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Chemical pollution peculiarities of the Nadiya mine rock dumps in the Chervonohrad Mining District, Ukraine

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Abstract

Purpose. The research purpose is to study the peculiarities of chemical pollution of the Nadiya mine rock dumps in the Chervonohrad Mining District, depending on the relief conditions and slope exposure, as well as to analyze the general trends in the distribution of chemical elements compared to the natural background.

Methods. The chemical pollution differentiation of the Nadiya mine rock dumps at the level of ecotopes is studied on the basis of dispersion analysis; multidimensional ordination of ecotopes in the space of geochemical indicators – based on the Principle Component Analysis; a typological scheme of mine rock dump ecotopes is constructed based on discriminant analysis; statistical processing of chemical pollution parameters.

Findings. It has been determined that the level of chemical pollution of the Nadiya mine rock dumps is characterized by significant heterogeneity even within the same slope exposure. Similarity in the distribution of chemical elements makes it possible to distinguish 6 of their associations, the main of which are I (Mg, Ca, S) and II (Al, Fe, K, Si). An analysis of the dependence between the chemical element concentrations indicates a close link between many parameters. It has been revealed that the closest dependence on the anthropogenic load intensity is demonstrated by such elements as Mg, Pb, Sn, Fe, Al, Cu, P, Ni, Zn. It has been determined that the difference between the ecotopes of different dump exposures is explained mainly by the level of Ca and Al concentration.

Originality. It has been revealed for the first time that the Nadiya mine rock dumps of the Chervonohrad Mining District are characterized by an ecological space, which is assessed on the basis of the ordination of ecotopes on the axes of complex geochemical gradients of the environment. The typological scheme of mine rock dumps reflects the gradient of soil cover chemical pollution compared to the natural background.

Practical implications. By determining the geochemical conditions of ecotopes in a certain period of time, it is possible to identify their position in the ecological-cenotic space of dump vegetation, as well as to predict the stability and possible changes in the vegetation cover as a result of various forms of anthropogenic impact.

Keywords: *mine rock dumps, chemical pollution, ecotope, complex environmental gradient, mathematical modeling*

1. Introduction

Research on the content of heavy metals in environmental components is given great attention in the global context. In particular, numerous studies are devoted to the industrial regions of the USA, China, Spain, Poland, Germany, Great Britain, etc. Heavy metal concentrations in soil have increased dramatically over the past three decades, posing a risk to the environment and human health. Some technologies have been used for a long time to eliminate hazardous heavy metals. The review [1] summarizes soil pollution with heavy metals on a global scale, the accumulation of heavy metals and their normative levels in soil.

Heavy metals transferred from soils to agricultural crops can pose a potential risk to human health. Similar to high levels of heavy metals in soil and corn, the concentrations of Cd, Cr, Cu, Pb, and Zn in moss samples collected from zinc smelting sites in Hezhang and Guizhou (China) range from 10 to 110, from 10 to 55, from 26 to 51, from 400 to 1200 and from 330 to 1100 mg/kg, respectively, demonstrating the local spatial pattern of metal deposition from the atmosphere [2].

In order to stabilize and isolate the toxic metal-bearing waste heap at the Park Mine, North Wales, in 1977-1978 it was covered with a 30-40 cm layer of quarry waste and seeded with a grass/clover mixture. The growth of roots on the dump flat top is more intense than on the slope, but the roots have not penetrated into the waste, and the Pb, Zn, and Cd content in surface vegetation remains low. Thus, covering the surface of toxic waste with coarse capillary-limiting materials is a valid disposal method if the lateral movement of the toxic filtrate can be controlled [3].

In the work [4], the genetic diversity and differentiation of two Echium vulgare L. populations, which originate from mining and metallurgical waste deposits of Zn-Pb (MP, MB populations) and one from the unpolluted soils (NM popula-

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tion), are studied. Harsh environmental conditions do not reduce the genetic diversity of Echium vulgare L., but, on the contrary, increase it. All markers indicate a differentiation between metallic and non-metallic plant populations. The molecular marker systems used do not provide unified information on the intra- and inter-population diversity of Echium vulgare L. It is concluded here that the use of only one method instead of a combination of several marker systems can give deceptive results.

A multi-element geochemical study of mining waste, soils, river sediments, water and air samples is conducted in the zone of influence of old mining and metallurgical plants in Asturias (Spain). The total Hg and As concentrations in soils reach values up to 502 and 19940 mg/kg, respectively, which are 500 and 2000 times higher than the local background levels. The effects of mining are intense both in water and river sediments, as well as in the local atmosphere, where mercury levels are 10 times higher than background levels in the area [5].

The concentration of trace elements Zn, Pb, Cu, and Cd in Scots pine needles in post-coal ecosystems does not differ from the data in natural areas. It is concluded that in this part of Europe, in forest areas, with impurities of hard coal, sand, brown coal and sulfur, there is no risk of concentration of trace elements in mine soils during mining. An exception is the case of Cd in the soils of a sandstone quarry and a coal dump located in the Upper Silesia region (Poland), which is more related to industrial pressure and pollutant deposition than to the initial Cd concentration in the parent rocks [6].

The areas around the non-ferrous metal mine in the south of China have been studied [7]. Three types of sampling sites (A-C) have been distinguished on mineral waste soil in the mining area and on adjacent agricultural lands (D), as well as along the riverbed (E) outside the mining area: A – the soil recently cultivated from mineral waste; B – a steep 6-month-old stack of waste soil; C – a gentle slope of the 12-month-old wasteland; D – the soil of agricultural lands within 1 km from the mine; E – the river water and adjacent soil. The average Pb, Zn, and Cd content in the mining area (types A-C) is 2028, 3794, and 14.8 mg/kg, respectively, which is 8, 19, and 49 times higher than the second level of the environmental quality standard for Chinese soils. The average Pb, Zn, and Cd content for D and E sites is 76.4, 131, and 0.18 mg/kg and 147, 194, and 0.95 mg/kg, respectively, all of which are below the second level limits.

The dynamics of oil pollution of the profile-differentiated soils of the Precarpathian region in the zone of influence of deep wells of the Vilkhiv oil exploration area in the Boryslav-Pokutsk oil-and-gas-bearing region of Ukraine has been studied. The highest concentration of pollutants has been found in the silts of elementary transsuperaquatic landscapes in the amount of up to 1750 mg/kg. In deeper horizons, pollutant concentrations are reduced in a non-linear manner, with different dynamics of this process in different elementary geochemical landscapes [8].

The peculiarities of the Lviv-Volyn coal basin as a center of industrial development in Western Ukraine are studied in [9], [10]. The characterization of the closed mine dumps within this basin is performed. The toxicological composition of the Novovolynska mine dumps is studied and their impact on the environment is determined. Mine rock dumps in the Lviv-Volyn region have an increased acidity, a significant content of various salts and sulphate-ions. In [11], the strength and microstructural properties of the backfill mass are studied and assessed when backfilling underground cavities, which pose a threat of mine rock caving in the process of mining mineral deposits.

Coal mining at the Nadiya mine in the Chervonohrad Mining District of Ukraine has led to significant environmental changes: the earth's surface subsidence, depletion of aquifers, pollution of the atmosphere, soil and water. These phenomena have a negative impact not only on vegetation and fauna, but also on the health of the population (mass fluorosis and hypoplasia of teeth, silicosis, etc.). Changes in the vegetation cover have led to the massive spread of ruderal plant species – weeds [12].

The research purpose is to study the peculiarities of chemical pollution of the Nadiya mine dumps in the Chervonohrad Mining District, depending on the relief conditions and slope exposure, as well as to analyze the general trends in the distribution of chemical elements compared to the natural background. In accordance with the purpose, it is envisaged to solve such tasks: in the course of the field studies, identify areas of burning on the rock dump and take rock and water samples for further analysis in the stationary laboratory; determine the species composition of the succession; analyze the content of chemical elements in each sample; study the peculiarities of the distribution of chemical elements using mathematical modeling by determining systematic bonds between them; assess the differences between the parameters of the mine dump ecotopes by dispersion analysis; verify the mathematical model based on a comparative assessment of the position of ecotopes on the axes of maximum variation (multidimensional ordination) with the results of geobotanical research; draw conclusions about the degree of chemical pollution of the rock dump and the peculiarities of the ecotope formation.

2. Research methods

The research area is located in the Male Polissia geobotanical district. It is characterized by a surface flatness, a large spread of sands and sod-podzolic sandy soils, pine and oak-pine forests, meadows, as well as significant swampiness. The most common sod-podzolic sandy soils are characterized by a low humus content (0.6-1.3%), an acidic reaction (pH = 5.33-6.14) and an insignificant amount of mobile nutrients [13]. The climate is Atlantic-continental, characterized by a significant amount of precipitation (620-750 mm), mild winters with frequent thaws and unstable snow cover, moderately warm summers, without persistent droughts and dry winds.

The geographical location of the Lviv-Volyn coal basin corresponds to the Male Polissia zone, the climate of which is influenced by the Atlantic air masses. Since the Chervonohrad Mining District was the first to be mined, the largest amount of rock is concentrated on its waste heaps. One of the largest mines in the district is Nadiya mine, the waste heap volume of which is 2869.4 thousand m^3. It is the waste heap of this mine that is the object of our research.

The Nadiya mine is located near the town of Sosnivka, Lviv region of Ukraine (geographic coordinates 50°18′35″ N, 24°13′03″ E). The dump is located next to the industrial mine facilities, surrounded by forest from two sides, and garden plots from the other two sides (Fig. 1).

A dump of a complex shape, composed mainly of burnt rocks. Its height is 42 m, the base area is 12 hectares [14]. The ash content in the rock is 83.1%, sulfur – 2.4%.

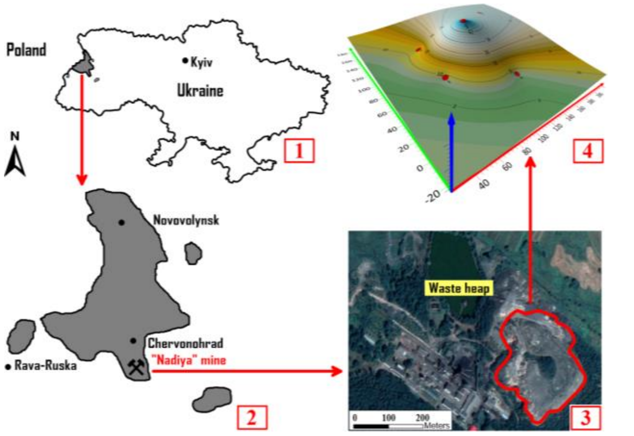

Figure 1. Layout of the study object: 1 – a map of Ukraine with the designation of the Lviv-Volyn coal basin; 2 – the Lviv-Volyn coal basin scheme with the designation of the Nadiya mine; 3 – the Nadiya mine map with the designation of a rock dump, made using Google Maps; 4 – 3-D rock dump model

The rock density is 2.25 kg/m^3. The rock dump base area is 120 thousand m^2, the height is 53 m, the rock dumping angle along the contour is 36°, the annual rock supply into the dump is 9.8 thousand m^3 (according to the Passport data of the Nadiya mine rock dump No.1, as updated in September, 2021). In general, the rock dumping began in August 1962, and the rock combustion began already in September 1963 and continues in a number of sources to this day. On the Nadiya mine dumps, mining-technical reclamation has been conducted with the application of about 40 cm of sandy or loamy layer. Thus, such factors as the age of dumping and the rock combustion processes prompted us to study the technogenic hazard of the Nadiya mine dump in the Lviv-Volyn coal basin. A general view of the rock dump is shown in Figure 2.

(a)

(b)

Figure 2. Slope exposition of the the Nadiya mine dump: (a) the southern exposition; (b) top

Analysis of samples for the content of chemical elements is performed in the chemical laboratory of the Freiberg University of Mining and Technology (Saxony, Germany). In total, 38 concentrations of chemical elements are analyzed, which represent 48 ecotopes of the Nadiya mine dumps and a pine forest control site located 3 km from the industrial facility.

Peculiarities of distribution of chemical elements are studied on the basis of mathematical modeling by determining systematic bonds between chemical elements. Each ecotope can be represented as a point in a multidimensional space of features, the coordinates of which correspond to the values of chemical element concentrations. In this case, the similarity of ecotopes according to the set of chemical element parameters can be determined based on the distances between the points. The essence of the further mathematical procedure is to identify the axes of maximum variation, determine their quantity, and assess the value of each chemical element for variation based on the principal components analysis [15], [16].

The differences between the ecotope parameters of the Nadiya mine dumps are assessed using dispersion analysis. Based on the canonical discriminant analysis, a typological scheme of mine ecotopes and a graphical visualization of the mathematical modeling results is constructed.

The mathematical model verification is performed on the basis of a comparative assessment of the ecotopes position on the axes of maximum variation (multidimensional ordination) with the results of geobotanical studies [16].

To assess the toxic impact of rock dumps on the hydrographic network, 5 water samples are taken and their content is analyzed for chemical elements. Water samples are taken from the following areas: 1 – wastewater from the southern side of the rock dump; 2 – puddle on the western side of the rock dump; 3 – the river of Rata; 4 – the river of Zahidny Bug; 5 – the river of Rata downstream 2.5 km from sample No. 3. Water samples are analyzed in the Laboratory of Industrial Toxicology in Lviv.

3. Research results

The concentration of chemical elements from the Nadiya mine dumps is highly heterogeneous. This is evidenced by the variability of the minimum, maximum and average concentration values, as well as their comparative analysis with the control site (Table 1). Comparing the maximum values of the chemical element concentrations, it is possible to conclude that the content of almost all chemical elements has significantly increased compared to the natural background. High concentrations are typical for the following chemical elements: Si, Al, Fe, K, S, Mg, Ca. The vast majority of the studied chemical elements have low concentrations: Lu, Tm, Cd, Ho, Tb, Eu, Yb, etc.

The site location (slope exposure, relief elements) and the substrate depth have a significant influence on the distribution of chemical elements. The similarity of locations in terms of the chemical element concentrations is assessed on the basis of cluster analysis. In this case, the Ward's method is used, in which the minimum dispersion is optimized within the clusters, resulting in clusters of approximately the same size. Euclidean distances are used as a measure of differences. The main result of the hierarchical cluster analysis is a dendrogram (Fig. 3).

Table 1. Concentration of chemical elements in the substrates of the Nadiya mine waste heap and on the control site

Chemical element	Waste heap				Control site			
	Mean	Minimum	Maximum	Mean	Minimum	Minimum	Mean	Minimum
Al	223290.2	32340.00	395000.0	19018.0	112883.8	24210.0	203100.0	33383.9
As	129.3	14.45	283.9	13.0	117.5	40.8	195.2	28.9
Ca	16240.9	2508.00	61240.0	2661.3	3043.8	1226.0	5349.0	644.1
Cd	2.3	1.60	3.2	0.1	2.4	1.5	3.4	0.3
Ce	234.5	36.15	378.5	16.6	22.2	20.9	23.3	0.3
Co	83.3	4.51	258.5	12.6	44.6	3.8	86.4	15.4
Cr	741.9	369.80	1100.0	43.3	643.4	342.1	950.6	112.6
Cu	268.4	19.49	603.0	29.8	194.0	13.9	379.4	68.0
Dy	13.5	2.33	27.1	1.1	3.7	1.3	6.2	0.9
Er	7.1	1.52	13.2	0.5	2.3	0.8	3.8	0.5
Eu	4.9	0.69	10.1	0.4	0.9	0.4	1.5	0.2
Fe	187963.8	14970.00	480100.0	23236.5	111257.5	12060.0	213100.0	37446.9
Ga	78.4	12.60	130.4	6.4	46.3	7.5	89.6	14.5
Gd	18.9	2.49	38.1	1.5	3.3	1.5	5.1	0.7
Ge	7.5	1.53	20.8	0.9	6.4	1.0	12.7	2.0
Ho	2.5	0.47	5.0	0.2	0.8	0.3	1.2	0.2
K	100214.3	55050.00	145300.0	4398.2	82890.0	53450.0	112200.0	10481.0
La	113.7	18.30	183.8	8.0	9.8	7.7	11.8	0.6
Lu	1.0	0.25	1.6	0.1	0.4	0.1	0.7	0.1
Mg	18140.2	1480.00	35780.0	1631.2	6160.7	1059.0	11390.0	1919.0
Mn	2874.0	275.60	9690.0	516.7	1246.6	203.4	2319.0	393.4
Nd	115.5	16.75	194.2	8.5	13.2	9.6	17.0	1.3
Ni	323.8	126.90	732.1	27.0	254.3	117.7	394.3	51.2
P	3803.7	1121.00	9151.0	382.1	2565.3	1548.0	3624.0	354.7
Pb	137.0	55.49	251.0	9.9	91.2	31.4	153.2	22.5
Pr	29.1	4.32	48.3	2.1	3.0	2.4	3.6	0.2
S	31223.4	445.30	69950.0	3511.1	29997.5	10240.0	49940.0	7431.1
Sc	49.7	4.87	92.7	4.5	15.7	3.6	27.7	4.5
Si	286184.2	10110.00	582700.0	24303.4	190537.5	108600.0	273600.0	30345.1
Sm	23.0	3.23	42.0	1.8	3.5	1.6	5.5	0.7
Sn	11.3	0.01	25.5	1.2	6.8	0.1	14.3	2.5
Tb	2.6	0.39	5.3	0.2	0.6	0.2	1.0	0.1
Th	53.1	6.58	85.0	3.8	6.0	4.0	8.1	0.7
Tm	1.0	0.23	1.8	0.1	0.4	0.1	0.6	0.1
U	21.1	2.37	54.4	2.3	11.5	1.3	22.4	3.9
Y	65.4	12.04	130.1	5.1	12.6	7.0	18.4	2.0
Yb	6.5	1.64	10.5	0.4	2.5	0.9	4.2	0.6
Zn	348.2	72.81	735.4	35.9	171.6	25.3	321.3	55.0

Visual analysis of the similarity dendrogram of the waste heap sites indicates a significant chaotic distribution of the chemical elements, which is caused by the substrate heterogeneity, fire, washout, etc. Therefore, the task of our research is precisely to reveal in a large array of numbers the peculiarities that characterize the specified distribution. Thus, for the control site, the eastern exposure slope foot (20 cm deep) and the waste heap top (15 cm deep) are the closest in terms of the concentration of the entire set of chemical elements. The significant substrate heterogeneity is evidenced, in particular, by the fact that the foot samples of the same eastern exposure, taken at different depths, are characterized by greatest difference in the chemical element concentrations. A large difference in the distribution of chemical elements is also characteristic of such areas: K_15 and E_15, S_15 and E_15. Thus, the cluster analysis testifies to the significant substrate heterogeneity of the eastern exposure foot.

A typical approach to the cluster analysis of the distribution of chemical elements is in using elementary waste heap sites as objects. But, an alternative approach is additionally use. The chemical elements themselves can also be objects of analysis, the features of which are their concentrations on the elementary waste heap sites. Using this approach, the similarity of chemical elements according to their distribution on the waste heap has been determined. In particular, the following associations (groups) of chemical elements have been distinguished:

I – Mg, Ca, S;
II – Al, Fe, K, Si;
III – Cu, Ni, Zn, Cr;
IV – P, Mn;
V – As, Pb, Co;
VI – Sn, Dy, Cd.

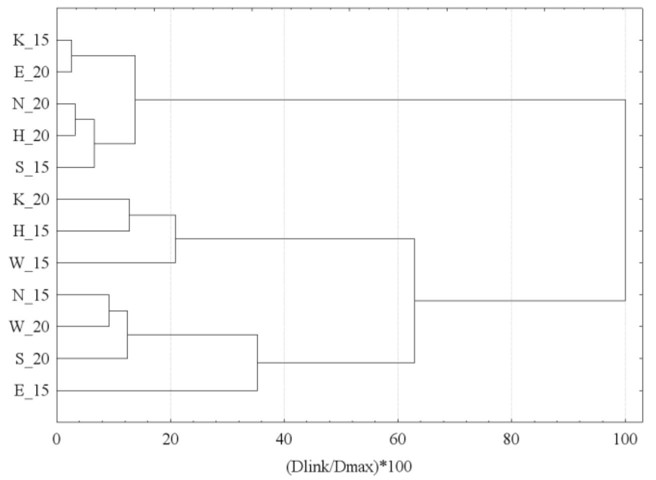

Figure 3. Similarity dendrogram of the sites on the Nadiya mine waste heap in terms of the chemical element concentrations depending on their location and the sampling depth; conventional signs: 15, 20 – sampling depth, cm; H – the waste heap top; exposure of the foot of the slopes: N – North; E – East; S – South; W – West; K – control site (pine forest)

Analysis of the dependence between the chemical element concentrations indicates the existence of a close link between many variables (Fig. 4). Thus, for concentrations of Mg and Pb correlation coefficient is *r* = 0.95, Mg and Al – *r* = 0.95, Al and K – *r* = 0.96, P and Fe – *r* = 0.95, Cr and Sn – *r* = 0.81, Fe and Co – *r* = 0.95, Cu and Ni – *r* = 0.92. The following chemical element pairs demonstrate a weak bond: Ca and P – *r* = 0.28, Si and S – *r* = 0.20, Fe and Ca – *r* = 0.35, K and Ca – *r* = 0.29, Fe and C – *r* = 0.21. The weakest bond in the chemical element concentrations is demonstrated by Si, for which the average value of the correlation coefficient is 0.36, as well as by Ca (average value is *r* = 0.43). Thus, the presence of an ordered structure is characteristic of the multidimensional ordination of the Nadiya mine waste heap locations according to the chemical element concentrations, which gives grounds for a mathematical procedure for reducing the measurability of space.

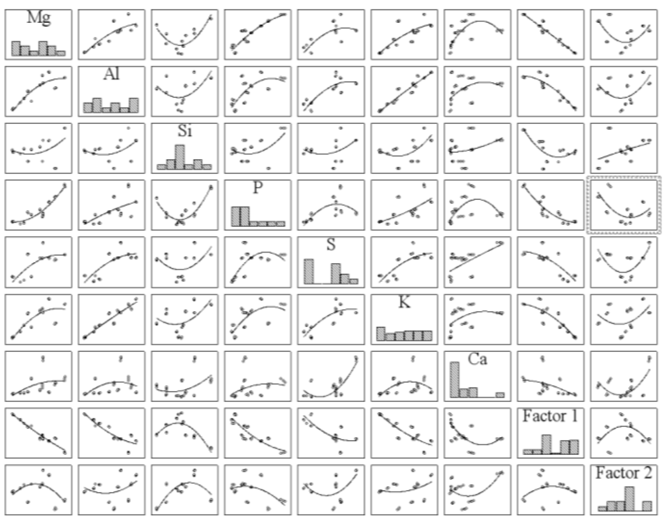

Figure 4. System of interrelations between chemical element concentrations and complex environmental gradients. Conventional signs: $Factor_{1-2}$ – the principal components, complex gradients of the environment

Since chemical element concentrations are correlated with each other, the results of observations can be explained by a small number of new variables that are not directly measured, but can be obtained through a linear combination of input data. This reduces the measurability of the observation space. Graphically, the calculation procedure consists in moving the origin of the coordinates to the data center so that the abscissa passes in the direction of the maximum dispersion of the data set.

The decrease in the measurability of the observation space is performed within the framework of the component analysis. The component analysis objective is in transforming the original system of interrelated variables into a new system of uncorrelated generalized indicators or orthogonal indicators. The new uncorrelated indicators are called components. The first component characterizes the largest share of variation in the output variables, and the second component explains the largest share of the dispersion that is not explained by the first component, etc. Each extracted component has a characteristic called an eigenvalue. The eigenvalue shows the share of the variation in the output variables that is explained by the component. The calculation results are shown in Figure 5.

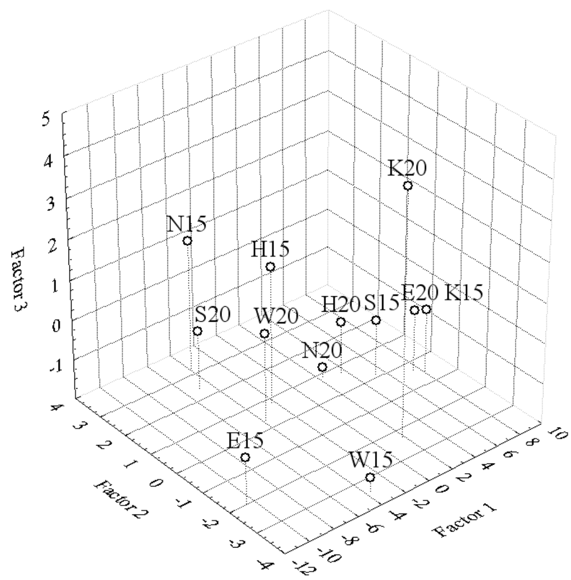

Figure 5. Three-dimensional projection of the Nadiya mine waste heap locations; conventional signs: 15, 20 – sampling depth; H – top; exposure of the slopes: N – North; E – East; S – South; W – West; K – control site; $Factor_{1-3}$ – the principal components, complex gradients of the environment

It follows from the analysis of the characteristics of eigenvalues λ_i that the first principal component of $Factor_1$ provides 76.3%, the two principal components of $Factor_{1-2}$ – 84.8%, and the three principal components of $Factor_{1-3}$ provide about 91.0% of the total dispersion. Thus, for many purposes of analysis, it is sufficient to use a two- or three-dimensional projection of the original data matrix. The correlation matrix eigenvectors make it possible to distinguish combinations of chemical element concentrations that determine the axes of maximum variation of the waste heap biogeocenotic cover. The main peculiarity of the formation of dump ecotopes (the first principal component) is in the following structure of bonds between the chemical element concentrations (Fig. 3): a decrease in $Factor_1$ function associated with an increase in the concentration of all chemical elements without exception. The closest bond with $Factor_1$ is typical of such chemical elements: Mg (correlation coefficient is r = -0.97), Pb, Sn (r = -0.96), Fe, Al (r = -0.90), Cu, P (r = -0.88), Ni, Zn (r = -0.83). The weakest bond with the first principal component is demonstrated by Ca (r = -0.49) and Si (r = -0.43). The values of the second principal component of $Factor_2$ demonstrate a positive bond with the concentration of such chemical elements as Si (r = 0.42), Ca (r = 0.32) and a negative bond with Mn (r = -0.66), Co (r = -0.58), Ni (r = -0.45), Fe (r = -0.40), Cu, As (r = -0.39), P (r = -0.38). The third principal component of $Factor_3$ depends mainly on concentration of Cr, S (r = 0.50), Cd (r = 0.47), K (r = 0.32), Mn (r = -0.25), Si (r = -0.22).

The first principal component reflects the intensity of anthropogenic load on the waste heap ecotopes. For example, control sites with natural forest stand are characterized by high values of the $Factor_1$ function. Locations with low values of the first principal component have high concentrations of chemical elements in the soil. This, in particular, is the foot of the western exposition waste heap. The results of the analysis of the principal components indicate a significant mosaic distribution nature of waste heap sites according to the intensity of anthropogenic load, since the concentration of chemical elements largely depends on the sampling depth. The waste heap top, which is located at the zero marks of the main components (Fig. 4), is characterized by average indicators of anthropogenic impact. It is possible to reduce the measurability of the observation space not only by calculating the principal components, but also by removing individual chemical elements from the analysis, taking into account their close bonds with each other (high correlation coefficient values). The dispersion analysis results are the basis for subsequent conclusions (Table 2).

Table 2. Dispersion analysis results of the chemical element concentrations by location in the relief

Chemical element	SS Effect	df Effect	MS Effect	SS Error	df Error	MS Error	F	p
Al	3.05E + 10	4	7.63E + 09	5.33E + 11	35	1.52E + 10	0.50	0.74
As	7.11E + 04	4	1.77E + 04	1.90E + 05	35	5.45E + 03	3.26	0.02
Ca	7.41E + 09	4	1.85E + 09	3.63E + 09	35	1.03E + 08	17.87	0.00
Cd	5.13E + 00	4	1.28E + 00	5.93E + 00	35	1.69E – 01	7.58	0.00
Ce	3.60E + 04	4	9.02E + 03	3.95E + 05	35	1.12E + 04	0.80	0.53
Co	9.46E + 04	4	2.36E + 04	1.53E + 05	35	4.39E + 03	5.39	0.00
Cr	9.91E + 04	4	2.47E + 04	2.82E + 06	35	8.06E + 04	0.31	0.87
Cu	3.73E + 05	4	9.34E + 04	1.01E + 06	35	2.89E + 04	3.23	0.02
Dy	2.76E + 02	4	6.90E + 01	1.51E + 03	35	4.32E + 01	1.60	0.20
Er	3.53E + 01	4	8.82E + 00	3.75E + 02	35	1.07E + 01	0.82	0.52
Eu	4.54E + 01	4	1.13E + 01	2.30E + 02	35	6.57E + 00	1.73	0.17
Fe	2.23E + 11	4	5.58E + 10	6.18E + 11	35	1.76E + 10	3.16	0.03
Ga	2.41E + 03	4	6.04E + 02	6.14E + 04	35	1.75E + 03	0.34	0.85
Gd	6.48E + 02	4	1.62E + 02	3.07E + 03	35	8.79E + 01	1.84	0.14
Ge	1.42E + 02	4	3.56E + 01	1.10E + 03	35	3.15E + 01	1.13	0.36
Ho	6.85E + 00	4	1.71E + 00	5.017E + 01	35	1.43E + 00	1.20	0.33
K	7.98E + 08	4	1.99E + 08	2.93E + 10	35	8.39E + 08	0.24	0.92
La	7.43E + 03	4	1.85E + 03	9.36E + 04	35	2.67E + 03	0.70	0.60
Lu	3.96E – 01	4	9.90E – 02	6.33E + 00	35	1.80E – 01	0.55	0.70
Mg	4.48E + 08	4	1.12E + 08	3.70E + 09	35	1.05E + 08	1.06	0.39
Mn	1.68E + 08	4	4.21E + 07	2.48E + 08	35	7.08E + 06	5.94	0.00
Nd	1.18E + 04	4	2.96E + 03	1.01E + 05	35	2.90E + 03	1.02	0.41
Ni	3.11E + 05	4	7.79E + 04	8.23E + 05	35	2.35E + 04	3.31	0.02
P	6.71E + 07	4	1.67E + 07	1.60E + 08	35	4.58E + 06	3.66	0.01
Pb	2.14E + 04	4	5.35E + 03	1.30E + 05	35	3.71E + 03	1.44	0.24
Pr	6.29E + 02	4	1.57E + 02	6.30E + 03	35	1.80E + 02	0.87	0.49
S	2.64E + 09	4	6.60E + 08	1.65E + 10	35	4.74E + 08	1.39	0.26
Sc	3.24E + 03	4	8.11E + 02	2.87E + 04	35	8.20E + 02	0.99	0.43
Si	3.35E + 11	4	8.38E + 10	5.85E + 11	35	1.67E + 10	5.01	0.00
Sm	6.51E + 02	4	1.62E + 02	4.29E + 03	35	1.22E + 02	1.33	0.28
Sn	1.18E + 02	4	2.96E + 01	2.00E + 03	35	5.72E + 01	0.52	0.72
Tb	1.20E + 01	4	3.00E + 00	5.75E + 01	35	1.64E + 00	1.83	0.15
Th	1.66E + 03	4	4.16E + 02	2.09E + 04	35	5.98E + 02	0.70	0.60
Tm	4.38E – 01	4	1.09E – 01	7.25E + 00	35	2.07E – 01	0.53	0.72
U	1.18E + 03	4	2.97E + 02	7.31E + 03	35	2.08E + 02	1.42	0.25
Y	5.14E + 03	4	1.28E + 03	3.51E + 04	35	1.00E + 03	1.28	0.30
Yb	1.68E + 01	4	4.20E + 00	2.81E + 02	35	8.04E + 00	0.52	0.72
Zn	3.55E + 05	4	8.89E + 04	1.65E + 06	35	4.73E + 04	1.88	0.14

Conventional signs: SS Effect and SS Error – intergroup and intragroup sum of squared deviations; MS Effect and MS Error – intergroup (factorial) and intragroup (residual) dispersion; df – degrees of freedom; F – Fisher's criterion; p – significance level

The one-factor dispersion analysis is based on the Fisher's criterion calculation, which is the ratio of intergroup and intragroup dispersions. The intergroup dispersion shows how the waste heap locations differ from each other in terms of the level of chemical element concentrations. The intergroup dispersion is zero when the average values of the chemical element concentrations are equal. Intragroup dispersion characterizes the difference in the concentration of chemical elements within the same location (the waste heap top or its foot of the specified exposure).

The maximum Fisher's criterion value is characteristic of the chemical elements Ca, Cd, Mn, Co, Si, P, Ni, As, Cu, Fe, which are the main factor in the ecological differentiation of the Nadiya mine waste heap locations (Table 2). With respect to the depth of sampling, one-dimensional dispersion analysis makes it possible to determine the following hierarchy of the significance of chemical elements: Zn, Cu, Co, Ni, Fe, As, Mn, Ca, Mg, U, Pb, Sn, S, Eu, Ga, Gd, Tb, Dy, Ho, Al, Sm.

Since the root-containing substrate layer on a waste heap can occupy a depth of more than 20 cm, the next step of our research is to construct a typological scheme of waste heap locations depending on the relief, without taking into account the sampling depth. For this purpose, the optimal combinations of 15 chemical element concentrations are calculated, with the help of which it is possible to determine the peculiarities of the anthropogenic load on the waste heap ecotopes.

The mathematical modeling results (Fig. 6) can be represented by the following equations:

$$Root_1 = 0.00351 \cdot Mg - 0.00033 \cdot Al - 0.00001 \cdot Si + 0.00098 \cdot P + 0.00052 \cdot Ca - 0.02481 \cdot Mn - 0.00043 \cdot Fe + 1.28240 \cdot Co + 0.02371 \cdot Ni - 0.09466 \cdot Cu + 0.05295 \cdot Zn - 0.67946 \cdot As + 4.59229 \cdot Cd + 0.96785 \cdot Sn + 1.21461 \cdot Pb - 46.39;$$

$$Root_2 = 0.00503 \cdot Mg + 0.00038 \cdot Al - 0.00011 \cdot Si - 0.00234 \cdot P - 0.00022 \cdot Ca - 0.02025 \cdot Mn - 0.00075 \cdot Fe + 1.98192 \cdot Co - 0.05513 \cdot Ni - 0.04604 \cdot Cu - 0.07979 \cdot Zn - 0.03759 \cdot As - 0.27732 \cdot Cd - 0.78038 \cdot Sn - 0.26774 \cdot Pb + 16.49,$$

where:

$Root_i$ – canonical discriminant functions, axes of the typological scheme of the biogeocenotic waste heap cover.

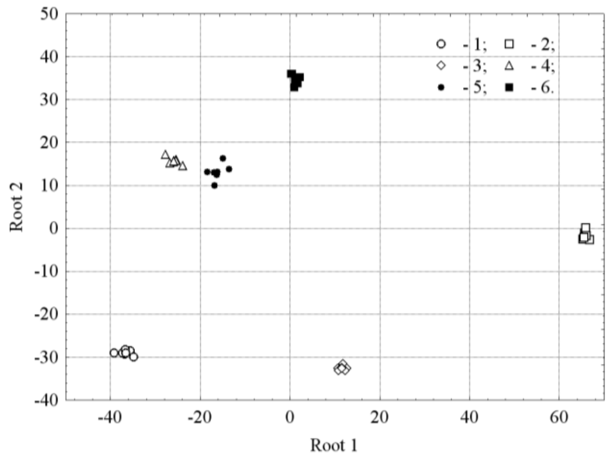

Figure 6. Typological scheme of the Nadiya mine waste heap locations: 1 – control site; slope exposure: 2 – North; 3 – East; 4 – South; 5 – West; 6 – waste heap top

The first axis of the $Root_1$ typological scheme (Fig. 6) explains 58.8% of the total dispersion. The minimum values of the canonical discriminant function $Root_1$ characterize the control site location, where the natural vegetation cover is formed by pine forest stand. The maximum $Root_1$ values are characteristic of the northern exposure ecotopes of the waste heap. The values of the first discriminant $Root_1$ function depend mainly on the Ca concentration (correlation coefficient is $r = 0.80$). Thus, on the control site, the Ca concentration is 3043 ± 644 ppm, and on the northern exposure slope it reaches 42355 ± 6088 ppm, which is 3 times higher than the average concentration value for the waste heap as a whole (14041 ± 2328 ppm). The bond of $Root_1$ function with other chemical elements is much weaker: Th – $r = 0.37$, U – $r = 0.36$, Si, Ce – $r = 0.33$.

The second axis of the $Root_2$ typological scheme (Fig. 5) additionally explains 30.7% of the total dispersion. Low values of the canonical discriminant function $Root_2$ characterize the control site location and eastern exposure ecotopes, and the maximum values of $Root_2$ characterize the waste heap top. The values of the second discriminant $Root_1$ function depend mainly on the Al concentration (correlation coefficient is $r = 0.33$). Thus, on the control site, the Al concentration is 112883 ± 33383 ppm, and on the waste heap top it reaches 245100 ± 42377 ppm.

The two-dimensional climate-edaphic grid (Fig. 5) explains 89.5% of the total dispersion, which is conditioned by the differences in the dump ecotopes in terms of the level of chemical pollution. Schematically, it can be depicted as a triangle, in the corners of which there are the control site (forest stand), the waste heap top and the northern exposure slope foot. The southern exposure slope occupies an intermediate position between the control site and the waste heap top, and the eastern exposure slope occupies an intermediate position between the control site and the northern exposure slope. To explain the peculiarities of the chemical pollution level between all types of dump ecotopes, the Mahalanobis distance has been determined – a multidimensional analogue of the Euclidean distance, taking into account the correlation between the chemical substance concentrations. As a result of the calculations, it has been determined that the western exposure slope forms the center of the ecological space of the dumps. This ecotope is characterized by the lowest values of Mahalanobis distances in relation to other types. The most remote in the hyperspace of ecological parameters is the location of the control site and the northern exposure slope.

The results of mathematical modeling are consistent with the data of phytocenological studies. Thus, on the northern exposure slope, there are numerous manifestations of water and wind erosion, places of ignition, draining of fuel and lubricant materials, as well as dumping of household waste. The increased density of the soil cover causes an almost complete absence of above-ground herbaceous cover. The substrate is bulk. In the herbaceous cover, only isolated groups of narrow-leaved bluegrass (Poa compressa L.) occur. The southern exposure slope is characterized by the smallest Mahalanobis distance relative to the control site (natural forest stand). There are quite favorable conditions for places of growing. The projective coverage of the herbaceous cover is 65%, and that of the tree layer is 55-60%. The species composition of the herbaceous cover is more diverse. In addition to narrow-leaved bluegrass (Poa compressa L.), common dandelion (Taraxacum officinale Webb. ex Wigg.), chimney sweep (Plantago lanceolata L.) and other species can be found in abundance here. The tree layer is dominated by drooping birch (Betula pendula Roth.) 7-8 (9) m high, common pine (Pinus sylvestris L.)

1-2 m (6-7 m higher along the slope), common locust (Robinia pseudoacacia L.) – 3-6 m. Among growing singly are common briar (Rosa canina L.), mayblossom (Crataegus monogyna Jacq.), pollard oak (Quercus robur L.) – 2-4 m, goat willow (Salix caprea L.) – 2-5 m.

The proposed variant of the typological scheme for the Nadiya mine rock dumps makes it possible to determine the coordinates of the ecotopes of plant groups by means of extrapolation. Thus, ecological information can be interpreted in the categories of direction and distance in a multidimensional space of features, solving the issues of patterns of dynamics or spatial distribution of vegetation cover, relationships between vegetation and the level of chemical pollution, assessing the intensity of anthropogenic impact, and environmental predicting.

It should be noted that partially or not forested rock dumps of liquidated coal mines lead to significant pollution of water bodies with various chemical elements and compounds. Table 3 presents the results of the research on the content of chemical elements in taken water samples.

Table 3. Content of chemical elements in the water samples taken in the impact zone of rock dumps

No.	Chemical elements, mg/dm³	Test sites					MPC* surface water for drinking purposes
		No. 1	No. 2	No. 3	No. 4	No. 5	
1	Cu	0.052	0.007	0.005	0.003	0.002	1
2	Pb	0.19	0.05	0.065	0.063	0.051	0.01
3	Cd	0.023	0.001	0.001	0.001	0.003	0.001
4	Zn	0.173	0.046	0.012	0.025	0.007	1
5	Cr	0.013	0.015	0.015	0.01	0.019	0.05
6	Sr	0.005	0.002	0.008	0.006	0.007	2
7	Co	0.13	0.005	0.005	0.005	0.005	0.1
8	Mn	4.61	2.53	1.69	0.19	0.21	0.1
9	Ni	0.65	0.031	0.021	0.017	0.017	0.01

* MPC (maximum permissible concentrations) is given in accordance with the analytical review (Kofanov et al., 2008 [17])

It has been determined that the most polluted waters with such chemical elements as Cu, Pb, Cd, Zn, Cr, Co, Mn, Ni are those taken in the immediate vicinity of the rock dump (samples No. 1 and 2). However, from Table 3, it can be stated that the water in the river of Rata and the river of Zahidny Bug, flowing through the Chervonohrad Mining District, is saturated with chemical elements (Pb, Cd, Mn, Ni), which in a number of indicators exceed the MPC. To overcome the negative consequences of chemical pollution, it is necessary to conduct an artificial phytomelioration of technogenic water bodies and create bioplateau systems at the foot of rock dumps.

Some scientists have also studied chemical pollution and other methods to detoxify wastewater from waste heaps. In particular, the environmental problems and chemical peculiarities of removal of toxic heavy metal ions (Cu^{2+}, Mn^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Cr^{3+}, Ni^{2+}, Fe^{2+}, Fe^{3+}) from the wastewater of mining enterprises are described in the paper [18]. The exceedance factor of the normative values has been quantified for each polluting component and its share in the overall level of environmental hazard has been calculated. The performed calculations [18] indicate a high environmental hazard of the underground mine wastewater for the environment. It is noted that the lack of effective methods of purification and universal methods for the utilization and recycling of mine wastewater, the unreliability of their accounting encourage research into the chemical binding of toxic components, optimizing the conditions for reactions of their precipitation. In the work [19], scientists have studied the increase in the level of environmental hazard of the hydrosphere as a result of improved adsorption processes for wastewater and mine water purification from pollution using natural sorbents and desalting processes by electrodialysis. The optimal parameters for improving the processes of sorption of pollutants with natural sorbents have been determined.

The prospects for further research are the analysis of heavy metals in vegetation and determination of physiological stability of the pioneer succession, which has developed on the rock dump. Also, for the regulation and conservation of phytocenoses, it is important to determine the stages of the rock dump overgrowing, as well as vertical and horizontal dynamics of their development. The rock dump natural phytoremediation is important for the renaturalization transformation of the subsystem of artificial objects and for improving the quality of the environment in the coal-mining region.

4. Conclusions

The distribution of chemical elements on the Nadiya mine rock dumps is characterized by significant heterogeneity. The mosaic nature of the chemical element concentrations depends on the sampling depth, slope exposure, site reclamation, and other factors. Even within the same exposure, ecotopes can differ significantly in the level of chemical pollution.

The similarity of chemical elements in their distribution on mine dumps makes it possible to distinguish 6 of their associations, the main of which are I (Mg, Ca, S) and II (Al, Fe, K, Si).

The presence of an ordered structure is characteristic of the multidimensional ordination of the Nadiya mine ecotopes according to the chemical element concentrations. Analysis of the dependence between the chemical element concentrations indicates the existence of a close link between many variables. The weakest bond in the chemical element concentrations is demonstrated by Si, for which the average value of the correlation coefficient is 0.36, as well as by Ca (average value is $r = 0.43$).

The main peculiarity of the dump ecotope formation is associated with an increase in the concentration of all chemical elements without exception compared to the natural background. The strongest link with anthropogenic load intensity is demonstrated by Mg, Pb, Sn, Fe, Al, Cu, P, Ni, and Zn.

The difference between the ecotopes of different dump exposures is mainly due to the level of Ca and Al concentrations.

Graphical visualization of geochemical information based on typological schemes and two-dimensional diagrams, where the chemical element concentrations are the axes, can be used to predict the dynamics of vegetation cover.

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Особливості хімічного забруднення породних відвалів шахти "Надія" Червоноградського гірничопромислового району, Україна

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Мета. Дослідження особливостей хімічного забруднення відвалів шахти "Надія" Червоноградського гірничопромислового району залежно від умов рельєфу та експозиції схилів, аналіз загальних тенденцій поширення хімічних елементів у порівнянні з природним фоном.

Методика. Диференціація хімічного забруднення відвалів шахти "Надія" на рівні екотопів досліджувалась на основі дисперсійного аналізу; багатовимірна ординація екотопів у просторі геохімічних показників – на основі аналізу головних компонент (Principle Component Analysis); побудова типологічної схеми екотопів відвалів шахти – на основі дискримінантного аналізу; статистична обробка параметрів хімічного забруднення.

Результати. Встановлено, що рівень хімічного забруднення відвалів шахти "Надія" характеризується істотною неоднорідністю навіть в межах однієї експозиції схилу. Подібність у розподілі хімічних елементів дозволила виділити 6 їх асоціацій, головними з яких є I (Mg, Ca, S) і II (Al, Fe, K, Si). Аналіз залежності між концентраціями хімічних елементів вказує на наявність тісного зв'язку між багатьма параметрами. Виявлено, що найбільш тісний зв'язок з інтенсивністю антропогенного навантаження демонструють елементи Mg, Pb, Sn, Fe, Al, Cu, P, Ni, Zn. Визначено, що відмінність між екотопами різних експозицій відвалу пояснюється в основному рівнем концентрації Ca і Al.

Наукова новизна. Вперше встановлено, що відвали шахти "Надія" Червоноградського гірничопромислового району характеризуються екологічним простором, оцінку якого виконано на основі ординації екотопів на осях комплексних геохімічних градієнтів середовища. Типологічна схема відвалів шахти відображає градієнт хімічного забруднення ґрунтового покриву у порівнянні з природним фоном.

Практична значимість. Визначення геохімічних умов екотопів у певний період часу дозволяє визначити їх положення в еколого-ценотичному просторі рослинності відвалів, прогнозувати стійкість і можливі зміни рослинного покриву унаслідок різноманітних форм антропогенного впливу.

Ключові слова: *відвали шахти, хімічне забруднення, екотоп, комплексний градієнт середовища, математичне моделювання*