

Hydro-ecological monitoring of heavy metal pollution of water bodies in the Western Bug River basin within the mining-industrial region

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Abstract

Purpose. This research aims to explore the peculiarities of chemical pollution with heavy metals of water in rivers and water bodies in the Chervonohrad mining-industrial region depending on the distance to the source of pollution and the type of landscape, as well as to analyze the general trends in the seasonal dynamics of chemical element concentration.

Methods. The paper uses statistical processing of the chemical pollution parameters of water and soil, such as correlation analysis and Data Mining methods. The similarity of ecotopes and grouping of chemical elements is assessed using cluster analysis. Multidimensional spatial ordination of ecotopes is described using geochemical indicators and graphical visualization based on Principle Component Analysis.

Findings. The highest level of pollution during the entire monitoring season was observed in water bodies at the foot of the Mezhyrichanska Mine waste heap near the city of Chervonohrad. Among the river bodies, the worst water condition in terms of heavy metal pollution was found in the Rata River (Silets village), which is located in the zone of influence of mining enterprises. The maximum excess of heavy metal content in water in seasonal dynamics in all sites is characterized by April variant of water samples. The analysis of the dependence between the concentrations of chemical elements indicates the presence of a close relationship between many parameters.

Originality. For the first time, it has been found that the multidimensional ordination of water bodies on the axes of complex geochemical gradients of the environment reflects the seasonal dynamics of the pollution level of natural water bodies with heavy metals within the mining-industrial region.

Practical implications. Based on the data obtained on the heavy metal content in water of natural water bodies, it is possible to predict the pollution level and implement measures to prevent the impact of negative factors on water quality. Knowing the geochemical conditions of ecotopes in a certain period of time, it is possible to determine their position in the ecological space on complex gradients of the medium, to predict the stability and possible changes in vegetation, fauna and microflora due to environmental pollution.

Keywords: heavy metals, ecotope, complex gradient of the medium, multidimensional ordination of ecotopes, mathematical modeling, ecological safety, technogenic pond

1. Introduction

The pollution of surface and groundwater bodies with high heavy metal concentrations is a global problem for humanity. The Global Goals were adopted by the United Nations in 2015 to reduce poverty, protect the planet, and ensure peace and prosperity by 2030. Global Sustainable Development Goal 6: Clean water and sanitation. More than 40% of people suffer from water shortages, and this figure is predicted to grow as temperatures rise. More and more countries are experiencing water shortages, and the rise of drought and desertification is already exacerbating these trends. It is predicted that by 2050, every fourth person will experience a constant shortage of water. Safe and affordable drinking water for all by 2030 requires investment in infrastructure,

sanitation and hygiene. Regarding water quality, the main criteria are given in [1]. Protecting and restoring water-related ecosystems is essential for all living organisms [2].

As a result of coal-mining and mine operation, the environmental situation in the regions is severe [3], [4]. In addition to the direct rock and coal extraction, dumping on the open surface, and altering the landscape, there is pollution of surface and underground aquifers [5]. Forest fires have a significant impact on the heavy metal migration in the environment [6]. Numerous scientific works devoted to the pollution of water bodies with heavy metals can be conditionally divided into the following directions: research into sources of heavy metals entering water bodies; research into the impact of heavy metals on water quality; research into the impact of

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heavy metals on the growth and development of aquatic organisms, plants and animals; the impact of water contaminated with heavy metals on the human body; purification of contaminated water from heavy metals. Coal mine waste dumps are a significant source of heavy metals entering water bodies [7], [8]. Based on data in [9], the highest heavy metal concentrations in water are observed where the thermal activity of waste rock dumps is high, since inorganic components are converted into more water-soluble forms.

Mine dumps are responsible for the risk of pollution of soil, air, and surface water used for drinking, irrigation, and domestic use. The undesirable effects of mine dumps are evident in the release of toxic substances, leading to serious health problems such as asthma. Managing acid drainage in mine dumps is a very important strategy to avoid environmental pollution and the spread of disease [10]. There is a peculiar seasonal dynamics of heavy metal accumulation in water [11], [12]. Soil and water data [13] from the Rudnik Pb-Zn mine area (central Serbia) show that areas near mining sites and those located remotely from them are heavily contaminated with toxic elements, especially As, Pb, Ni and Cr. As a result of the interaction of water and rock, mine tailings and mining activities at the Küre sulfide Pb-Zn-Cu mine (Kastamonu), it was found that SO₄, Al, As, Ba, Mn, Ni, Sb, Pb concentrations in some groundwater and surface water exceed the Maximum Permissible Concentration (MPC) in terms of compliance with Turkish and World Health Organization (WHO) standards for water intended for human consumption [14].

Paper [15] assesses the impact of gold mining on surface water quality in the Batouri region (East, Cameroon). The results of the heavy metal analysis show that the content of nickel, iron, chromium, selenium, lead, arsenic, mercury and cadmium exceed the limits recommended by the World Health Organization. The results of the hydrochemical test show that these waters are chlorinated with calcium and calcium sulfate and are unsuitable for consumption. In addition, there were attempts to model the spread of pollutants in river water and to statistically process the results obtained for determining the impact of polluted water on the vital activity of living organisms [16]-[19].

Waste causes environmental pollution, namely: groundwater pollution due to leaching of organic, inorganic and various other problematic substances (SoC) contained in waste; air pollution due to suspended particles; odor pollution from solid waste disposal; sea pollution from any potential effluents [20]. In addition, health impact may arise from groundwater pollution and gas emissions, resulting in carcinogenic and non-carcinogenic effects for exposed populations living in the vicinity [21], [22]. A study [23] shows that waste near water bodies has a significant impact on water quality, leading to groundwater pollution through leaching. The results show that EC, TDS, chloride, Fe and Zn levels in the Bariga waste exceed the Nigerian Drinking Water Quality Standard (NSDWQ-2007) [23]. The conditions of the dumpsites range from acidic to alkaline, so the elements studied have different mobility for different dumpsites. The elements that pose environmental risks differ from one type of dumpsite to another, so different dumpsites have different potential for pollution of water bodies [24]. The results obtained from the physical-chemical analyses of the filtrate lead to the conclusion about varying degrees of severe groundwater pollution

with organic matter, salts, and heavy metals [25]. Therefore, the use of such water is dangerous to human health [26].

Mining of metals such as gold, silver and copper results in the exposure of water and air to sulfide-containing ore. This leads to the formation of several harmful products, such as sulfuric acid. If water drainage from these mines is uncontrolled, it can drain into streams/ rivers or seep into groundwater, thus eventually reaching underground water systems (groundwater) that are interconnected over vast areas [28]. In this regard, 11 metals, including Al, Cr, Mn, Fe, Ni, Co, Cu, Zn, Sr, Cd and Pb, were identified in different water samples (well, spring, river and lake) collected from three specific geographical mining sites. The level of toxic/carcinogenic metals, including Pb, Cd and Ni, in water samples is higher than WHO recommendations and poses a real risk to human health, especially for children [29].

Grasses and trees added with organic matter have proven to be effective in controlling erosion and stabilizing the slopes of waste dumps, as well as improving aesthetics. It has been found that species selection based on root morphology, intended use, and point of application (in the case of slopes) determines the effectiveness of reclamation programs, which requires further research [30]. The chemical composition of the soil material indicates a low degree of weathering of the utilized post-coal waste and homogeneity, while the higher Ca and Mg content may be the result of plant decomposition [31].

To monitor groundwater quality, samples from 3 observation wells near the red sludge dumps were analyzed. Soil monitoring results show no values of analyzed parameters above those prescribed by national legislation on soil quality [32].

Many scientific papers are devoted to the adsorption of heavy metals from water [33]-[35], as well as to methods of water purification by chemical [36] and biological methods [37], in particular in the study region. However, this topic will be the prospect for our further research.

Having reviewed a number of scientific papers on the impact of various pollutants on water quality, it can be stated that such studies do not lose their relevance over time and require comprehensive and further development. Monitoring of pollution of rivers and hydrographic networks with heavy metal should be conducted continuously and regardless of the season.

2. Materials and methods

2.1. Study area

The Western Bug River flows in the western part of Ukraine near the border with Poland through the territory of the Chervonohrad mining-industrial region. The Western Bug River basin is located in the territory of the Malye Polissya geobotanical area, which borders on the Western Forest-Steppe of Ukraine.

Water quality in the rivers and water bodies of the mining-industrial region largely depends on surface runoff from the territory of cities, industrial areas and agricultural landscapes, as well as on the distance to the probable source of pollution [38]-[40]. Taking this factor into account, 5 research objects were selected (Fig. 1).

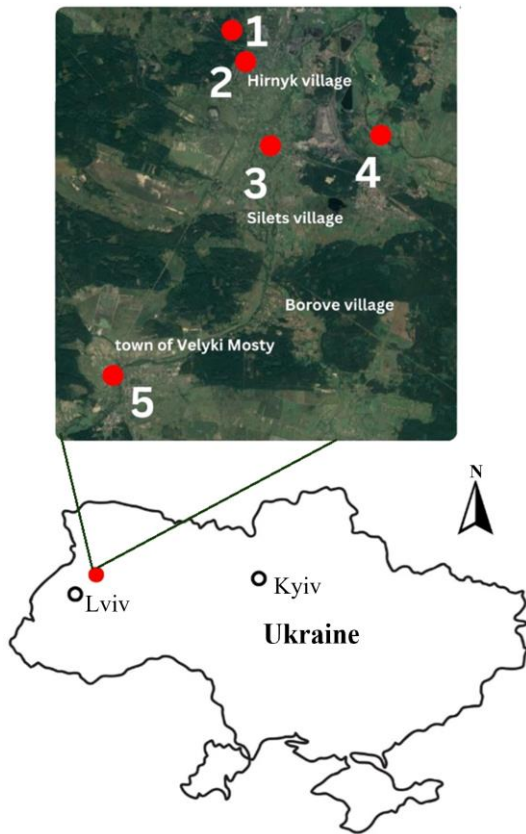


Figure 1. Localization of sampling within the mining-industrial region: 1-5 – sites No. 1-5

Site No. 1 is a small water body located at the foot of the waste heap belonging to the Vidokremenyi Pidrozdil Shakhta Mezhyrichanska or Mezhyrichanska Mine (until 2001 – Velykomostivska Mine No. 3), which is a separate subdivision of the Derzhavne Pidpriemstvo “Lvivvuhillia” (geographical coordinates – 50.3398690°N; 24.1950900°E). The waste heap is located near the city of Chervonohrad, Lviv Oblast. This territory belongs to the Lviv-Volyn coal basin. In the course of long-term coal mining, this site has undergone a significant level of landscape transformation. This is where the formation of waste heaps as waste rock storage facilities occurs, which is accompanied by significant surface compaction, soil, water and vegetation pollution.

Site No. 2 is a technogenic pond at the foot of the waste heap, where natural phytomelioration has been taking place for many years, and is located near Site No.1 (geographical coordinates – 50.3398690°N; 24.1950900°E). There is a significant compaction of the soil surface caused by truck movement, a pronounced rugged relief with alternating flat areas, bulk hills (mainly made of rock and technozem) and lowered relief. Rainwater collects in many places of the lowered relief, and filtrates at the foot of the waste heap itself, posing a significant environmental hazard. On the slopes, there are signs of water erosion (gullies 0.5-1.0 m wide and 0.5-1 m deep), deflations (from wind erosion), and noticeable places for draining fuels and lubricants, as well as household waste dumping.

Site No. 3 – the Rata River, outside the village of Silets, near the confluence of the Bolotnia River (geographical coordinates – 50.3103030°N; 24.1973610°E). The width of the Rata River is 40-45 m. The site is located 11 km from the city of Chervonohrad, 50 m below the automobile road con-

necting the highway (P 15) and the city of Sosnivka. The territory is predominantly flat, with insignificant anthropogenic impact. The site is used for recreation (for kayaking). The village of Silets is located nearby. The site is without significant digression damage, but is in the zone of influence of the territory where significant changes in natural landscapes have occurred as a result of the mining complex operation. They consist in the earth’s surface subsidence in places of mining coal seams up to 2-4 m. This has led to flooding and water-logging of large areas on the territory of the Silets Village Council, and the failure of engineering communications. The tailings dump of the Chervonohrad Central Processing Plant near the city of Sosnivka, coal storage facilities, storage ponds, and mine water sumps also pose a significant regional environmental hazard. According to rough estimates, 30 years of the Chervonohrad Central Processing Plant operation have resulted in the formation of a waste heap over 70 m high and several kilometers long. Based on the estimates of the Chervonohrad CPP administration, about 40 million tons of waste from coal beneficiation are buried here.

Site No. 4 – the Western Bug River, at a distance of about 500 m east of the border of Horodyshche village, Chervonohrad District, Lviv Oblast, near the bridge, the automobile road leading to Volsvyn village (geographical coordinates 50.3144420°N; 24.2493800°E). The traffic intensity of road transport is insignificant. Among the anthropogenic sources of impact on the Western Bug River, it is worth highlighting individual private households, which are a source of organic waste. The Western Bug River in this area is characterized by a wavy channel. The width of the river in this area is 30-40 m. On both banks of the river, there is a significant diversity of woody vegetation, characterized by high density and, in places, unsatisfactory sanitary condition.

Site No. 5 – the Rata River within the boundaries of the city of Velyki Mosty, Chervonohrad District, Lviv Oblast, at a distance of 200 m from the highway (P 15) leading to Chervonohrad (geographical coordinates 50.2448170°N; 24.1352160°E). The width of the riverbed is about 40 m. There are small household waste dumps on the banks of the river.

2.2. Sampling

The level of chemical pollution of water in technogenic ponds and rivers in the mining-industrial region is assessed using indicators developed on the basis of geochemical and hygienic environmental studies. These indicators include: concentration coefficient K_c and total index of water pollution level Z_c [41], [42].

The concentration coefficient K_c is determined as the ratio of the actual content of a chemical substance C (mg/dm^3) to its maximum permissible concentration C_{MPC} [43], [44]:

$$K_{C_i} = \frac{C_i}{C_{MPC_i}}, \quad (1)$$

where:

i – the chemical substance serial number.

The total index of water pollution level Z_c is equal to the sum of the concentration coefficients of chemical elements K_c . In a modified form, it is expressed by the Formula:

$$Z_c = \sum_1^n K_{C_i}, \quad (2)$$

where:

n – the amount of chemical elements-pollutants.

The peculiarities of seasonal dynamics of water pollution in technogenic ponds and rivers are studied by data-fetching methods [45], [46]. Data-fetching method – is the process of analytically examining large amounts of information in order to identify certain patterns and dependences between variables (hidden knowledge) that can be applied to new data sets, as well as to reliably predict processes and phenomena [46]. The research includes three main stages: studying the structure of the relative location of elemental sites in the multidimensional space of heavy metal content signs, mathematical modeling of the structure, and verification of the mathematical model.

The environmental information is based on the level of water pollution in 5 sites with 9 heavy metals: Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr. Mathematical modeling is performed by identifying systematic relationships between heavy metal concentrations. Each site can be represented as a point in a multidimensional space of signs, the coordinates of which correspond to the values of chemical element concentrations. In this case, the similarity of sites in terms of a set of environmental pollution parameters can be determined based on the distances between points. The essence of the subsequent mathematical procedure is to identify the axes of maximum variation, determine their number, and assess the contribution of each environmental parameter to the variation based on principal component analysis [47], [48]. The mathematical model is verified based on a comparative assessment of the position of the sites on the axes of maximum variation (multidimensional ordination) with the results of the seasonal dynamics of chemical water pollution.

Water samples are taken according to the procedure described in DSTU ISO 5667-6:2009 “Water quality. Sampling. Part 6. Guidelines for sampling water from rivers and streams”. Water sampling vessels are selected in accordance with DSTU ISO 5667-3-2001 “Water quality. Sampling. Part 3. Guidelines for sample storage and handling”.

The analysis of heavy metal content in water samples is conducted at the Laboratory of Industrial Toxicology, which is a structural unit of Danylo Halytsky Lviv National Medical University (Certificate No. RL 068/22 dated 01.12.2022 on compliance of the measurement control system with DSTU ISO 10012:2005). Measuring equipment used during testing: laboratory electronic scales TVYe-1-0.01 (Certificate of calibration No. KLM 978 dated 26.12.2022); atomic absorption spectrophotometer S-115. M1 (Certificate of calibration No. UA/37/221219/001359 dated 19.12.2022).

The paper uses methods of mathematical modeling of the location structure of the site temporal variants in the hyper-space of signs. Since it is visually impossible to recognize a structure in multidimensional space, the main focus is on multidimensional ordination methods. Mathematical modeling consists in replacing an array of numbers (heavy metal concentrations) with such a spread of points that would help to reveal its structure as a reflection of the temporal peculiarities of water pollution in a certain site. Mathematical modeling is performed using MathLab software.

3. Results and discussion

The distribution of heavy metals in water of the rivers and water bodies of the mining-industrial region during the year is characterized by great heterogeneity. Even within the same site, there is a significant variation in the level of chemical water pollution compared to the maximum permissible concentration of a chemical element (Table 1).

Cadmium compounds are toxic even in small concentrations, and are classified as hazard class II. A significant excess of the maximum permissible concentration of cadmium in water (14-23 times) was observed in Sites No. 1 and 2 (water bodies located at the foot of the waste heap belonging to the Mezhyrichanska Mine, near the city of Chervonohrad). In other sites, the maximum excess of the maximum permissible cadmium concentration during the year was 2-3 times (Table 1).

Zinc is a heavy metal of hazard class III. High humidity conditions are characterized by high zinc migration in the soil, which creates the prerequisites for its entry into water bodies and rivers with surface and underground runoff. The maximum permissible concentration of zinc was exceeded by 1.6-2.2 times only in Sites No. 1 and 2 in November 2022 (Table 1). Lead is also considered one of the most toxic chemical elements, even in small amounts, and belongs to the hazard class II. The maximum level of water pollution with lead in the rivers and water bodies of the mining-industrial region was observed in the summer and spring in all study sites.

Copper is a chemical element that belongs to the heavy metals of hazard class III. It has low phytotoxicity, but is very toxic to the human body. In case of excess entry into the body of people and animals, it is carcinogenic and has toxic effects on the heart, blood and other organs. In no site did the copper content in the water exceed the maximum permissible concentration (Table 1). The content of chromium (hazard class III) and strontium (hazard class II) in the water of rivers and water bodies in the mining-industrial region was also characterized by low levels. Maximum cobalt concentrations (hazard class II) were recorded only in Site No. 1 (a small water body at the foot of the waste heap, near the city of Chervonohrad).

Nickel is a hazard class III chemical element. In contact with the skin and respiratory system, it can cause acute and chronic poisoning. A very high nickel concentration level in water was observed in April 2023 in Sites No. 1 and 2 (water bodies located at the foot of the Mezhyrichanska Mine waste heap, near the city of Chervonohrad).

Manganese belongs to chemical substances of hazard class III. It affects the organoleptic characteristics of water, in particular, its color. Its maximum permissible concentration in water is 0.1 mg/l. Abnormally high manganese concentrations in water were observed in April 2023 in Sites No. 1 and 2 (water bodies located at the foot of the Mezhyrichanska Mine waste heap, near the city of Chervonohrad).

The main problem of water quality monitoring research is the need to conduct a comparative assessment of studied sites in terms of many parameters (chemical concentrations) in space and time. In fact, we are dealing with a multidimensional space, the axes of which reflect the content of nine chemical elements, namely Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr in water. This paper focuses on studying the seasonal (temporal) dynamics of water pollution in the context of individual sites.

The analysis of the dependence between the heavy metal concentrations in the water of rivers and water bodies in the mining-industrial region indicates that there is a close relationship between individual chemical elements. For example, for Site No. 1 (a small water body at the foot of the waste heap) for Cu and Cd concentrations, the correlation coefficient is $r = 0.84$, for Cu and Pb – $r = 0.94$, for Cu and Co – $r = 0.99$, for Mn and Ni – $r = 0.97$, for Mn and Sr – $r = 0.99$.

Table 1. Water pollution level in the rivers and water bodies of the mining-industrial region

Site No.	Date*	Heavy metal content in water, mg/l								
		Cu	Cd	Zn	Pb	Cr	Co	Mn	Ni	Sr
1	VI	0.052	0.023	0.173	0.19	0.013	0.13	4.61	0.65	0.005
	XI	0.0065	0.014	1.6	0.012	0.025	0.025	62.5	0.025	0.025
	II	0.004	0.001	0.042	0.012	0.014	0.017	21.4	0.21	0.002
	IV	0.029	0.019	0.062	0.042	0.002	0.06	326.7	6.75	0.08
2	VI	0.007	0.001	0.046	0.05	0.015	0.005	2.53	0.031	0.002
	XI	0.012	0.02	2.2	0.022	0.046	0.098	0.025	0.29	0.17
	II	0.001	0.001	0.045	0.01	0.01	0.008	15.7	0.23	0.004
	IV	0.026	0.016	0.062	0.046	0.003	0.062	203.35	4.31	0.1
3	VI	0.005	0.001	0.012	0.065	0.015	0.005	1.69	0.021	0.008
	XI	0.0039	0.0017	0.08	0.005	0.025	0.005	0.011	0.005	0.74
	II	0.003	0.001	0.004	0.01	0.01	0.013	0.11	0.005	0.006
	IV	0.001	0.002	0.014	0.037	0.002	0.016	8.35	0.17	0.09
4	VI	0.003	0.001	0.025	0.063	0.01	0.005	0.19	0.017	0.006
	XI	0.06	0.0019	0.13	0.0075	0.025	0.0064	0.23	0.01	0.7
	II	0.002	0.001	0.003	0.025	0.014	0.007	0.01	0.002	0.005
	IV	0.002	0.003	0.006	0.036	0.002	0.016	0.12	0.09	0.05
5	VI	0.002	0.003	0.007	0.051	0.019	0.005	0.21	0.017	0.007
	XI	0.0039	0.0014	0.08	0.0025	0.025	0.006	0.003	0.005	0.46
	II	0.002	0.001	0.003	0.012	0.012	0.007	0.04	0.007	0.008
	IV	0.002	0.002	0.007	0.038	0.002	0.015	0.59	0.13	0.12
MPC, mg/l	–	1	0.001	1	0.03	0.05	0.1	0.1	0.1	7
Exceeding the maximum permissible concentration, times										
1	VI	0.052	23.0	0.173	6.333	0.26	1.30	46.10	6.50	0.0007
	XI	0.006	14.0	1.600	0.400	0.50	0.25	625.00	0.25	0.0036
	II	0.004	1.0	0.042	0.400	0.28	0.17	214.00	2.10	0.0003
	IV	0.029	19.0	0.062	1.400	0.04	0.60	3267.00	67.50	0.0114
2	VI	0.007	1.0	0.046	1.667	0.30	0.05	25.30	0.31	0.0003
	XI	0.012	20.0	2.200	0.733	0.92	0.98	0.25	2.90	0.0243
	II	0.001	1.0	0.045	0.333	0.20	0.08	157.00	2.30	0.0006
	IV	0.026	16.0	0.062	1.533	0.06	0.62	2033.50	43.10	0.0143
3	VI	0.005	1.0	0.012	2.167	0.30	0.05	16.90	0.21	0.0011
	XI	0.004	1.7	0.080	0.167	0.50	0.05	0.11	0.05	0.1057
	II	0.003	1.0	0.004	0.333	0.20	0.13	1.10	0.05	0.0009
	IV	0.001	2.0	0.014	1.233	0.04	0.16	83.50	1.70	0.0129
4	VI	0.003	1.0	0.025	2.100	0.20	0.05	1.90	0.17	0.0009
	XI	0.060	1.9	0.130	0.250	0.50	0.06	2.30	0.10	0.1000
	II	0.002	1.0	0.003	0.833	0.28	0.07	0.10	0.02	0.0007
	IV	0.002	3.0	0.006	1.200	0.04	0.16	1.20	0.90	0.0071
5	VI	0.002	3.0	0.007	1.700	0.38	0.05	2.10	0.17	0.0010
	XI	0.004	1.4	0.080	0.083	0.50	0.06	0.03	0.05	0.0657
	II	0.002	1.0	0.003	0.400	0.24	0.07	0.40	0.07	0.0011
	IV	0.002	2.0	0.007	1.267	0.04	0.15	5.90	1.30	0.0171

*Date of sampling for chemical analysis: VI – 07.06.2022; XI – 01.11.2022; II – 24.02.2023; IV – 25.04.2023

The idea of our further research is to mathematically model the location structure of the site temporal variants in the hyperspace of signs. Since it is impossible to visually recognize a structure in a multidimensional space, the main focus is on multidimensional ordination methods. The task of the mathematical modeling is to replace an array of numbers (heavy metal concentrations) with such a spread of points that would help to reveal its structure as a reflection of the temporal peculiarities of water pollution in Site No. 1.

Since the heavy metal concentrations in the water of Site No. 1 (a small water body at the foot of the waste heap) are correlated with each other, it can be concluded that the

observational data can be explained by a small number of new variables that are not directly measured, but can be obtained through a linear combination of the original data. This makes it possible to reduce the dimensionality of the observation space.

Graphically, the calculation procedure is reduced to moving the origin of coordinates to the data center and rotating the coordinate axes so that abscissa passes towards the maximum data set variance. The results of the principal component analysis based on the correlation matrix are as follows (Fig. 1).

$$\text{Factor}_1 = -0.386 \cdot \text{Cu} - 0.355 \cdot \text{Cd} + 0.273 \cdot \text{Zn} - 0.265 \cdot \text{Pb} + 0.397 \cdot \text{Cr} + 0.390 \cdot \text{Co} - 0.299 \cdot \text{Mn} - 0.369 \cdot \text{Ni} - 0.289 \cdot \text{Sr}; \quad (1)$$

$$\lambda_1 = 4.39;$$

$$\text{Factor}_2 = 0.324 \cdot \text{Cu} - 0.195 \cdot \text{Cd} + 0.001 \cdot \text{Zn} + 0.458 \cdot \text{Pb} + 0.194 \cdot \text{Cr} - 0.549 \cdot \text{Co} + 0.418 \cdot \text{Mn} - 0.349 \cdot \text{Ni} - 0.401 \cdot \text{Sr}; \quad (2)$$

$$\lambda_2 = 3.29,$$

where:

Factor_i – the component coordinates, complex gradients of the medium;

Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – the standardized values of heavy metal concentrations in water;

λ_i – eigenvalues of vectors.

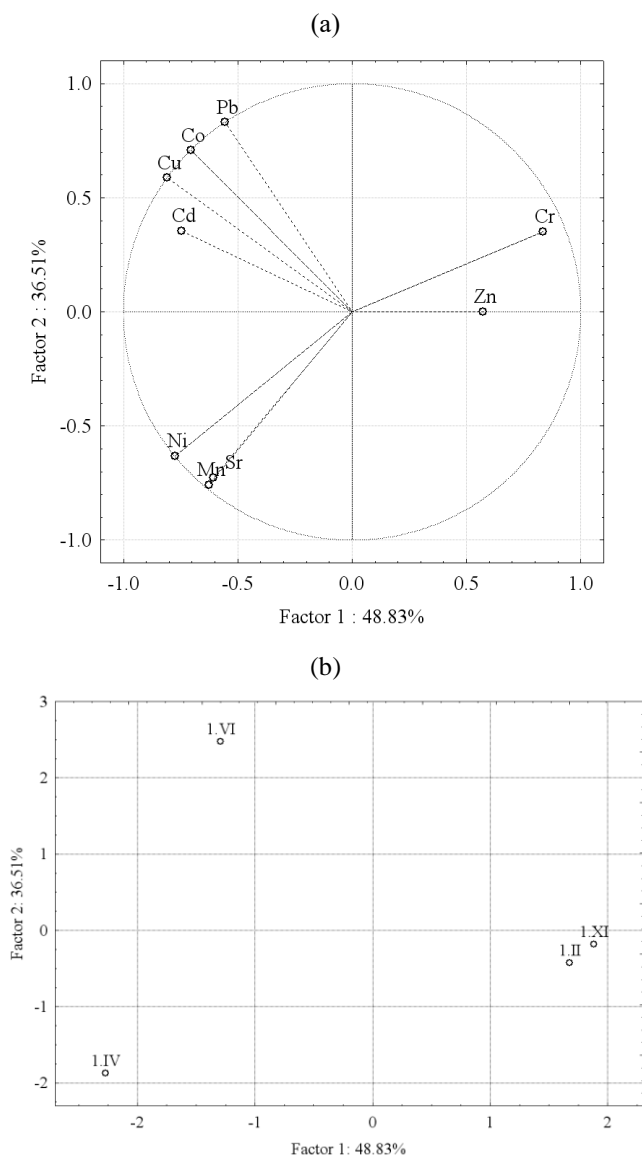


Figure 1. Results of analysis of the principal components of heavy metal content in water of Site No. 1 (a small water body at the foot of the waste heap): (a) the system of relationships between the concentrations of chemical elements and complex gradients of the medium; (b) a location of temporal variants of the site in the coordinate system of complex gradients of the medium; Factor₁₋₂ – the principal components, complex gradients of the medium; Arabic numerals indicate site numbers, Roman numerals indicate the calendar month serial numbers (Table 1)

The analysis of the eigenvalues λ_i shows that the two principal components already provide 85.3% of total variance, therefore, for many analysis purposes, it is sufficient to use a two-dimensional projection of the original data matrix. Eigenvectors of the correlation matrix (1)-(2) make it possible to identify combinations of environmental factors that determine the axes of maximum variation in the seasonal dynamics of chemical water pollution. The main pattern of formation of water medium quality in site No. 1 (the first principal component of Factor₁) is the following structure of relationships between chemical elements (Fig. 1a): with a decrease in Cu concentration (correlation coefficient is $r = -0.81$), the concentrations of Cd ($r = -0.74$), Co ($r = -0.71$), Ni ($r = -0.77$) decrease, and the concentrations of Cr ($r = 0.83$) increase. The first principal component explains only 48.8% of the total variance, but its values clearly reveal the main pattern of temporal dynamics of water medium quality in Site No. 1. Thus, the April 1.IV and June 1.VI temporal variants of Site No. 1 are characterized by low values of the first principal component of Factor₁, distinguished by high heavy metal concentrations: Cd, Co, Ni, Pb, Mn and Sr (Table 1). The November 1.XI and February 1.II temporal variants of Site No. 1 are distinguished by maximum values of the first principal component, where Cr and Zn have relatively higher concentrations in water (Table 1).

The second axis of maximum Factor₂ variation additionally explains 36.5% of the total data variance. The Factor₂ function value mainly depends on the content of Pb ($r = 0.83$), Co ($r = 0.71$), Mn ($r = -0.76$) and Sr ($r = -0.73$). Thus, in June, the highest Pb concentrations (exceeding the MPC by 6.3 times) and Co (exceeding the MPC by 1.3 times) are observed in Site No. 1, as a result of which the June 1.VI variant has the maximum value of the second principal component. At the same time, the June 1.VI variant of Site No.1 is characterized by the lowest level of pollution in terms of total indices of exceeding the maximum permissible concentrations of 9 chemical elements. The minimum value of the second principal component is the April 1.IV variant of the site, which is characterized by high concentrations of Mn (exceeding the MPC by 3267 times) and Ni (exceeding the MPC by 67.5 times) and generally the worst water quality indicators (Table 1).

The least distant in hyperspace of complex gradients of the water medium according to the heavy metal content (Fig. 1b) are the November 1.XI and February 1.II variants of Site No. 1 (Euclidean distance is 2.83). The most distant relative to other variants are the April 1.IV and June 1.VI variants (Euclidean distance is 4.37-4.66).

Based on the correlation between the heavy metal content and complex gradients of the water medium (Fig. 1a), the following associations (groups) of chemical elements can be distinguished:

- I – Cu, Co, Pb, Cd;
- II – Zn, Cr;
- III – Mn, Sr, Ni.

The most distant in the hyperspace of complex gradients of the water medium are the chemical elements Cr and Ni (Euclidean distance is 1.92), Cr and Mn (Euclidean distance is 1.85), Cr and Sr (Euclidean distance is 1.80), Cu and Sr (Euclidean distance is 1.70).

The analysis of the dependence between the heavy metal concentrations in water of Site No. 2 (a technogenic pond at the foot of the waste heap) also indicates that there

$$\text{Factor}_1 = -0.336 \cdot \text{Cu} - 0.466 \cdot \text{Cd} - 0.332 \cdot \text{Zn} - 0.033 \cdot \text{Pb} - 0.243 \cdot \text{Cr} - 0.459 \cdot \text{Co} - 0.181 \cdot \text{Mn} - 0.215 \cdot \text{Ni} - 0.458 \cdot \text{Sr};$$

$$\lambda_1 = 4.59;$$

$$\text{Factor}_2 = -0.358 \cdot \text{Cu} + 0.001 \cdot \text{Cd} + 0.364 \cdot \text{Zn} - 0.335 \cdot \text{Pb} + 0.431 \cdot \text{Cr} + 0.089 \cdot \text{Co} - 0.468 \cdot \text{Mn} - 0.452 \cdot \text{Ni} + 0.101 \cdot \text{Sr};$$

$$\lambda_2 = 3.69,$$

where:

Factor_{*i*} – the component coordinates, complex gradients of the medium;

Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – the standardized values of heavy metal concentrations in water;

λ_i – eigenvalues of vectors.

From the analysis of the characteristics of eigenvalues λ_i , it follows that already the two principal components provide 91.9% of the total variance, therefore, for many analysis purposes, it is sufficient to use a two-dimensional projection of the original data matrix. The main pattern of formation of water quality in the water medium of Site No. 2 (the first principal component of Factor₁) is the following structure of relationships between chemical elements (Fig. 2a): with a decrease in Cd concentration (correlation coefficient is $r = -1.00$), the concentrations of Co ($r = -0.98$), Sr ($r = -0.98$), Cu ($r = -0.72$), Zn ($r = -0.71$) decrease. The first principal component explains 51.0% of the total variance, and its values clearly show the main pattern of the temporal dynamics of water medium quality in Site No. 2.

Thus, the April 2.IV and November 2.XI temporal variants of Site No. 2 are characterized by low values of the first principal component of Factor₁, distinguished by high heavy metal concentrations: Cd, Zn, Co, Mn and Ni (Table 1). The February 2.II and June 2.VI temporal variants of Site No. 2 are distinguished by maximum values of the first principal component, where Cu, Cd, Zn, Co, Ni, Sr have relatively lower concentrations in the water (Table 1).

The second axis of maximum Factor₂ variation additionally explains 41.0% of the total data variance. The Factor₂ function value mainly depends on the content of Mn ($r = -0.90$), Ni ($r = -0.87$), Zn ($r = 0.70$) and Cr ($r = 0.83$). Thus, in April 2023, abnormally high concentrations of Mn (exceeding the MPC by 2033 times) and Ni (exceeding the MPC by 43 times) were observed in Site No. 2, which resulted in April 2.IV variant having the lowest value of the second principal component. According to total indices of exceeding the maximum permissible concentrations of 9 chemical elements, the April 2.IV variant of Site No. 2 is characterized by the highest pollution level (Table 1). In terms of seasonal dynamics of water pollution level, Site No. 2 is similar to Site No. 1 due to its spatial proximity.

The least distant in hyperspace of complex gradients of the water medium by the heavy metal content (Fig. 2b) are the June 2.VI and February 2.II variants of Site No. 2 (Euclidean distance is 2.18). The most distant relative to other variants are the April 2.IV and November 2.XI variants (Euclidean distance is 4.17-4.68).

is a close relationship between many chemical elements. Thus, for the concentrations of Cu and Ni, the correlation coefficient is $r = 0.91$, for Cu and Mn – $r = 0.88$, for Cd and Co – $r = 0.99$, for Mn and Ni – $r = 0.99$, for Cd and Sr – $r = 0.98$, for Zn and Cr – $r = 0.96$, for Co and Sr – $r = 0.99$, for Cd and Sr – $r = 0.98$.

The results of principal component analysis based on the correlation matrix are as follows (Fig. 1):

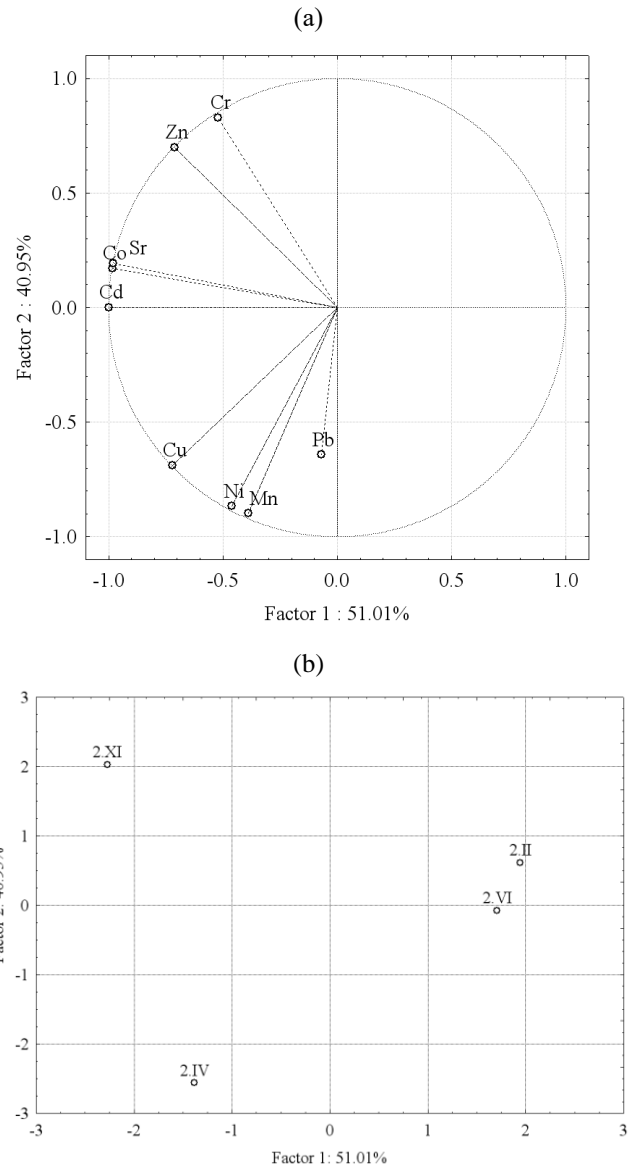


Figure 2. Results of analysis of the principal components of heavy metal content in water of Site No. 2 (technogenic pond at the foot of the waste heap): (a) the system of relationships between the concentrations of chemical elements and complex gradients of the medium; (b) a location of temporal variants of the site in the coordinate system of complex gradients of the medium; Factor₁₋₂ – the principal components, complex gradients of the medium; Arabic numerals indicate site numbers, Roman numerals indicate the calendar month serial numbers (Table 1)

Based on the correlation between the heavy metal content and complex gradients of the water medium (Fig. 2a), as well as cluster analysis, the following associations (groups) of chemical elements can be distinguished:

I – Mn, Ni, Cu, Pb;

II – Co, Sr, Cd;

III – Zn, Cr.

The most distant in the hyperspace of complex gradients of the water medium are the chemical elements Cr and Mn (Euclidean distance is 1.78), Cr and Ni (Euclidean distance is 1.74), Zn and Mn (Euclidean distance is 1.65), Pb and Cr (Euclidean distance is 1.64).

$$\text{Factor}_1 = 0.375 \cdot \text{Cu} - 0.184 \cdot \text{Cd} + 0.282 \cdot \text{Zn} - 0.122 \cdot \text{Pb} + 0.429 \cdot \text{Cr} - 0.394 \cdot \text{Co} - 0.400 \cdot \text{Mn} - 0.400 \cdot \text{Ni} + 0.268 \cdot \text{Sr};$$

$$\lambda_1 = 5.10;$$

$$\text{Factor}_2 = 0.276 \cdot \text{Cu} - 0.527 \cdot \text{Cd} - 0.454 \cdot \text{Zn} + 0.364 \cdot \text{Pb} - 0.133 \cdot \text{Cr} - 0.060 \cdot \text{Co} - 0.144 \cdot \text{Mn} - 0.190 \cdot \text{Ni} - 0.478 \cdot \text{Sr};$$

$$\lambda_2 = 2.74,$$

where:

Factor_{*i*} – the component coordinates, complex gradients of the medium;

Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – the standardized values of heavy metal concentrations in water;

λ_i – eigenvalues of vectors.

From the analysis of the characteristics of eigenvalues λ_i , it follows that already the two principal components provide 87.1% of the total variance, therefore, for many analysis purposes, it is sufficient to use a two-dimensional projection of the original data matrix. The main pattern of formation of water quality in the water medium of Site No. 3 (the first principal component of Factor₁) is the following structure of relationships between chemical elements (Fig. 3a): with an increase in Cu concentration (correlation coefficient is $r = 0.85$), Cr concentration ($r = 0.97$) increases, Co ($r = -0.89$), Mn ($r = -0.90$), Ni ($r = -0.90$) concentrations decrease. The first principal component explains only 56.7% of the total variance. The April 3.IV temporal variant of Site No. 3 is characterized by low values of the first principal component of Factor₁, distinguished by high concentrations of heavy metals: Cd, Co, Ni, Pb, Mn, and generally the worst water quality indicators (Table 1). The November 3.XI variant of Site No. 3 is distinguished by the maximum value of the first principal component, where only Cd exceeded the maximum permissible concentration in water (1.7) (Table 1).

The second axis of maximum Factor₂ variation additionally explains 30.5% of the total data variance. The Factor₂ function value mainly depends on the content of Cd ($r = -0.87$), Sr ($r = -0.79$), Zn ($r = -0.75$) and Pb ($r = 0.60$). Thus, in June, the highest concentrations of Pb (exceeding the MPC by 2.2 times) and Mn (exceeding the MPC by 16.9 times) were observed in Site No. 3, which resulted in June 3.VI variant having the maximum value of the second principal component. According to total indices of exceeding the maximum permissible concentrations of 9 chemical elements, the November

$$\text{Factor}_1 = 0.421 \cdot \text{Cu} - 0.091 \cdot \text{Cd} + 0.423 \cdot \text{Zn} - 0.281 \cdot \text{Pb} + 0.429 \cdot \text{Cr} - 0.259 \cdot \text{Co} + 0.255 \cdot \text{Mn} - 0.270 \cdot \text{Ni} + 0.410 \cdot \text{Sr};$$

$$\lambda_1 = 5.08;$$

$$\text{Factor}_2 = -0.190 \cdot \text{Cu} - 0.586 \cdot \text{Cd} - 0.158 \cdot \text{Zn} + 0.225 \cdot \text{Pb} + 0.115 \cdot \text{Cr} - 0.474 \cdot \text{Co} - 0.189 \cdot \text{Mn} - 0.468 \cdot \text{Ni} - 0.229 \cdot \text{Sr};$$

$$\lambda_2 = 2.79,$$

where:

Factor_{*i*} – the component coordinates, complex gradients of the medium;

The analysis of the dependence between the heavy metal concentrations in water of Site No. 3 (the Rata River, outside the village of Silets, near the confluence of the Bolotnia River) also indicates that there is a close relationship between many chemical elements.

Thus, for the concentrations of Cu and Co, the correlation coefficient is $r = -0.92$, for Cu and Mn – $r = -0.78$, for Cu and Ni – $r = -0.83$, for Cu and Cr – $r = 0.75$, for Zn and Sr – $r = 0.99$, for Co and Cr – $r = -0.89$, for Mn and Ni – $r = 0.99$, for Zn and Cr – $r = 0.80$.

The results of principal component analysis based on the correlation matrix are as follows (Fig. 3):

3.XI and February 3.II temporal variants of Site No. 3 are characterized by the lowest water pollution level (Table 1).

The least distant in hyperspace of complex gradients of the water medium by the heavy metal content (Fig. 3b) are the June 3.VI and February 3.II variants of Site No. 3 (Euclidean distance is 2.81). The most distant relative to other variants are the April 3.IV and November 3.XI variants (Euclidean distance is 3.95-5.45).

Based on the correlation between the heavy metal content and complex gradients of the water medium (Fig. 3a), as well as cluster analysis, the following associations (groups) of chemical elements can be distinguished:

I – Cu, Cr, Zn, Sr;

II – Mn, Ni, Co, Cd;

III – Pb.

The most distant in the hyperspace of complex gradients of the water medium are the chemical elements Cu and Co (Euclidean distance is 1.96), Cr and Co (Euclidean distance is 1.95), Cu and Ni (Euclidean distance is 1.91), Cr and Mn (Euclidean distance is 1.89). For Site No. 4 (the Zakhidnyi Buh River, Horodyshche village), the analysis of dependences between heavy metal concentrations in water also revealed a close relationship between individual chemical elements. For Cu and Zn concentrations, the correlation coefficient is $r = 0.99$, for Cu and Pb – $r = -0.71$, for Cu and Cr – $r = 0.85$, for Cu and Sr – $r = 0.99$, for Cd and Co – $r = 0.90$, for Zn and Cr – $r = 0.85$, for Zn and Sr – $r = 0.98$, for Cr and Sr – $r = 0.82$, for Co and Ni – $r = 0.95$. Since the heavy metal concentrations in water of Site No. 4 are correlated with each other, the observational data can be explained by a small number of new variables that are not directly measured, but can be obtained through a linear combination of the original data. This makes it possible to reduce the dimensionality of the observation space.

The results of principal component analysis based on the correlation matrix are as follows (Fig. 4):

Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – the standardized values of heavy metal concentrations in water;

λ_i – eigenvalues of vectors.

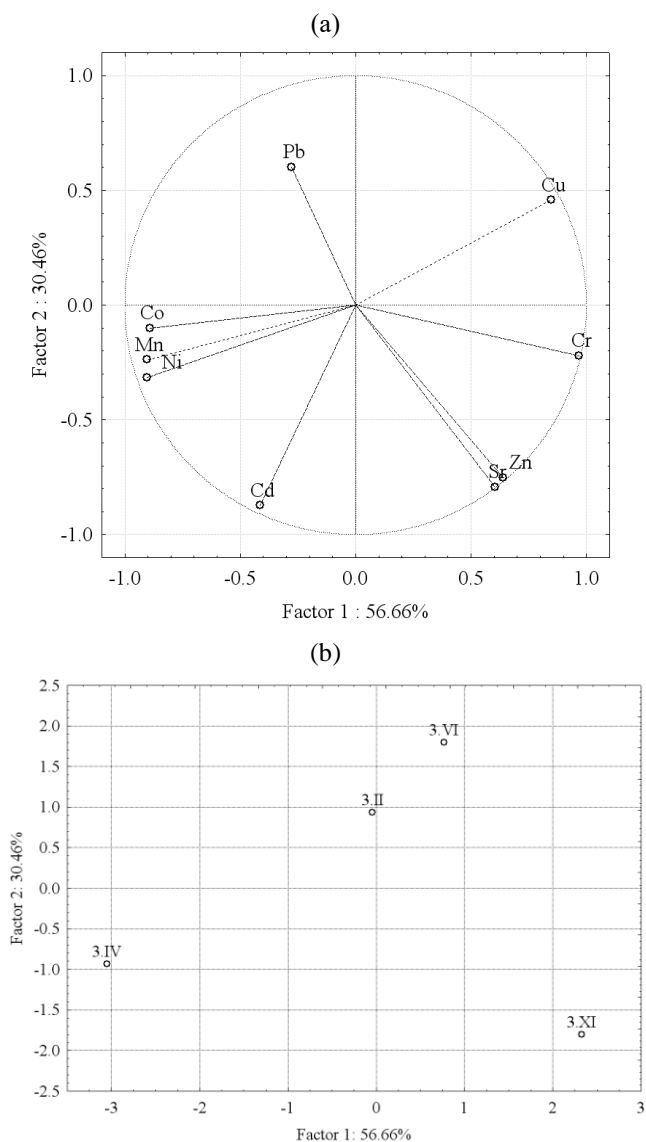


Figure 3. Results of analysis of the principal components of heavy metal content in water of Site No. 3 (the Rata river, Silets village): (a) the system of relationships between the concentrations of chemical elements and complex gradients of the medium; (b) a location of temporal variants of the site in the coordinate system of complex gradients of the medium; Factor_{1,2} – the principal components, complex gradients of the medium; Arabic numerals indicate site numbers, Roman numerals indicate the calendar month serial numbers (Table 1)

From the analysis of the characteristics of eigenvalues λ_i , it follows that already the two principal components provide 87.5% of the total variance, therefore, for many analysis purposes, it is sufficient to use a two-dimensional projection of the original data matrix. Eigenvectors of the correlation matrix make it possible to identify combinations of environmental factors that determine the axes of maximum variation in the seasonal dynamics of chemical water pollution. The main pattern of formation of water medium quality in site No. 4 (the first principal component of Factor₁) is the following structure of relationships between chemical elements (Fig. 4a): with the increase in Cr concentration (correlation coefficient is $r = 0.97$), the concentrations of Zn ($r = 0.95$), Cu ($r = 0.95$), Sr ($r = 0.92$) increase, and the concentrations of Pb ($r = -0.63$), Ni ($r = -0.61$) decrease.

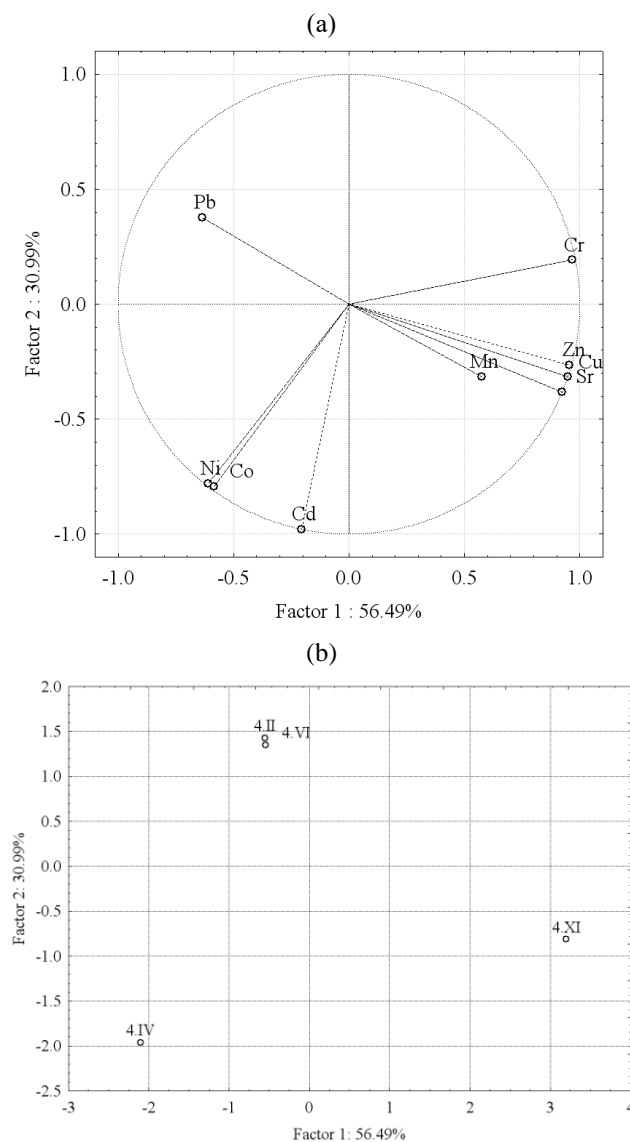


Figure 4. Results of analysis of the principal components of heavy metal content in water of Site No. 4 (the Zakhidnyi Buh River, Horodyshche village): (a) the system of relationships between the concentrations of chemical elements and complex gradients of the medium; (b) a location of temporal variants of the site in the coordinate system of complex gradients of the medium; Factor_{1,2} – the principal components, complex gradients of the medium; Arabic numerals indicate site numbers, Roman numerals indicate the calendar month serial numbers (Table 1)

The first principal component explains 56.5% of the total variance. The April 4.IV temporal variant of site No. 4 is characterized by low values of the first principal component of Factor₁, distinguished by high heavy metal concentrations: Cd, Mn and Ni (Table 1). The November 4.XI temporal variant of Site No. 4 is distinguished by maximum values of the first principal component, where Cd, Zn, Cr, Mn and Sr concentrations in water are relatively higher (Table 1).

The second axis of maximum Factor₂ variation additionally explains 31.0% of the total data variance. The Factor₂ function value mainly depends on the content of Cd ($r = -0.98$), Co ($r = -0.79$), Ni ($r = -0.78$) and Sr ($r = -0.73$). The maximum values of the second principal component are characteristic of the February 4.II and June 4.VI temporal variants of site No. 4. According to total indices of exceeding

the maximum permissible concentrations of 9 chemical elements, the February 1.II temporal variant of Site No. 4 is characterized by the lowest water pollution level. The minimum value of the second principal component is observed in the April 1.IV variant of the site, which is characterized by high concentrations of Cd (exceeding the MPC by 3 times), Pb (exceeding the MPC by 1.2 times) and Mn (exceeding the MPC by 1.2 times) (Table 1). Site No. 4 is characterized by high stability of the seasonal level of water pollution with heavy metals. The standard deviation of the total excess of the maximum permissible concentrations for 9 chemical elements is characterized by the lowest value of 1.81.

The least distant in the hyperspace of complex gradients of the water medium by heavy metal content (Fig. 4b) are the June 4.VI and February 4.II variants of Site No. 4 (Euclidean distance is 2.83). The most distant relative to other variants are the April 1.IV and November 1.XI variants (Euclidean distance is 3.90-5.42).

Based on the correlation between the heavy metal content and complex gradients of the water medium (Fig. 4a), as well as cluster analysis, the following associations (groups) of chemical elements can be distinguished:

$$\text{Factor}_1 = 0.374 \cdot \text{Cu} - 0.191 \cdot \text{Cd} + 0.366 \cdot \text{Zn} - 0.333 \cdot \text{Pb} + 0.376 \cdot \text{Cr} - 0.298 \cdot \text{Co} - 0.375 \cdot \text{Mn} - 0.333 \cdot \text{Ni} + 0.313 \cdot \text{Sr};$$

$$\lambda_1 = 5.41; \tag{9}$$

$$\text{Factor}_2 = -0.260 \cdot \text{Cu} + 0.322 \cdot \text{Cd} - 0.264 \cdot \text{Zn} + 0.278 \cdot \text{Pb} + 0.251 \cdot \text{Cr} - 0.483 \cdot \text{Co} - 0.263 \cdot \text{Mn} - 0.404 \cdot \text{Ni} - 0.393 \cdot \text{Sr};$$

$$\lambda_2 = 2.23, \tag{10}$$

where:

Factor_i – the component coordinates, complex gradients of the medium;

Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – the standardized values of heavy metal concentrations in water;

λ_i – eigenvalues of vectors.

From the analysis of the characteristics of eigenvalues λ_i , it follows that already the two principal components provide 84.9% of the total variance, therefore, for many analysis purposes, it is sufficient to use a two-dimensional projection of the original data matrix. Eigenvectors of the correlation matrix (1)-(2) make it possible to identify combinations of environmental factors that determine the axes of maximum variation in the seasonal dynamics of chemical water pollution. The main pattern of formation of water medium quality in site No. 5 (the first principal component of Factor₁) is the following structure of relationships between chemical elements (Fig. 5a): with a decrease in Mn concentration (correlation coefficient $r = -0.87$), the concentrations of Ni ($r = -0.78$), Pb ($r = -0.78$), Co ($r = -0.69$) decrease, and the concentrations of Cr ($r = 0.87$), Cu ($r = 0.87$), Zn ($r = 0.85$), Sr ($r = 0.73$) increase. The first principal component explains only 60.1% of the total variance, but its values clearly reveal the main pattern of temporal dynamics of water medium quality in Site No. 5. Thus, the April 5.IV temporal variant of Site No. 5 is characterized by low values of the first principal component Factor₁, distinguished by high heavy metal concentrations: Mn, Ni (Table 1). The November 5.XI temporal variant of Site No. 5 is distinguished by maximum values of the first principal component, where Cu, Zn, Cr and Sr have relatively higher concentrations in water compared to the monthly average (Table 1).

The second axis of maximum Factor₂ variation additionally explains 24.8% of the total data variance. The Factor₂

I – Cu, Sr, Zn, Cr, Mn;

II – Cd, Co, Ni;

III – Pb.

The most distant in the hyperspace of complex gradients of the water medium are the chemical elements Cr and Ni (Euclidean distance is 1.88), Pb and Sr (Euclidean distance is 1.86), Cu and Pb (Euclidean distance is 1.85), Cr and Co (Euclidean distance is 1.84).

The presence of a close relationship between chemical elements is also characteristic of Site No. 5 (the Rata River, the city of Velyki Mosty). Thus, for Cu and Zn concentrations, the correlation coefficient is $r = 0.99$, for Cu and Sr – $r = 0.97$, for Cd and Pb – $r = 0.90$, for Zn and Sr – $r = 0.97$, for Pb and Cd – $r = 0.90$, for Cr and Co – $r = -0.88$, for Co and Ni – $r = 0.97$, for Mn and Ni – $r = 0.97$. As in previous cases, the observational data can be explained by a small number of new variables that are not directly measured, but can be obtained through a linear combination of the original data, which reduces the dimensionality of the observation space.

The results of the principal component analysis based on the correlation matrix are as follows (Fig. 5):

function value mainly depends on the content of Co ($r = -0.72$), Ni ($r = -0.60$), Sr ($r = -0.59$), Cd ($r = 0.48$) and Pb ($r = 0.42$). Thus, in June, the highest concentrations of Pb (exceeding the MPC by 1.7 times) and Cd (exceeding the MPC by 3.0 times) were observed in Site No. 5, which resulted in June 5.VI variant having the maximum value of the second principal component. According to total indices of exceeding the maximum permissible concentrations of 9 chemical elements, the June 5.VI temporal variant ranks second. The minimum value of the second principal component is for the April 5.IV variant of the site, which is characterized by the worst water quality indicators (Table 1).

The least distant in hyperspace of complex gradients of the water medium by the heavy metal content (Fig. 5b) are the June 5.VI and February 5.II variants of Site No. 5 (Euclidean distance is 3.07). The most distant relative to other variants are the April 5.IV and November 5.XI variants (Euclidean distance is 3.86-5.63).

Based on the correlation between the heavy metal content and complex gradients of the water medium (Fig. 5a), the following associations (groups) of chemical elements can be distinguished:

I – Cu, Zn, Sr, Cr (Cr can be distinguished into a separate group);

II – Cd, Pb;

III – Co, Ni, Mn.

The most distant in the hyperspace of complex gradients of the water medium are the chemical elements Cr and Co (Euclidean distance is 1.94), Cr and Ni (Euclidean distance is 1.92), Cr and Mn (Euclidean distance is 1.91), Cu and Pb (Euclidean distance is 1.84). Multidimensional statistical analysis and graphical visualization of the information made it possible to identify some common features in seasonal dynamics of the level of water pollution with heavy metals (Figs. 1-5).

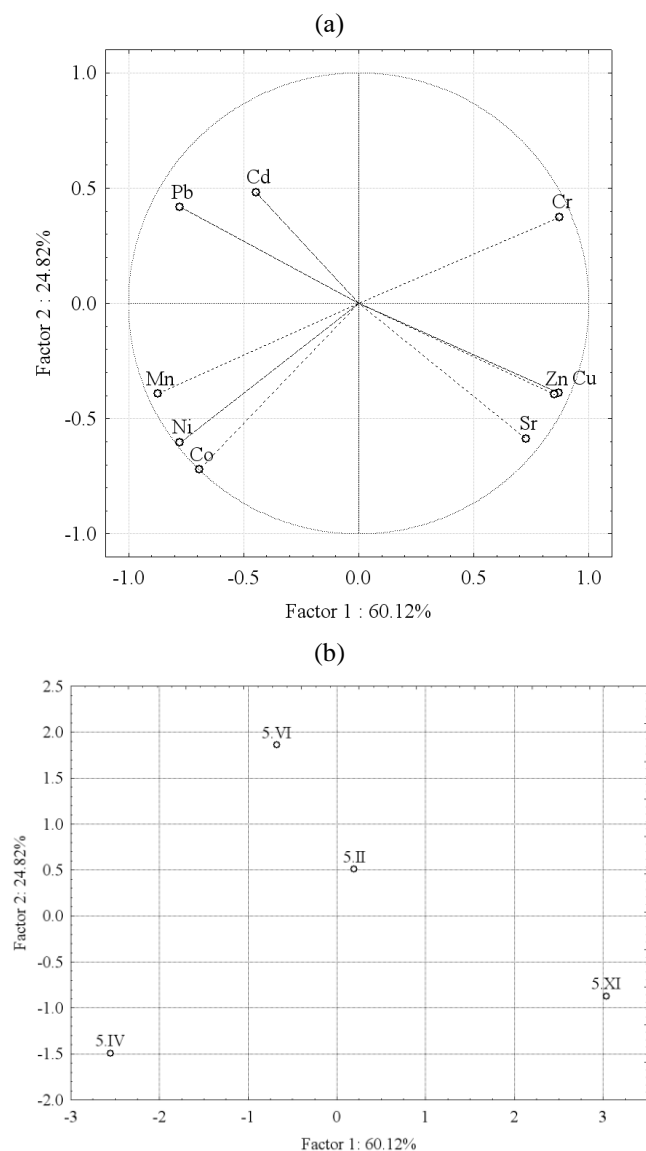


Figure 5. Results of analysis of the principal components of heavy metal content in water of Site No. 5 (the Rata river, the city of Velyki Mosty): (a) the system of relationships between the concentrations of chemical elements and complex gradients of the medium; (b) a location of temporal variants of the site in the coordinate system of complex gradients of the medium; Factor₁₋₂ – the principal components, complex gradients of the medium; Arabic numerals indicate site numbers, Roman numerals indicate the calendar month serial numbers (Table 1)

The highest level of pollution during the entire monitoring season (Table 1) was observed in Sites No. 1 and 2 (small and technogenic ponds at the foot of the slope of the Mezhyrichanska Mine waste heap near the city of Chervonohrad). In seasonal dynamics, the April variant in all sites is characterized by a similar location on the axes of complex gradients of the medium (Figs. 1-5b) in the third coordinate quarter. The reason for this location is the maximum value of exceeding the heavy metal content in water compared to the maximum permissible concentration. Chemical elements form similar associations (groups):

- Ni, Mn – in sites No. 1, 2 (Figs. 1-5a);
- Ni, Mn, Co – in sites No. 3, 5;
- Cu, Zn, Sr – in sites No. 3-5;
- Cu, Zn – in sites No. 1-5;

– Pb on the axes of complex gradients of the medium most often was maximally distant from Zn, Sr (Figs. 1-5a).

The total index of water pollution level Z_c makes it possible to consider in more detail the peculiarities of water pollution with heavy metals (Table 2). In this case, 3 variants of the index are considered. The first variant of the calculations includes the values of exceeding the maximum permissible concentration of all 9 chemical elements. Since Mn shows abnormal dynamics of its content in water, the second variant of the total water pollution level Z_c does not use the values of this chemical element. The third variant of the calculations takes into account only 4 chemical elements (Cd, Pb, Co, Sr), which are classified as hazard class II. The first place for water pollution with heavy metals belongs to site No. 1, the second – to site No. 2 (Table 2). Both sites are represented by water bodies located at the foot of the Mezhyrichanska Mine waste heaps near the city of Chervonohrad.

Table 2. Total water pollution level in the rivers and water bodies of the mining-industrial region

Site No.	Date*	Total index of water pollution level Z_c					
		9 chemical elements (Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr)		8 chemical elements (Cu, Cd, Zn, Pb, Cr, Co, Ni, Sr)		4 chemical elements of hazard class II (Cd, Pb, Co, Sr)	
		Z_c , times	Rank	Z_c , times	Rank	Z_c , times	Rank
1	VI	83.7	4	37.6	2	30.6	1
	XI	642.0	2	17.0	3	14.7	3
	II	218.0	3	4.0	4	1.6	4
	IV	3355.6	1	88.6	1	21.0	2
2	VI	28.7	3	3.4	3	2.7	3
	XI	28.0	3	27.8	2	21.7	1
	II	161.0	2	4.0	3	1.4	4
	IV	2094.9	1	61.4	1	18.2	2
3	VI	20.6	2	3.7	2	3.2	2
	XI	2.8	3	2.7	3	2.0	3
	II	2.8	3	1.7	4	1.5	4
	IV	88.7	1	5.2	1	3.4	1
4	VI	5.4	2	3.5	2	3.2	2
	XI	5.4	2	3.1	2	2.3	3
	II	2.3	3	2.2	3	1.9	4
	IV	6.5	1	5.3	1	4.4	1
5	VI	7.4	2	5.3	1	4.8	1
	XI	2.3	3	2.2	3	1.6	3
	II	2.2	3	1.8	4	1.5	3
	IV	10.7	1	4.8	2	3.4	2
Mean values of Z_c							
1	mean	1074.8	1	36.8	1	17.0	1
2	mean	578.1	2	24.1	2	11.0	2
3	mean	28.7	3	3.3	3	2.5	3
4	mean	4.9	5	3.5	3	2.9	3
5	mean	5.6	4	3.5	3	2.8	3

*Date of sampling for chemical analysis: VI – 07.06.2022; XI – 01.11.2022; II – 24.02.2023; IV – 25.04.2023

Depending on the chosen variant of calculating the total index of water pollution level Z_c , the rank of the temporal variant of the site in the seasonal dynamics of heavy metal content in water changes (Table 2). Most often, the worst

water quality conditions are observed in the warm season, and the best – in winter and late autumn. This peculiarity is clearly visible in the third variant of calculations, where only hazard class II chemical elements are taken into account. The greatest difference in the values of the total index of water pollution level Z_c , depending on the calculation variant, is observed in Sites No. 1-2. For example, in site No. 2, without taking into account Mn, the worst water quality indices move from April to November variants. For the third variant of the total index of water pollution level Z_c , sites No. 3-5 have the identical rank (Table 2). For the first variant of calculating the total index of water pollution level Z_c , taking into account all 9 chemical elements, the worst condition of water in the river in terms of heavy metal pollution is observed in Site No. 3 (the Rata River, Silets village). This is due to the fact that it is located in the zone of influence of mining enterprises (the earth's surface subsidence in places of coal seam mining up to 2-4 m, flooding and water-logging of large surface areas) (Table 2). Thus, the distance to a potential source of pollution has a significant impact on the seasonal dynamics of heavy metal content in the water of rivers and water bodies of the mining-industrial region.

It is extremely important to study the factors of pollution of natural water bodies with heavy metals within the mining-industrial complex. Promising directions for further research is to study the content of heavy metals in snow samples from the studied sites, as well as those located in close proximity to coal mine waste dumps, industrial buildings and structures. The study of heavy metals in snow samples will provide an opportunity to have a clear idea of heavy metal pollution of the surface air in the mining area, as well as the level of acidity and toxicity of precipitation. An integral part of environmental monitoring is the study of heavy metal and a nitrate content in vegetation, including fruits consumed by the population. The issue of pollution of food fruit vegetation is an important problem in coal-mining regions.

4. Conclusions

The level of chemical pollution of water in the rivers and water bodies of the Chervonohrad mining-industrial complex with heavy metals during the season is characterized by significant heterogeneity. The main role in the deterioration of the ecological state of water bodies is associated with an increase in the concentration of Mn, Ni, Cd, and Pb, compared to the maximum permissible concentration. The highest level of pollution during the entire monitoring season was observed in water bodies at the foot of the Mezhyrichanska Mine waste heap near the city of Chervonohrad. Among the river bodies, the worst water condition in terms of heavy metal pollution was found in the Rata River (Silets village), which is located in the zone of influence of mining enterprises. The maximum excess of heavy metal content in water in seasonal dynamics in all sites is characterized by April variant of water samples.

The analysis of the dependence between the concentrations of chemical elements indicates the presence of a close relationship between many parameters. Based on the similarity of chemical elements in terms of their distribution in water, the following associations (groups) have been identified: I – Cu, Zn – in all water bodies; II – Cu, Zn, Sr – in the rivers of the Western Bug basin; III – Ni, Mn – in water bodies at the foot of the waste heap; IV – Ni, Mn, Co – in the rivers of the Western Bug basin.

The practical significance of the results obtained is that predicting dynamic trends, protecting and restoring ecosystem components are impossible without taking into account their interrelationships with environmental conditions, including the level of chemical water pollution. Knowing the geochemical conditions of ecotopes in a certain period of time, it is possible to determine their position in the ecological space on complex gradients of the medium, to predict the stability and possible changes in all ecosystem components due to environmental pollution.

Author contributions

Conceptualization: VP; Data curation: VS, OK; Formal analysis: VS; Investigation: VS, OT; Methodology: VP, VS; Project administration: VS; Resources: OT, OK; Software: VS; Supervision: VP; Validation: VP, VS, OK; Visualization: VP, VS; Writing – original draft: VP, VS, OT, OK; Writing – review & editing: VP. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interests

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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Гідроекологічний моніторинг забруднення важкими металами водойм басейну Західного Бугу в межах гірничопромислового району

В. Попович, В. Скробала, О. Тиндик, О. Каспрук

Мета. Дослідити особливості хімічного забруднення води рік і водойм на території Червоноградського гірничопромислового району важкими металами залежно від відстані до джерела забруднення та типу ландшафту, проаналізувати загальні тенденції сезонної динаміки концентрації хімічних елементів.

Методика. У роботі використано статистичну обробку параметрів хімічного забруднення води і ґрунтів, таких як кореляційний аналіз, методи добування даних (Data Mining Methods). Оцінку подібності екоотопів та групування хімічних елементів виконано за допомогою кластерного аналізу. Багатовимірна ординація екоотопів у просторі описана за допомогою геохімічних показників та графічної візуалізації на основі аналізу головних компонент (Principle Component Analysis).

Результати. Найвищий рівень забруднення упродовж всього сезону спостережень мав місце у водоймах біля підніжжя терикону шахти "Межирічанська" поблизу міста Червоноград. Серед річкових об'єктів найгірший стан води за рівнем забруднення важкими металами встановлено у р. Рата (с. Сілець), яка перебуває у зоні впливу підприємств гірничо-видобувного комплексу. Максимальним перевищенням вмісту важких металів у воді у сезонній динаміці на всіх об'єктах характеризувався квітневий варіант водних об'єктів. Аналіз залежності між концентраціями хімічних елементів вказує на наявність тісного зв'язку між багатьма параметрами.

Наукова новизна. Вперше встановлено, що багатовимірна ординація водних об'єктів на осях комплексних геохімічних градієнтів середовища відображає сезонну динаміку рівня забруднення природних водойм важкими металами у межах гірничопромислового району.

Практична значимість. На основі отриманих даних вмісту важких металів у воді природних водойм можна здійснити прогнозування рівня забруднення, а також запровадити заходи щодо попередження впливу негативних чинників на якість води. Знаючи геохімічні умови екоотопів у певний період часу, можна визначити їх положення в екологічному просторі на комплексних градієнтах середовища, прогнозувати стійкість і можливі зміни рослинності, тваринного світу та мікрофлори унаслідок забруднення довкілля.

Ключові слова: важкі метали, екоотоп, комплексний градієнт середовища, багатовимірна ординація екоотопів, математичне моделювання, екологічна безпека, техногенна водойма

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