significant amounts of CO , CO_2 , SO_2 , H_2S , NO , and NO_2 , totaling 9758 kg of CO , 154170 kg of CO_2 , 1476 kg of SO_2 , 339 kg of H_2S , and 72 kg of $NO+NO_2$ [Qi Li et al., 2014]. Over 400 tons of rocks containing toxic elements, such as Hg, Pb, As, Se, Cd, Ni, Mo, Zn, Mn, V, Be, and Te, are blown from each factory and spoil tip into the surrounding area. This poses a significant health risk for both humans and wildlife in the area [Reshetnyak et al., 2022].

The research on environmental pollution and monitoring has identified over 40 elements in D. I. Mendeleev’s periodic system with an atomic mass greater than 40 atomic units as heavy metals, including V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo,

Cd, Sn, Hg, Pb, Bi, and others. N. Reimers' classification (1990) defines the metals with a density of more than 8 g/cm³ as heavy. The categorization of heavy metals, however, depends not only on their density but also on their toxicity to living organisms at relatively low concentrations, as well as their ability to bioaccumulate and biomagnify [Bulygin et al., 2020]. According to medical and sanitary studies, the morbidity and mortality rates in the areas affected by spoil tips are significantly higher compared to other areas [Reshetnyak et al., 2022; Forghani et al., 2023; Munir et al., 2022].

Within a radius of 0.5 km from the industrial spoil tip, the chernozems soil type loses properties completely up to a depth of 0.6 m. Heavy metals accumulate in the soil up to a distance of 5 km, causing a loss of both the amount and structure of humus, leading to soil degradation in the affected areas [Jiaorong Lv et al., 2020; Kachmar et al., 2018]. Heavy metals are mainly concentrated in the surface layer of the soil up to 15 cm in depth [Kotaiah & Kiran, 2022; Petrova et al., 2022]. Heavy metals such as exchangeable ions and those that are part of humic substances, carbonates, aluminum oxide, iron, and manganese accumulate in the soil, suppressing the development of vegetation and various microorganisms, and adversely affecting the development of fauna in the affected area. The intensity of the accumulation of heavy metals depends on soil properties, including the content of organic matter, pH of the environment, absorption capacity, and mechanical composition of the soil [Kucher et al., 2022].

Increased acidity of soils contributes to more intensive dissolution of heavy metals, soil absorption and greater available toxicity. Chemical and biochemical processes of oxidation of sulfides in the waste rock of mines contribute to the intensification of the migration of heavy metals to the territory adjacent to the spoil and pollute those areas [Xiaoyang Liu et al., 2016]. The soils with high humus content accumulate more heavy metals [Kotaiah & Kiran, 2022]. The presence of a finely dispersed fraction in the mechanical composition of soil contributes to greater fixation strength and the content of heavy metals. However, various elements behave differently. For instance, zinc penetrates deeper into the soil than cadmium and mercury [Zhang et al., 2020; Kravchenko et al., 2022].

The spoil tips of coal mines located in the geological and industrial district of the South Donbas consist of fragments of clay shales and sandstones originating from the Lower and

Middle Carboniferous geologic periods of the Paleozoic era. They contain up to 34% of combustible substances consisting of coal, carbonaceous substances, coal dust, sulfur, and sulfurous compounds. The lithological composition of the Carboniferous includes argillites (clay shales), which turn into fragments of a tile structure during weathering and then into a clay mass, siltstones (sand shales), sandstones, limestones, and coal [Popovych et al., 2018].

Heavy metals accumulate more intensively in the soils with a heavy mechanical composition such as loams and clays. The soil firmly binds heavy metals, which in turn protects soil, drinking water, and plant products from contamination. The soils with a light mechanical composition, on the other hand, are more susceptible to pollution. They weakly bind heavy metals, which can easily be absorbed by plants or pass through the soil layer during the process of filtering precipitation. On such soils, the risk of contamination of plants and groundwater increases [Sperdouli, 2022]. Trace elements are heavy metal salts that are found in small concentrations in soil. They play a vital role in many essential physiological and biochemical processes of plants. A deficiency in these elements can result in the slowdown or cessation of certain growth processes. Conversely, an excess of trace elements can also have negative effects on soil properties and plant growth [Żukowska et al., 2021; Forghaniet et al., 2023; Singh et al., 2011; Slobodianyk et al., 2022; Karpenko et al., 2020; Nobis & Kenyon, 2022].

The harmful effects of existing mine spoil tips, such as the emission of gaseous substances, radioactivity, and migration of heavy metals due to erosion by water and wind, can be reduced through the process of biological reclamation using grass and woody plants. Heavy metals in the soil are primarily present in colloidal suspensions or in compounds with organic and mineral substances, and they cannot remain in a dissolved form for an extended period. Therefore, the concentration of heavy metals in the sediment can often serve as an indicator of pollution [Kucher et al., 2022; Singh et al. 2011; Makarenko & Budak, 2017; Biswas et al., 2022]. Heavy metals have a dual role in plant life: they are essential components in plant metabolism, but their accumulation in high concentrations in the soil solution can lead to toxicity in various parts of plants. Determining the chemical composition of plants can establish the criteria for the indicator capacity

of plant species, their potential use as highly sensitive bioindicators, and as biomonitors for soil pollution levels with heavy metals. Additionally, plants can be used as a component of fertilizers or as material [Zykova et. al., 2016; Ulianych et. al., 2018; Korzhenevska et. al., 2021; Abuova et. al., 2021; Rebezov et. al., 2020; Rebezov et. al., 2021a; Rebezov et. al., 2021b; Rebezov et. al., 2021c; Tretyak et. al., 2021; Beregniak et. al., 2023; Munir et. al., 2022; Zykova et. al., 2019; Kachanovska & Kondakova, 2017; Yakovenko, 2017; Kuramshina et. al., 2019; Yamborko et. al., 2018; Bondar & Makarenko, 2019; Felix-Henningsen et. al., 2010; Yermishev et. al., 2019; Voitsitskiy et. al., 2019; Ruban et. al., 2017, Cherkasova et. al., 2021].

The accumulation of heavy metals in plants is a result of the active interaction between the roots and soil particles and minerals through contact absorption. This process occurs due to the exchange of hydrogen ions and organic acids that are released by the roots of plants for metal ions. The intensity of metal ion absorption from the solid phase by plants can vary greatly, ranging from hundreds to thousands of times. This absorption depends on various factors, including climatic conditions, physicochemical properties, and morpho-anatomical and physiological-biochemical features of the plant [Okhremchuk, 2018; Kuramshina et. al., 2018; Mazhayskiy et. al., 2022; Imeri et. al., 2019; Bondar et. al., 2020; Das et. al., 2008; Olkhovych et. al., 2022; Min-iailo, 2018; He & Chen, 2014].

Given the information presented above, several research questions need to be addressed regarding the accumulation of heavy metals in soils and plants because of their migration to adjacent territories from spoil tips. Therefore, this study

aimed to investigate the extent of heavy metal accumulation and migration in soils and plants during the spread of heavy metal pollution from spoil tips in the Donbas region of Ukraine.

MATERIALS AND METHODS

The testing site was located in the Donbas region of southeastern Ukraine. The region has a continental climate with strong, dry winds and hot summers, and an annual precipitation rate of 400-420 mm. However, on the Donetsk ridge, the precipitation rate increases to 540 mm [Small Mining Encyclopedia, 2004]. At the “South Donbaska-1” mine, which has a rock composition of 53 years and a height of 65 meters, the trace element composition of the spoil tips was analyzed (see Fig. 1).

The content of mobile and total forms of heavy metals was determined by the atomic absorption method using an S-115-M-1, JSC “SELM-1” spectrometer, made in Sumy, Ukraine. The maximum permissible concentration for metals in the soil: Cd – 1.0, Cu – 55.0, Mn – 1500.0, Ni – 85.0, Pb – 30.0, Zn – 115.0, Co – 55, Cr – 100 mg in 1 kg of air-dry soil. Cd, Pb, Zn are included in the I class of danger; where as the II class of danger includes – Co, Ni, Cu, Cr; in turn, Mn is assigned to the III class of danger. The total content of heavy metals was determined by dissolving the mine rock in 1N nitric acid with addition of hydrogen peroxide. Mobile forms were determined using an acetate-ammonium buffer with a pH of 4.8, in accordance with State Standard of Ukraine 4770.4:2007 and 4770.5:2007. The total content of heavy metals in plants (selected from the protective zone around the spoil tip) was determined by extracting the wet ashed sample with



Fig. 1. Spoil tip of the “South -Donbaska-1” mine (aerial photos of Google Earth)

nitric acid. Separate original samples were used for each extraction, and the “sample-solution” mass ratio was 1:10. The content of mobile forms of heavy metals was determined in the samples of the “South Donbaska-1” spoil tip from the top, middle, and bottom tiers, located to the southwest of the spoil tip at distances of 0.5 km and every 0.1 km further along the reclamation territory. The soil type is typical chernozem. The degree of contamination of soil, rocks, and plants by heavy metals was assessed based on the threshold limit values (TLV) regulated by [Bulygin et al., 2020].

STATISTICAL ANALYSIS

The results were statistically evaluated using the Analysis of Variance. All assays were performed in triplicate, and the results are expressed as mean ± SD. All calculations were made using the Microsoft Office 2019 software package. A Pearson correlation and linear model analysis were conducted according to standard methods [France & Thornley, 2007].

RESULTS AND DISCUSSION

The distribution of the total content of heavy metals in sedimentary rocks of the Lower Carboniferous period is presented in Table 1. Among them are the heavy metals of hazard class 1 (Zn, Pb, Cd) and 2 (Ni, Co, Cu, Cr). The data show that the rock samples of the “South Donbaska-1” mine exceed their content of Co, Cr, Cu and Fe in the background soils. Excessive values of the gross forms of heavy metals in the presented samples according to the TLV were not detected.

Soil pollution caused by heavy metals results in a significant decrease in soil fertility, and this phenomenon is most intense in the immediate surrounding area, up to a radius of 0.5 km from the pollution source. The intensity of pollution reduces continuously with increasing distance, disappearing entirely at a range of 30–40 km. The direction of the wind also plays a role in the spread of pollution. In the case of the “South Donbaska-1” mine, fluctuations in the concentration of heavy metals in the rock are shifted towards an increase in the lower part due to erosive

Table 1. The total content of heavy metals in the top layer 0–10 sm from the surface, mg/kg

Object	The content of the element								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Black soil is ordinary	0.25	3.72	1.45	6.71	252.26	336	8.46	10.24	5.49
Dump of the mine “Pivdenno-Donbaska-1”	0.05	5.06	1.8	10.14	1757.1	159.5	6.44	9.39	15.64

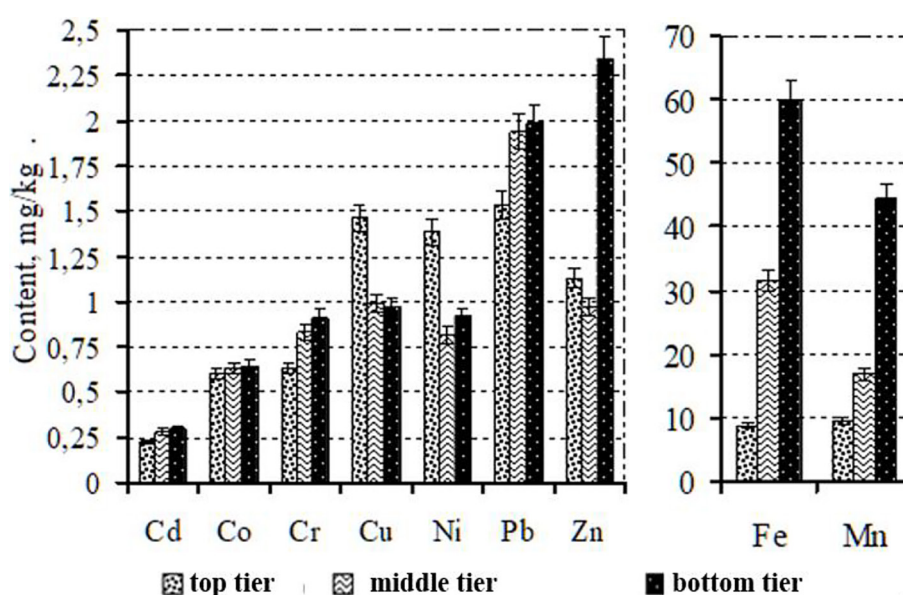


Fig. 2. Distribution of the content of mobile forms of heavy metals in the spoil tip of the “Pivdenno-Donbaska-1” mine, mg/kg

washing and the granulometric composition of the rock. This is illustrated in (Fig. 2). To assess the impact of coal mining waste on the natural environment, a study was conducted on the accumulation of mobile forms of heavy metals at varying distances from the spoil tip. Samples were collected every 0.5 km, starting from 0.05 km away from the beginning of the spoil tip. As the distance from the spoil tip increased, the concentration of heavy metals in the soil gradually decreased, as shown in Fig. 3. However, the levels of heavy metals in both the rock samples collected from the spoil tip and the soils surrounding the spoil tip exceeded the allowed concentration limits. The pH level of the soil away from the spoil tip was similar to that of ordinary medium-humus chernozems (pH=6.7).

The studies have shown that lead, which is classified as a first-class hazardous heavy metal, actively migrates beyond the source of pollution. This is evidenced by its almost identical content in both rock samples and the studied soil, especially at the bottom of the spoil tip, where its concentration is as high as 1.99 mg/kg of soil. This situation raises concerns about the chemical aggressiveness of lead and its potential danger to the environment, as confirmed by other researchers [Knysh & Karabyn, 2014; Kabata-Pendias & Pendias, 2010; Han & Singer, 2007].

Heavy metals cannot disappear from the soil, but they can move from one natural layer to another, interacting with various living organisms and maintaining their negative impact on them. Heavy metals pose the greatest danger to the humans who consume plant products with concentrations of heavy metals 10–10,000 times higher than the safe levels considered for such products. Chemical transformations of heavy metals containing compounds increase the risk of the appearance of new forms of heavy metals that are characterized by a more pronounced degree of toxicity. The ingestion of such toxic substances through food creates a predisposition for the cumulative, carcinogenic, and mutagenic effects of heavy metals on living organisms [Skok, 2018]

The mobility of metal salts in soil depends largely on the soil acidity, which is influenced by various processes, such as physical, chemical, and biochemical oxidation of sulfides in the waste rock. To determine the pH of the soil samples, tests were conducted in different areas of the spoil tip. The samples collected from the closest area to the spoil tip (30–40 m) had a slightly acidic pH of 5.2. However, the pH increased to 6.3 at a distance of up to 800 m from the bottom of the spoil tip. It was observed that under weakly acidic and neutral conditions, there were no reactions

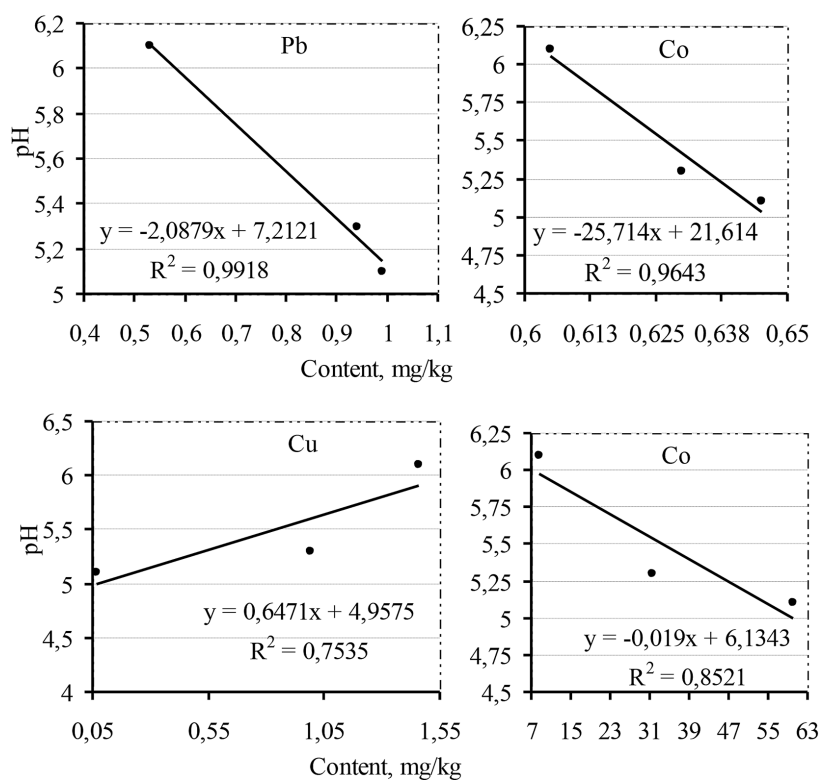


Fig. 3. Heavy metal content depending on soil pH, mg/kg

for Cu, Cr, Mo, Ni, Co, which resulted in their immobility and intensive accumulation in the soil [Xiang et al., 2016; Sintorini et al., 2021; Król et al., 2020; Schubert et al., 2019].

Through correlational analysis (Pearson), the relationships between the mobile forms of heavy metals in the different layers of the spoil tip at the South Donbaska-1 mine were investigated. It was observed that the concentration of all the studied metals showed proportional co-dependence. On the basis of the data presented in Table 2, it can be inferred that the salts of all heavy metals are released quite intensively from the rock. A weak relationship ($r=0.1-0.47$) was found between Mn and Cd, Cu, and Fe; Ni and Cu and Fe; as well

as Zn and Mn and Ni. In these cases, the release from the rock occurs unevenly, depending on the intensity of oxidation processes and the natural weathering, and microbiological intensity in the waste rock [Kucher et. al., 2022; Small mining encyclopedia, 2004].

An analysis was conducted on samples of different parts of plant biomass taken from areas of natural overgrowth in the protective zone of the adjacent territory. The vegetative mass analyzed included seed oats (*Avena sativa* L.), fruit pulp of the forest apple (*Malus sylvestris* Mill.), common raspberry (*Rubus sdaeus* L.), common apricots (*Armeniassa vulgaris* Lam.), and common apricot pits (Table 3).

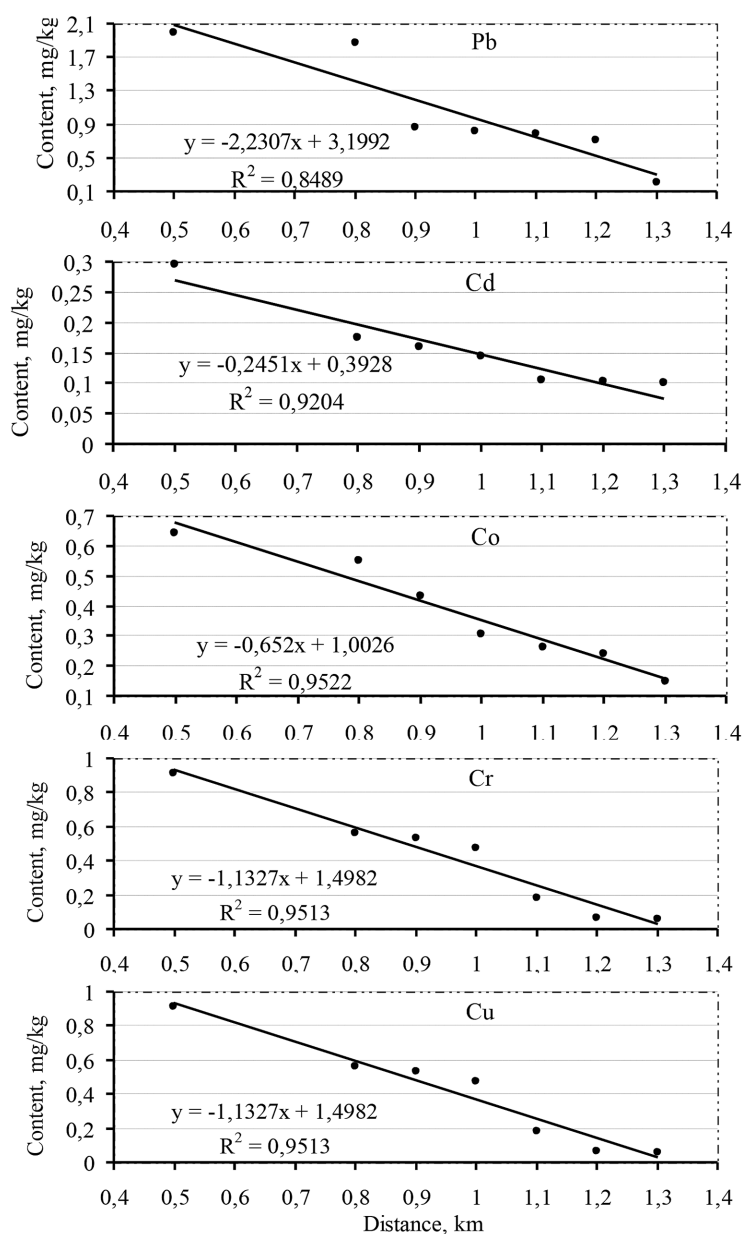


Fig. 4. Correlation dependence of the content of heavy metals depending on the distance from the mine dump

Table 2. Relationship of mobile forms of heavy metals in the soil of the spoil tip of the “South Donbaska-1” mine

Chemical	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cd	1.00								
Co	0.91±0.10	1.00							
Cr	0.94±0.09	0.94±0.13	1.00						
Cu	0.94±0.15	0.75±0.21	0.78±0.16	1.00					
Fe	0.90±0.12	0.68±0.17	0.73±0.21	0.99±0.16	1.00				
Mn	0.47±0.21	0.75±0.12	0.68±0.16	0.16±0.11	0.07±0.11	1.00			
Ni	0.62±0.11	0.84±0.14	0.76±0.13	0.34±0.14	0.27±0.15	0.87±0.19	1.00		
Pb	0.85±0.09	0.95±0.12	0.84±0.17	0.72±0.09	0.65±0.23	0.73±0.21	0.71±0.13	1.00	
Zn	0.92±0.12	0.71±0.15	0.75±0.13	0.99±0.19	0.99±0.16	0.10±0.11	0.30±0.18	0.68±0.17	1.00

Table 3. Content of heavy metals in plant products, mg/kg (per dry mass)

Plants	The content of the element								
	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
<i>Avena sativa L.</i> vegetative mass	0.26	0.43	4.21	7.21	636.7	99.17	3.2	6.65	21.94
<i>Malus sylvestris Mill.</i> fruit pulp	0.09	0.51	0.16	1.85	81.42	12.76	0.94	1.04	7.35
<i>Rubus idaeus L.</i> berry pulp	0.18	0.37	0.37	5.36	143.74	344.22	8.34	2.38	25.44
<i>Armeniassa vulgaris</i> Lam. fruit pulp	0.08	0.12	0.22	0.91	1.83	5.3	1.17	1.89	9.01
<i>Armeniassa vulgaris</i> Lam. seed of drupe	0.09	0.42	0.35	4.55	18.51	4.65	1.02	0.05	14.26
TLV	0.03	1.00	0.20	10.00	50.00	44.00	0.50	0.30	50.00

After analyzing the biomass of various plants, it was determined that the levels of Co, Cu, and Zn were below the threshold limit values (TLV). However, there were excessive amounts of certain heavy metals in some plants. For example, the vegetative mass of seeded oats had 8.6 times the TLV of Cd, 21 times the TLV of Cr, 12.8 times the TLV of Fe, 2.2 times the TLV of Mn, 6.4 times the TLV of Ni, and 22.2 times the TLV of Pb. The fruits of the forest apple tree had 3 times the TLV of Cd, 1.5 times the TLV of Fe, 1.8 times the TLV of Ni, and 3.5 times the TLV of Pb, but no excessive amounts of Cr and Mn. Common raspberry fruits had 6 times the TLV of Cd, 1.8 times the TLV of Cr, 2.9 times the TLV of Fe, 7.8 times the TLV of Mn, and 7.9 times the TLV of Pb. The fruits (pulp) of common apricot had 2.6 times the TLV of Cd, 1.1 times the TLV of Cr, 2.3 times the TLV of Ni, and 6.3 times the TLV of Pb, but no excessive amounts of Fe and Mn. Common apricot pits had no excessive amounts of Fe and Mn, but had 1.7 times the TLV of Cd, 6.3 times the TLV of Pb, 1.7 times the TLV of Cr, and 2.3 times the TLV of Ni. The use of these areas for grazing poses a hazardous accumulation of heavy

metals in animal products. The fruits obtained from these plants are not suitable for consumption or processing.

CONCLUSIONS

The conducted research shows that rock samples taken from the “South Donbaska-1” mine have higher contents of Co, Cr, Cu, and Fe than the background soils. The concentration of heavy metals decreases with an increase in the distance from the spoil tip. A close relationship was observed between pH and the accumulation of some heavy metals. The analysis of the plant biomass samples collected from the spoil tip revealed that all investigated heavy metals, except for Co, Cu, and Zn, exceed the TLV. Hence, the results of the research indicated that spoil tips are permanent sources of pollution for the surrounding area, although the concentration of gross forms of heavy metals does not exceed the TLV. The study of the content of mobile forms of heavy metals in the spoil tip of the coal mine showed an increase in the integral index of the amount of TLV, which

makes it hazardous for human and animal consumption. The obtained data should be considered when planning reclamation and recreational work for the restoration as well as utilization of lands near spoil tips for agricultural purposes.

REFERENCES

1. Abuova, A.B., Rebezov, M.B., Mukhamedyarova, L.G. et. al. 2021. Results of Studies of Wheat Bread for Lead Content Using the Additive Method. IOP Conf. Ser. Earth Environ. Sci., 677, 052050. DOI: 10.1088/1755-1315/677/5/052050
2. Artemov, I.A., Popov, Yu.V., Sharova, T.V. 2022. Mineralo-petrographic zonation of the burning terraces of the sand-clay composition of eastern Donbas. Successes of modern natural science, (11). DOI: 10.17513/use.37936
3. Beregniak, E., Beregniak, M., Myronycheva, O. et. al. 2023. Ecological Analysis of the Current State of Forest Resources in Forest Steppe of Ukraine. J. of Ecological Engineering, 24(1), 87–96. DOI: 10.12911/22998993/155951
4. Biswas, A., Hendry, M.J., Essilfie-Dughan, J. et. al. 2022. Geochemistry of zinc and cadmium in coal waste rock, Elk Valley, British Columbia, Canada. Applied Geochemistry, 136. DOI: 10.1016/j.apgeochem.2021.105148
5. Bondar, V., Makarenko, N. 2019. Impact of winter wheat cultivation technologies on lead accumulation and translocation. Biological Resources and Nature Management, 11(1–2), 41–49. DOI: 10.31548/bio2018.03.030 (in Ukrainian)
6. Bondar, V.S., Fursa, A.V., Gumentyk, M.Ya., Svystunova, I.V. 2020. Climate Change: Apocalyptic Prognosis and Reality. Ukrainian Journal of Ecology, 10(2), 273–278. DOI: 10.15421/2020_96
7. Bulygin, S.Yu., Tonkha, O.L., Vitvitskyi, S.V., Kucher, L.I., Bulany, O.V. 2020. Evaluation and management of soil quality. Vinnychenko Publishing House, 478.
8. Cherkasova, E.I., Rebezov, M.B., Shariati, M.A. et. al. 2021. Monitoring the Stability of the Results of Studies of Chilled River Fish for Cadmium Content Using the Method of Additions. IOP Conf. Ser. Earth Environ. Sci., 677, 052060. DOI: 10.1088/1755-1315/677/5/052060
9. Das, N., Vimala, R., Karthika, P. 2008. Biosorption of heavy metals – an overview. Indian J. of Biotechnology, 7, 159–169.
10. Dold, B. 2017. Acid rock drainage prediction: A critical review. J. of Geochemical Exploration, 172, 120–132. DOI: 10.1016/j.gexplo.2016.09.014
11. Doulati, A.F., Jodeiri S.B., Bagheri, M., Soleimani, E. 2010. Investigation of pyrite oxidation and acid mine drainage characterization associated with Razi active coal mine and coal washing waste dumps in the Azad shahr-Ramian region, northeast Iran. Environmental Earth Sciences [https://link.springer.com/journal/12665\(61\)](https://link.springer.com/journal/12665(61)). DOI: 10.1007/s12665-010-0469-7
12. Felix-Henningsen, P., Urushadze, T., Steffens, D., Kalandadze, B., Narimanidze, E. 2010. Uptake of heavy metals by food crops from highly-polluted Chernozem-like soils in an irrigation district south of Tbilisi, eastern Georgia. Agronomy Research, 8(1), 781–795.
13. France, J., Thornley, J.H.M. 2007. Mathematical models in agriculture. London: Butterworths, 335.
14. Forghani, T.G., Rubinos, D., Kelm, U., Ghadimi, S. 2023. Environmental and human health risks of potentially harmful elements in mining-impacted soils: A case study of the Angouran Zn-Pb Mine. J. of Environmental Management, 334. DOI: 10.1016/j.jenvman.2023.117470
15. Goncharova, N.V. 2015. Structuring of complex coal deposits with respect to quality. J. of Mining Science, 51, 1220–1225. DOI: 10.1134/S1062739115060514
16. Han, F.X., Singer, A. 2007. Trace Element Distribution In Arid Zone Soils. In: Biogeochemistry of Trace Elements in Arid Environments. Environmental Pollution, 13. DOI: 10.1007/978-1-4020-6024-3_2
17. He, J., Chen, J.P. 2014. A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry, and modeling simulation tools. Bioresource Technology, 160, 67–78. DOI: 10.1016/j.biortech.2014.01.068
18. Imeri, R., Kullaj, E., Duhani, E., Millaku, L. 2019. Impact of rootstock on heavy metal bioaccumulation in apple plant grown near an industrial source in Obiliq, Kosovo. Agronomy Research, 17(1), 100–110. DOI: 10.15159/AR.19.012
19. Islam, K., Yokoi, R., Motoshita, M., Murakami, S. 2022. Ecological footprint accounting of mining areas and metal production of the world. Resources Conservation and Recycling, 183. DOI: 10.1016/j.resconrec.2022.106384
20. Jamieson, H.E., Walker, S.R., Parsons, M.B. 2015. Mineralogical characterization of mine waste. Applied Geochemistry, 57, 85–105. DOI: 10.1016/j.apgeochem.2014.12.014
21. Jiaorong, L., Han L., Yongsheng X. 2020. Impact of rock fragment size on erosion process and micro-topography evolution of cone-shaped spoil heaps. Geomorphology, 350. DOI: 10.1016/j.geomorph.2019.106936
22. Kabata-Pendias, A., Pendias, H. 2010. Trace Elements in Soil and Plants. CRC Press, Boca Raton, FL. DOI: 10.1201/b10158

23. Kachanovska, L.O., Kondakova, M.A. 2017. Agro-ecological assessment of soils of administrative area of the Herson regions. Scientific reports of NULES of Ukraine, 6(70). DOI: 10.31548/dopovid2017.06.004 (in Ukrainian)
24. Kachmar, N.V., Snitynskyi, V.V., Dydiv, A.I. 2018. Influence of fertilizers and meliorants on the phytoproductivity of white cabbage dining in case soil contamination lead. Plant and Soil Science, (268), 329–338. agriculturalscience.com.ua/web/uploads/pdf/10877-23570-1-SM.pdf (in Ukrainian)
25. Karpenko, V., Slobodyanyk, G., Ulianych, O. et. al. 2020. Combined application of microbial preparation, mineral fertilizer and bioadhesive in production of leek. Agronomy Research, 18(1), 148–162. DOI: 10.15159/AR.20.014
26. Knysh, L., Karabyn, V. 2014. Heavy metals distribution in the waste pile rocks of Chervonogradska mine of the Lviv-Volyn coal basin. Pollution Research, 33(4), 663–670. (in Ukraine).
27. Kravchenko, Y.S., Zhang, X., Song, C. et. al. 2022. Seasonal Dynamics of Organic Carbon and Nitrogen in Biomasses of Microorganisms in Arable Mollisols Affected by Different Tillage Systems. Land, 11, 486. DOI: 10.3390/land11040486
28. Kříbek, B., Bičáková, O., Sýkorová, I. et. al. 2021. Experimental pyrolysis of metalliferous coal: A contribution to the understanding of pyrometamorphism of organic matter and sulfides during coal waste heaps fires. International J. of Coal Geology, 245. DOI: 10.1016/j.coal.2021.103817
29. Król, A., Mizerna, K., Bożym, M. 2020. An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag. J. of Hazardous Materials, 384, 121502. DOI: 10.1016/j.jhazmat.2019.121502
30. Korzhenevska, P.O., Sharamok, T.S., Marenkov, O.N. 2021. Content of heavy metals in tsyogorych fishery of Dnipropetrovsk region. Scientific reports of NULES of Ukraine, 2(90). (in Ukrainian)
31. Kotaiah, D., Kiran, R. 2022. Numerical Analysis of High Wall and Dumps Slope Stability. J. of Mines, Metals and Fuels, 70(6). DOI: 10.18311/jmmf/2022/30801
32. Kucher, L.I. 2018. Estimation of potassium reserves in zonal chernozemic soils of Ukraine's forest-steppe Polish Journal of Soil Scienc., 51, 1. DOI: 10.17951/pjss.2018.51.1.83
33. Kucher, L., Poltoretskyi S., Vasylenko, O., et. al. 2022. Peculiarities of the Primary Process of the Soil Formation on the Mine Rock Dumps under the Influence of Biotic Factors. J. of Ecological Engineering, 23(11), 101–108. DOI: 10.12911/22998993/153399
34. Kuramshina, N., Rebezov, M., Kuramshin, E. et. al. 2018. Heavy Metals Contamination of Soil in Urban Areas of Southern Ural Region of Russia. International J. of Engineering and Technology, 7(4.42), 14–18.
35. Kuramshina, N., Rebezov, M., Kuramshin, E. et. al. 2019. Heavy metals content in meat and milk of orenburg region of Russia. International J. of Pharmaceutical Research, 11(1), 1031–1035.
36. Landa, P., Cyrusova, T., Jerabkova, J. et. al. 2016. Effect of Metal Oxides on Plant Germination: Phytotoxicity of Nanoparticles, Bulk Materials, and Metal Ions. Water, Air & Soil Pollution, 227, 448. DOI: 10.1007/s11270-016-3156-9
37. Lin, H., Tang, Y., Dong, Y. et. al. 2022. Characterization of heavy metal migration, the microbial community, and potential bioremediating genera in a waste-rock pile field of the largest copper mine in Asia. J. of Cleaner Production, 351. DOI: 10.1016/j.jclepro.2022.131569
38. Makarenko, N.A., Budak, O.O. 2017. Improvement of the environmental monitoring system rural areas which are located in the zone of influence of municipal solid waste landfills. Biological Resources and Nature Management, 9, 5–6, 89–97. (in Ukrainian)
39. Mazhayskiy, Yu.A., Guseva, T.M., Kurchevskiy, S.M., Vcherashnyaya, V.V. 2022. Agrochemical methods for reducing the translocation ability of heavy metals in sod-podzolic soil. Agronomy Research, 20(2), 310–317. DOI: 10.15159/AR.22.014
40. Mianovski, A., Butuzova, L., Radko, T., Turchanina, O. 2005. Thermokinetic analysis of the decomposition of Ukrainian coals from the Donetsk Basin. Bulletin of Geosciences, 80, 1, 39–43 www.researchgate.net/publication/287422798
41. Miniailo, N.V. 2018. Assessment methods of ecological condition of agrolandscapes. Biological Resources and Nature Management, 10(3–4), 92–97. DOI: 10.31548/bio2018.03.011 (in Ukrainian)
42. Munir, N., Jahangeer, M., Bouyahya, A. et. al. 2022. Heavy metal contamination of natural foods is a serious health issue: A review. Sustainability (Switzerland), 14(1), 161. DOI: 10.3390/su14010161
43. Nobis, B., Kenyon, Z. 2022. Reclaiming waste rock piles at Bingham Canyon Mine. Proceedings of the International Conference on Mine Closure, 1, 15th International Conference on Mine Closure, Mine Closure Brisbane. DOI: 10.36487/ACG_repo/2215_77
44. Olkhovych O., Taran N., Hrechishkina S. et. al. Evaluation of hyper-tolerance of aquatic plants to metal nanoparticles. Journal of Ecological Engineering, 23(8), 249–259. doi.org/10.12911/22998993/150719
45. Okhremchuk, I. 2018. Integrates assessment models for modeling of climate mitigation policies. Biological Resources and Nature Management, 10(1–2),

- 73–78. (in Ukrainian)
46. Opara, C.B., Kamariah, N., Spooren, J., Pollmann, K., Kutschke, S. 2023. Interesting Halophilic Sulphur-Oxidising Bacteria with Bioleaching Potential: Implications for Pollutant Mobilisation from Mine Waste. *Microorganisms*, 11(1). DOI: 10.3390/microorganisms11010222
47. Petrova, T., Rudzisha, E., Alekseenko, A., Bech, J., Pashkevich, M. 2022. Rehabilitation of Disturbed Lands with Industrial Wastewater Sludge. *Minerals*, 12(3). DOI: 10.3390/min12030376
48. Popovych, V., Kuzmenko, O., Voloshchyshyn, A., Petlovanyi, M. 2018. Influence of man-made edaphotopes of the spoil heap on biota. *E3S Web of Conferences*, 60. DOI: 10.1051/e3sconf/20186000010
49. Qi, Li, Wenbin, Fei, Xuehao, Liu et al. 2014. Challenging combination of CO₂ geological storage and coal mining in the Ordos basin, China Greenhouse Gases. *Science and Technology*, 4(4). DOI: 10.1002/ghg.1408
50. Rebezov, M.B., Shariati, M.A., Ryskina, E.A. et al. 2020. Monitoring the Research Results on the Toxic Elements Content (Lead, Cadmium and Arsenic) in Food. *IOP Conf. Ser. Earth Environ. Sci.*, 613, 012123. DOI: 10.1088/1755-1315/613/1/012123
51. Rebezov, M.B., Shariati, M.A., Shinkarev, I.K. et al. 2021a. Results of Comparative Research Methods for Arsenic Content in Meat Samples of Broiler Chickens. *IOP Conf. Ser. Earth Environ. Sci.*, 677, 052053. DOI: 10.1088/1755-1315/677/5/052053
52. Rebezov, M.B., Kudryavtseva, T.M., Meshcheryakova, G.V. et al. 2021b. Control of the Stability of the Results of Studies of Cadmium Content Using the Method of Additions in Cow's Milk Samples. *IOP Conf. Ser. Earth Environ. Sci.*, 677, 052051. DOI: 10.1088/1755-1315/677/5/052051
53. Rebezov, M.B., Assirzhanova, Z.B., Dautova, A. et al. 2021c. Control by the Accuracy of the Results of Studies for the Lead Content in Samples Applying the Microwave Laboratory System PLP-01M. *IOP Conf. Ser. Mater. Sci. Eng.*, 1047, 012188. DOI: 10.1088/1757-899x/1047/1/012188
54. Ruban, Yu., Illienko, V., Nesterova, N., Pareniuk, O., Shavanova, K. 2017. Estimation of the effect of radionuclide contamination on *Vicia sativa* L. induction of chlorophyll fluorescence parameters using "Floratest" optical biosensor," *Proc. SPIE 10592, Biophotonics-Riga, 105920M*. DOI: 10.1117/12.2297563
55. Reshetnyak, V.N., Zakrutkin, V.E. Gibkov, E.V. 2022. Integral assessment of river sediments technogenic contamination within Eastern Donbass coal-mining area *Theoretical and Applied Ecology*, 4. DOI: 10.25750/1995-4301-2022-4-080-087
56. Schubert, J., Radeke, C., Fery, A., Chanana, M. 2019. The role of pH, metal ions and their hydroxides in charge reversal of protein-coated nanoparticles. *Physical Chemistry Chemical Physics*, 21(21), 11011–11018. DOI: 10.1039/C8CP05946B
57. Sidkina, E., Soldatova, E., Cherkasova, E. et al. 2022. Fate of Heavy Metals in the Surface Water-Dump Rock System of the Mine Lupikko I (Karelia): Field Observations and Geochemical Modeling. *Water (Switzerland)*, 14(21). DOI: 10.3390/w14213382
58. Singh, B.R., Gupta, S.K., Azaizeh, H. et al. 2011. Safety of food crops on land contaminated with trace elements. *J. of the Science of Food and Agriculture*, 91(8), 1349–66. DOI: 10.1002/jsfa.4355
59. Sintorini, M.M., Widyatmoko, H., Sinaga, E., Aliyah, N. 2021. Effect of pH on metal mobility in the soil. *IOP Conf. Series: Earth and Environmental Science*, 737, 012071. DOI: 10.1088/1755-1315/737/1/012071
60. Shi-Lei, Y., Xin, L. 2022. Study on Multi-Indicator Quantitative Risk Evaluation Methods for Different Periods of Coal Spontaneous Combustion in Coal Mines Combustion. *Science and Technology*. DOI: 10.1080/00102202.2022.2121608
61. Skok, S. 2018. Spatial heterogeneity of soil contamination of urban systems with heavy metals. *Scientific reports of NULES of Ukraine*, 3(73). DOI: 10.31548/dopovidi2018.03.005 (in Ukrainian)
62. Slobodianyk, H., Zhilyak, I., Mostovyak, I., Shchetyna, S., Zabolotnyi, O. 2022. Effectiveness of different groups of preparations for pre-sowing treatment of winter wheat seeds. *Scientific Horizons*, 25(9), 53–63. DOI: 10.48077/scihor.25(9).2022.53-63
63. Small mining encyclopedia. 2004: 1t. za red. V.S. Biletskoho. Donetsk: Skhidnyi vydavnychiy dim, 640. (in Ukrainian)
64. Sperdoui, I. 2022. Heavy Metal Toxicity Effects on Plants. *Toxics*, 10, 715. DOI: 10.3390/toxics10120715
65. Tretyak, L.N., Rebezov, M.B., Korablev, A.V. et al. 2021. Control by the Accuracy of the Results of Studies for the Cadmium Content in Samples Applying the Microwave Laboratory System PLP-01M. *IOP Conf. Ser. Mater. Sci. Eng.*, 1047, 012183. DOI: 10.1088/1757-899x/1047/1/012183
66. Tubis, A., Werbińska-Wojciechowska, S., Wroblewski, A. 2020. Risk assessment methods in mining industry-A systematic review. *Applied Sciences (Switzerland)*, 10(15). DOI: 10.3390/app10155172
67. Ulianych, O.I., Schetyna, S.V., Slobodianyk, G.Ya., et al. 2018. Ecological Status of Soils and Vegetable Products in Cherkasy Region. *Ukrainian J. of Ecology*, 8(2), 10–15.
68. Vaziri, V, Sayadi, A.R., Parbhakar-Fox, A., Mousavi, A., Monjezi, M. 2022. Improved mine waste dump planning through integration of geochemical and mineralogical data and mixed integer programming:

- Reducing acid rock generation from mine waste. *J. of Environmental Management*, 3091. DOI: 10.1016/j.jenvman.2022.114712
69. Voitsitskiy, V.M., Midyk, S.V., Poltavchenko, T.V. et. al. 2019. Ecosystem monitoring: goals and necessity, role of bioindication. *Biological Resources and Nature Management*, 11(3–4), 39–46. DOI: 10.31548/bio2019.03.005 (in Ukrainian)
70. Xiang, Y., Xiang, Y., Wang, L. Zhang Z. 2016. Effects of Modified Excess Sludge on the Growth of *Artemisia ordosica* and Transformation of Heavy Metals. *Water Air Soil Pollut.*, 227, 123. DOI: 10.1007/s11270-016-2818-y
71. Xiaoyang L., Wei Z., Zhongke B. 2016. Vegetation coverage change and stability in large open-pit coal mine dumps in China during 1990-2015. *Ecological Engineering*, 95, 447–451. DOI: 10.1016/j.ecoleng.2016.06.051
72. Yamborko, N.A., Iutynska, G.A., Svistunova, I.V. 2018. Biodestruction of Hexahorocyclohexane Isomers by Natural and Artificial Created Microbial Associations. *Mikrobiolohichni Zhurnal*, 80(5), 15–24. DOI: 10.15407/mikrobiolj80.05.015
73. Yakovenko, A.V. 2017. Geochemistry of heavy metals in soils of the zone of influence of the non-ferrous metallurgy enterprises Scientific reports of NULES of Ukraine, 6(10). DOI: 10.31548/dopovid2017.06.002 (in Ukrainian)
74. Yao, H., Lu, J., Yuan, X. 2014. Concentrations, Bioavailability, and Spatial Distribution of Soil Heavy Metals in a Long-Term Wastewater Irrigation Area in North China. *CLEAN - Soil, Air, Water*, 42. DOI: 10.1002/clen.201200574
75. Yermishev, O.V., Mudrak, O.V. 2019. Environmental and comparison analysis of functional health of men of different age groups in radiation contaminated and conditionally pure regions. *Biological Resources and Nature Management*, 11(5–6), 108–118. DOI: 10.31548/bio2019.04.012 (in Ukrainian)
76. Zhang, X., Dayton, E.A., Basta, N.T. 2020. Predicting the modifying effect of soils on arsenic phytotoxicity and phytoaccumulation using soil properties or soil extraction methods. *Environmental Pollution*, 263. DOI: 10.1016/j.envpol.2020.114501
77. Zykova, I., Rebezov, M., Maksimiuk, N., Kuramshina, N. 2016. The interaction of metals with humic acid of activated sludge and biological treatment facilities sludge. *International J. of Chem. Tech. Research*, 9(3), 372–378.
78. Zykova, I., Maksimuk, N., Rebezov, M. et. al. 2019. Interaction between heavy metals and microorganisms during wastewater treatment by activated sludge. *ARPJ. of Engineering and Applied Sciences*, 14(11), 2139–2145.
79. Zhenqi, Hu, Qing, Xia. 2017. An integrated methodology for monitoring spontaneous combustion of coal waste dumps based on surface temperature detection. *Applied Thermal Engineering*, 122, 27–38. DOI: 10.1016/j.applthermaleng.2017.05.019
80. Żukowska, T., Chomeczyńska, M., Myszura, M., 2021. Influence of diversified anthropogenic pressure on heavy metals contents in soils and plants of garden allotments. *J. of Physics: Conference Series*, 1736, 1. DOI: 10.1088/1742-6596/1736/1/012055