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Modelling the seasonal dynamics of heavy metal pollution of water bodies within a mining area

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Abstract

Waste heaps from coal mines pollute the environment through spontaneous combustion of waste and contaminated wastewater leaking into underground and surface aquifers. Together with pollutants, a large concentration of heavy metals gets into the water. The object of this research is water bodies in the impact zone of the Chervonohrad mining district, a part of the Lviv-Volyn coal basin (Ukraine). Water chemical contamination level of anthropogenic reservoirs in the mining district was measured by indicators developed based on geochemical and hygienic environmental investigations. Methods of statistics of parameters of chemical pollution of water and soil; correlation analysis; data mining methods; assessment of similarity of ecotopes and grouping of chemical elements based on cluster analysis; multidimensional ordination of ecotopes in the space of geochemical indicators and graphical visualization based on Principle Component Analysis were used in the research. Chemical pollution of rivers and reservoirs in Male Polissia with heavy metals during the season is characterized by significant heterogeneity. The main reason of the deterioration of the ecological state of water bodies is related to the increase in the content of Mn, Ni, Cd, Pb compared to the maximum permissible concentration. The highest level of pollution during the entire monitoring season was observed in the water bodies at the foot of the Mezhyrichanska mine spoil tip near the city of Chervonohrad. Based on the correlation between the heavy metal content and the complex gradients of the aquatic environment, the following associations (groups) of chemical elements were identified: I - Cu, Pb, Co, Cd; II - Mn, Ni; III - Zn, Cr, Sr. The multidimensional ordination of water bodies on the axes of complex geochemical gradients of the environment reflects the seasonal dynamics of water pollution and its spatial features. The practical significance of the results obtained lies in the fact that forecasting dynamic trends, protection and restoration of ecosystem components are impossible without taking into account their relationships with environmental conditions, in particular, with the level of chemical pollution of water.

Keywords:
heavy metals, chemical pollution, ecotope, complex environmental gradient, multidimensional ordination of ecotopes, mathematical modelling, environmental safety

1. Introduction

Mining complexes cause direct and irreversible biogeochemical processes in the environment. Open pit coal mining creates significant voids on the ground surface, that are filled with appropriate materials and reclaimed decades after mining. Underground coal mining results in significant areas of fertile land being allocated for spoil piles, the reclamation of which is not currently being fully implemented (**Popovych et al., 2019**). Coal mine spoil piles pollute the environment through spontaneous combustion of rock and the discharge of contaminated wastewater into underground and surface aquifers (**Petlovanyi et al., 2021**). Together with pollutants, a large concentration of heavy metals gets into the water.

On a global scale, many researchers investigate the problem of heavy metal pollution in water bodies and methods of water purification. The pollution of aquatic ecosystems with some heavy metals may lead to envi-

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ronmental problems and, consequently, to negative health effects. Heavy metals, as persistent toxicants, are deposited in the ecosystem and subsequently infect food chains (**Kapoor et al., 2021**). The results (**Jara, et al., 2014**) indicate that coastal waters with mining activities and the highest concentrations of copper and iron caused a greater antioxidant response and oxidative damage to lipids in *E. peruviana*. Research on the impact of heavy metals on living organisms, including human health, is of considerable importance. Heavy metal intoxication is a serious threat, and several health risks are associated with it (**Popovych, et al., 2021a; Serhiyenko, et al., 2021; Serhiyenko, et al., 2022b**). The toxic effects of these metals, even though they do not have any biological role, persist in one form or another and threaten the human body and its proper functioning (**Sankhla et al., 2016**). Acute and chronic illnesses are caused by high concentrations of heavy metals in drinking water that exceed the permissible limits set by several national and international organizations. They can range from non-lethal, such as muscle and physical weakness, to lethal, such as brain, nervous system, and even cancer (**Nersesyan, et al., 2021; Serhiyenko, et al., 2022a; Singh, et al. 2022**).

Besides the global crisis of drinking water shortage, the pollution of water bodies and rivers due to industrial and mining operations is an urgent problem (**Petlovanyi et al., 2022**). Notably, the main pollutants from mining found near Baia Mare (Romania) are heavy metals Pb, Zn, Cd, Cu, Ni, and As. High concentrations of heavy metals have been detected in groundwater from wells in villages located downstream of mining facilities (**Modoi et al., 2014**). According to the Heavy Metal Pollution Index and the Heavy Metal Assessment Index of surface water samples, the middle part of the Aryesh River basin, near and downstream of the gold mine reservoir, was characterized by high levels of pollution (**Moldovan et al., 2022**).

While in Ghana, in water bodies around gold mining sites, the hazard quotients (HQs) for ingestion and dermal contact for virgin and mine-derived samples ranged from 3.00E-04 (Cu) to 0.84 (Cr) and from 2.40E-06 (Cu) to 7.44 (As), respectively (**Hadzi et al., 2018**). Lead, cadmium, arsenic, and mercury are highly carcinogenic, while others are toxic. The levels of these metals in the water resources of the lead-zinc mining communities of Enyigba, Mkpuma Akpatakpa, Ameka, Amori, Amanchara, and Alibaruhu were assessed and the potential health risks were investigated. Seasonal analysis shows a decrease in the content of chemical components in the rainy season compared to the dry season (**Obasi et al., 2020**).

Researchers have assessed the impact of arsenic and heavy metals on the environment in the 105 km^2 area of the historic and recent Villa de la Paz Matejuala mine, San Luis Potosí (Mexico). It was determined that the maximum concentration of arsenic in pluvial water bodies (265 μg/l), near the main potential sources of pollution, is 5 times higher than the Mexican drinking water quality standard (50 μg/l). Arsenic concentrations in reservoirs and stream sediments decrease with increasing distance from potential sources (**Razo et al., 2004**). The impact of heavy metals has led to an unacceptable risk level for human health in two age groups of people, both carcinogenic ($TCR > 1\times10^{-5}$) and non-carcinogenic ($HI > 1$) through consumption of tap water and accidental ingestion of surface water. Sensitivity analysis showed that As concentration in water and frequency of exposure were the main risk factors (**Jiménez-Oyola et al., 2021**). In the Bolkar mining area of the Nigde province in south-central Turkey, water hazard index (WHI) values indicate that 100% of samples collected in both winter and autumn are extremely toxic (WHI > 15). Arsenic is the dominant PTE contaminant in soil and water samples. The bioconcentration coefficient of PTEs in most fruit plants is > 1, indicating a very high level of transfer of the metal from soil and water to plants (**Lermi et al., 2023**).

In Datuku in the Talensi-Nabdam District of Upper East Ghana, research (**Cobbina et al., 2013**) was conducted to assess the impact of small-scale gold mining on the quality of drinking water in the community. Some parameters exceeded WHO limits. Levels of turbidity, nitrate, cadmium, total iron, manganese, and arsenic were all above the WHO recommended drinking water quality limits. Turbidity ranged from 1 to 447 NTU (55 NTU), nitrates ranged from 0.15 to 595 (47.1), cadmium ranged from 0.005 to 0.029 mg/L (0.014 mg/L), etc.

In **Prasad et al. (2014**), the concentrations of 7 heavy metals were evaluated at 20 important groundwater sampling stations in the town of Dhanbad, located very close to the Jharia coal fields. The concentrations of heavy metals were generally below acceptable levels, although at several stations the concentrations of iron and manganese exceeded the permissible limits.

In humid regions, leaching of heavy metals from both tailings and overburden sulfides leads to environmental pollution. The use of impermeable layers is highly recommended. Climatic factors (temperature, wind, and precipitation) largely control the distribution and mobility of heavy metals in the Cu mining region (**Punia, 2021**).

Overall, 48 water samples (groundwater (27) and surface water (21)) are analyzed for heavy metals. Eighty-eight percent of groundwater and 90% of surface water samples are contaminated with Hg. High concentrations of Pb and Cd were also found in the samples. Surprisingly, in all water samples As concentrations exceeded the WHO limit of 10 ppb. In addition, 95% of the samples have an HPI score of more than 100, indicating high heavy metal pollution. The CD value means that 89% of the samples are contaminated with heavy metals (As, Hg, Cd, Pb). Due to the spatial distribution, it can be understood that most of the contaminated samples are located near thermal power plants, ash and slag dumps, and coal mines (**Bhardwaj et al., 2020**).

The results of **Igwe et al. (2021)** revealed the presence of some chemical pollutants in the range of mg/L, namely: Cd (0.18-4.37), Pb (0.06-10.11), Zn (0.13-7.11), Ni (0.02-1.21), Mn (0.04-1.16), Fe (0.03-2.04) and Cr (0.02-0.48) in the surface water regime, as well as Cd (0.02-2.00), Pb (0.16-3.18), Zn (0.13-5.16), Ni (0.01) -1.54), Mn (0.01-2.17), Fe (0.01-2.50) and Cr (0.01-0.28) in the groundwater system. Except for Mn and Ni, which showed higher pollution levels in groundwater than in typical surface water samples.

The natural causes include the migration and redistribution of soil debris and hydraulic migration of the parent rock of the high background soil by wind; human causes include mining, abandoned mines, fertilizer and pesticide applications, and wastewater irrigation (**Zhang et al., 2020**). Metal concentrations were higher in the pre-monsoon season than in the post-monsoon season, regardless of location, but there was more seasonal variation in water from open pit mines than from underground mines. Concentrations of Al, Ba, Fe, Mn, and Ni exceeded both desirable and permissible drinking water standards in both seasons (**Tiwari et al., 2017**). The results of **Othmani et al. (2015)** confirm that wind is the main agent capable of dispersing metals in the W-E direction, with concentrations exceeding soil quality standards for Cd, Pb, and Zn at a distance of several hundred meters from the source, facilitated by the fine fraction and low cohesion of tailings particles.

This research assesses the concentration(s) of heavy metals in groundwater and pollution in the Agbara and Ota industrial areas of Ogun State. The concentration of heavy metals was found to increase in the following order of Pb > Cr > Fe > Ni > Cd > Cu and Fe > Pb > Ni > Cu > Cr > Cd for Agbara and Ota locations respectively. The spatial distributions of HPI contamination ranged from 171.25 to 734.11 and from 95.11 to 1393 for Ota and Agbar, respectively (**Ojekunle et al., 2023**).

An investigation (**Abraham et al., 2017**) showed that the average concentrations (mg/kg) of Co (112), Cu (3320), Ni (131), As (8.6) in mine tailings were significantly higher than the global average and were eroded and discharged to water bodies within the catchment. Underground mine water and leachate contained higher mean concentrations (µg/L) of Cu (9470), Co (3430), and Ni (590) compared to background concentrations (µg/L) in uncontaminated water of 1.9, 0.21, and 0.67 for Cu, Co, and Ni, respectively.

It was found that *Hyophila involuta* accumulates Mn, Cr, Cd, Pb, Fe, and Hg, while *Barbula arcuata* accumulates Mn, As, and Cu in SP1. *Hyophila involuta* and *Trematodon longicollis* accumulate Mn, Cr, Cd, Pb, Fe, Hg, Zn in SP2. *Trematodon ambiguous* accumulates Cd, Fe, and Ni, while *Fissidens diversifolius* accumulates Mn, Cr, Hg, As, Cu, and Zn in SP3. There is a high probability of monitoring heavy metal pollution in moss as a potential bioindicator (**Nanda et al., 2024**).

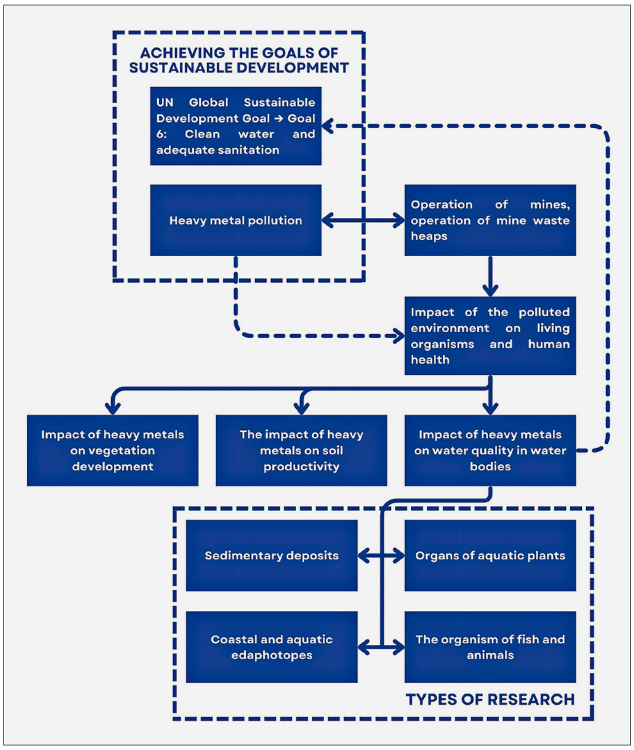

Figure 1. Algorithm for measuring the heavy metal content in water bodies within mining areas (developed by Popovych V.V.)

Heavy metal toxicity indices indicate that sediments in the Niger Delta pose a significant environmental risk, especially for Cd. None of the three pathways of heavy metal exposure to muscles and age groups of molluscs (*Callinectes amnicola, Uca tangeri, Tympanotonus fuscatus, Peneaus monodon*) poses a non-carcinogenic risk. The values of the total cancer risk for Cd and Cr exceeded the acceptable range (from 10^{-6} to 10^{-4}) established by the USEPA for children and adults, which raises concerns about the potential cancer risks after exposure to these metals in the region (**Jonjev et al., 2024**).

Figure 1 shows the algorithm for examining the heavy metal content in water bodies within mining areas, based on the water quality studies, influenced by the level of research on bottom sediments, aquatic plant organs, fish and animal organisms, and coastal and aquatic edaphotopes.

Considering the numerous scientific publications on the quality of fresh water in reservoirs, rivers and lakes, as well as the factors of its deterioration, the relevance of research within mining regions is undeniable.

Having considered a number of scientific works on the impact of various pollutants on water quality, we can state 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 metals should be carried out constantly and regardless of the season. In scientific studies by other authors, the modelling of the distribution of

Figure 2. Location of the studied sites in the mining region

heavy metals in the hydrographic network of the mining region has not been fully implemented. At the same time, new results of the content of heavy metals in water can be included in the state environmental monitoring system.

2. Overview of the research object and Methodology

2.1. Site investigation in mining regions

Water bodies of the Chervonohrad mining district, which is a part of the Lviv-Volyn coal basin, are the object of this research. The basin operates within the geographical area of Male Polissia. The landscape structure of Male Polissia is mainly dominated by natural and territorial complexes of the Polissia type. In some places, forest-steppe landscapes are common. In terms of climate, Male Polissia is significantly different from Ukrainian Polissia. Winter is mild, cloudy, with frequent thaws and small precipitation. Spring is long, at this time the weather is characterized by great variability. Summer is warm, rainy, with a predominance of westerly winds. The highest average July temperatures for Male Polissia are +18.8°C, in Roztochchya +17.5°C. Average January temperatures, for example, in the town of Rava-Ruska are -4.1°C, in the town of Brody -4.3°C. More precipitation falls here, especially on the southern border, at the foot of the Podolsk Upland, in particular, the average annual precipitation in the town of Rava-Ruska is 720 mm, in the town of Brody is 742 mm. There are 160-180 days with precipitation during the year. The total amount of precipitation in the Western Bug basin reaches 600 mm per year. The greatest amount of precipitation (per year) falls in the upper part of the basin (700-750 mm), which can be explained by the proximity of the Carpathian zone. The unevenness of precipitation throughout the year is characteristic, in particular, about 40% falls in the summer months, and in winter - only 16% of the annual norm.

Chemical pollution of water in man-made reservoirs of the mining district was assessed by indicators developed on the basis of geochemical and hygienic environmental research. These indicators include the concentration coefficient K_c and the total pollution index Z_c (**Bogolyubov et al., 2018; Bosak et al., 2020; Khilchevskyi**

Table 1: Study sites within the mining district

Study site No.	Location coordinates	Description of the study site
Site No.1	50.340802°N; 24.193898°E	A small reservoir located at the foot of a spoil pile belonging to the Mezhyrichanska Mine (until 2001 - Velykomostivska Mine No. 3), which is a separate subdivision of the State Enterprise Lvivvuhillya. The spoil pile is located near Chervonohrad, Lviv region. This area has undergone a significant landscape transformation during the long-term extraction of coal raw materials.
Site No.2	50.3398690°N; 24.1950900°E	A man-made reservoir at the foot of the spoil pile, where a process of natural phytomelioration has been taking place for many years, is located near Site No. 1. Rainwater collects in many places in the lowered relief, and leachate at the foot of the spoil pile itself, which poses a significant environmental hazard.
Site No.3	50.3103030°N; 24.1973610°E	Rata River, outside the village of Silets, near the confluence of the Bolotna River. The width of the Rata River is 40-45 meters. The site is located at a distance of 11 km from Chervonohrad city, 50 m below the road connecting the highway (P 15) and the town of Sosnivka. The territory is predominantly flat, with little anthropogenic impact. The site is without significant degradation damage, but is located in the impact zone of the territory affected by significant changes in natural landscapes as a result of mining and extraction enterprises.
Site No.4	50.3144420°N; 24.2493800°E	The Western Bug River, at a distance of about 500 meters to the east of the border of Horodyshche village, Chervonohrad district, Lviv region, near the bridge, the road to Volsvyn village. Among the anthropogenic sources of impact on the Western Bug are individual private households, which are a source of organic waste.
Site No.5	50.2448170°N; 24.1352160°E	The Rata River is located within the town of Velyki Mosty, Chervonohrad district, Lviv region, 200 meters from the road (P 15) to Chervonohrad. The riverbed is about 40 meters wide. There are small household waste dumps on the river banks.

et al. 2022; Popovych et al. 2021). The concentration coefficient K_c is defined as the ratio of the actual content of the substance C (mg/dm^3) to its maximum permissible concentration C_{MPC}:

$$K_{ci} = \frac{C_i}{C_{MPCi}} \tag{1}$$

Where:

i – is the serial number of the chemical substance.

The total pollution index Z_c equals the sum of the concentration coefficients of chemical elements K_c. In a modified form, it is represented by the formula:

$$Z_c = \sum_{1}^{n} K_{Ci} \tag{2}$$

Where:

n– is the serial number of the chemical substance.

The environmental information is based on data on the level of water pollution at 5 sites in 4 periods of time by 9 heavy metals: Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr. The location of the studied sites in the mining region (see **Figure 2**).

Mathematical modelling was done by establishing systematic relationships between heavy metal concentrations (**Skrobala et al., 2020; Skrobala et al., 2022**). The differences between ecotopes in terms of water pollution by heavy metals in space and time were assessed based on univariate analysis of variance and multivariate discriminant analysis. Mathematical models were tested using a comparative assessment of the position of sites on the axes of maximum variation (multidimensional ordination) with the results of seasonal dynamics and spatial features of chemical water pollution (**Aggarwal, 2015 Kantardzic et al., 2020**).

2.2. *Quality and distribution of heavy metals in the hydrological network of mining regions*

Water quality in the hydrographic network of a mining area depends on surface runoff from coal mine spoil piles, industrial structures, and anthropogenic landscapes, as well as on the distance to the probable source of pollution. Considering this factor, we selected 5 study sites (see **Table 1**).

Water samples were taken according to the method described in DSTU ISO 5667-6:2009 "Water quality. Sampling. Part 6. Guidelines for sampling water from rivers and streams". The selection of containers for water sampling was carried out in accordance with DSTU ISO 5667-3-2001 "Water quality. Sampling. Part 3. Guidelines for storage and handling of samples".

The analysis of the content of heavy metals in water samples was carried out in the Laboratory of Industrial Toxicology, which is a structural unit of the Danylo Halytskyi Lviv National Medical University (certificate No. RL 068/22 dated 01.12.2022 on the compliance of the measurement management system in accordance with DSTU ISO 10012:2005). Measuring equipment used during testing: electronic laboratory scales TVE-1-

Table 2. Level of water pollution in rivers and reservoirs of Male Polissia

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
	Concentration coefficients *Kc*, exceeding the maximum permissible concentration									
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

Conventions. *Numbering of sites: 1 - a small water body located at the foot of the spoil pile, near Chervonohrad; 2 - anthropogenic water body at the foot of the spoil pile, near Chervonohrad; 3 - the Rata River, Silets village; 4 - the Western Bug River, Horodyshche village; 5 - the Rata River, Velyki Mosty town. **Date of sampling for chemical analysis: VI - 07.06.2022; XI - 01.11.2022; II - 24.02.2023; IV - 25.04.2023.

0.01 (calibration certificate No. KLM 978 dated 12/26/2022); atomic absorption spectrophotometer S-115. M1 (calibration certificate No. UA/37/221219/001359 dated 12/19/2022).

Distribution of heavy metals in the hydrological network of mining complexes during the year is heterogeneous. Within one study area, there is a significant fluctuation in the level of chemical water pollution compared to the maximum permissible concentration of a chemical element (see **Table 2**).

The heavy metals content in the studied areas varies and the pattern of their distribution is also different. Specifically, a significant exceedance of the maximum permissible concentration of cadmium in water (14-23 times) was observed at sites No. 1 and No. 2. At other sites, the maximum exceedance of the maximum permissible concentration of cadmium during the year made up 2-3 times (see **Table 2**). Exceedance of the maximum permissible concentration of zinc by 1.6-2.2 times was observed only at sites No. 1 and No. 2 in November

2022 (see **Table 2**). The maximum level of lead pollution in the water bodies of the mining complex was observed in the summer and spring at all study sites. At no site did the copper content in water exceed the maximum permissible concentration (see **Table 2**). The content of chromium (hazard class III) and strontium (hazard class II) in the water bodies was characterized by low levels. Maximum concentrations of cobalt were recorded only in site No. 1 (a small reservoir at the foot of the spoil pile, near Chervonohrad).

A very high concentration of nickel in water was observed in April 2023 at sites No. 1 and No. 2 (water bodies located at the foot of the Mezhyrichanska mine spoil pile, near Chervonohrad). Abnormally high concentrations of manganese in water were observed in April 2023 at sites 1 and 2 (water bodies located at the foot of the Mezhyrichanska mine spoil heap near Chervonohrad).

3. Results

3.1. Analysis of spatial features of heavy metal content in water

Analyzing the differences between the sites with regard to chemical water pollution is easiest based on the average values of heavy metal content during the season, concentration factors (exceeding the maximum permissible concentration, times), and total pollution indicators Z_c (sum of concentration factors). Thus, sites No. 1-5 are characterized by the following average values of total pollution indicators Z_c for 9 chemical elements: 1074.8, 578.1, 28.7, 4.9, and 5.6, respectively. The values of the total Z_c pollution indicators mainly depend on the concentration coefficients of Mn, which demonstrated anomalous dynamics of its content in water. Since Mn belongs to the third hazard class and the limiting feature of its harmfulness is the organoleptic properties of water, additionally, the total Z_c pollution indicators only for 4 chemical elements (Cd, Pb, Co, Sr), classified as hazard class II, was determined. In this case, sites No. 1-5 are characterized by the following average values of Z_c indicators: 17.0, 11.0, 2.5, 2.9, and 2.8, respectively. Thus, sites No. 1 and No. 2 (reservoirs at the foot of the Mezhyrichanska mine spoil pile, near Chervonohrad) are most affected by high levels of chemical water pollution.

The one-factor analysis of variance is based on the calculation of the Fisher's criterion, which is the ratio of intergroup and intragroup variances. The intergroup variance shows how the concentrations of heavy metals vary in different areas. It is zero when the average concentrations of heavy metals are equal. The intragroup variance characterizes the difference in heavy metal concentrations within a site during the season. According to the analysis of variance, the greatest significance of differences in the average values of heavy metals in water is characteristic of Cd concentration. The maximum value of Fisher's criterion, which is inherent in Cd, indicates that this chemical element is the main factor in the differentiation of water bodies in Male Polissia (see **Table 3**). Thus, sites No. 1-5 are characterized by the following concentration coefficients *Kc* (exceedance of the maximum permissible concentration, times) for Cd: 14.3, 9.5, 1.4, 1.7, 1.9, respectively. Post hoc comparisons of mean Cd concentrations by the least significant difference test (LSD test) show a difference in Cd concentrations between site No. 1, on the one hand, and sites No. 3, 4, and 5, on the other.

The seasonal dynamics of heavy metal water pollution is characterized by a more complex pattern. The maximum total water pollution indicators Z_c for 9 chemical elements were observed in the April. The average values of Z_c water pollution indicators for different periods of time were as follows: 22.06.2023 – 29.2; 22.11.2022 – 136.1; 23.02.2023 – 77.3; 23.04.2023 – 1111.3. Only the April and June results differ significantly at the $p<0.05$ level of significance. For 4 chemical ele-

Table 3. Results of the dispersion analysis of spatial features of heavy metals content in the water of rivers and reservoirs of Male Polissia

Chemical element	SS Effect	df Effect	MS Effect	SS Error	df Error	MS Error	F	p
Cu	0.00	4	0.00	0.00	15	0.00	1.06	0.412
Cd	545.72	4	136.43	577.50	15	38.50	3.54	0.032
Zn	1.22	4	0.30	5.20	15	0.35	0.88	0.499
Pb	4.24	4	1.06	31.45	15	2.10	0.51	0.732
Cr	0.04	4	0.01	0.88	15	0.06	0.15	0.959
Co	0.88	4	0.22	1.42	15	0.09	2.32	0.104
Mn	3438397.68	4	859599.42	9739245.95	15	649283.06	1.32	0.306
Ni	1208.31	4	302.08	4429.83	15	295.32	1.02	0.427
Sr	0.00	4	0.00	0.02	15	0.00	0.42	0.794

Conventions: SS Effect and SS Error – intergroup and intragroup sums of squares of deviations; MS Effect and MS Error – mean value of intergroup (factor) and intragroup (residual) squared deviations; df – degrees of freedom; F – Fisher's test; p – significance level.

Table 4. Results of the analysis of variance of temporal (seasonal) dynamics of heavy metals content in the water of rivers and reservoirs of Male Polissia

Chemical elment	SS Effect	df Effect	MS Effect	SS Error	df Error	MS Error	F	p
Cu	0.001	3	0.000	0.005	16	0.000	0.65	0.594
Cd	0.000	3	0.000	0.001	16	0.000	0.94	0.443
Zn	2.307	3	0.769	4.108	16	0.257	3.00	0.062
Pb	0.017	3	0.006	0.015	16	0.001	6.29	0.005
Cr	0.002	3	0.001	0.000	16	0.000	24.14	0.000
Co	0.002	3	0.001	0.021	16	0.001	0.40	0.753
Mn	38191.490	3	12730.497	93584.946	16	5849.059	2.18	0.131
Ni	17.975	3	5.992	38.406	16	2.400	2.50	0.097
Sr	0.582	3	0.194	0.404	16	0.025	7.69	0.002

Conventions: SS Effect and SS Error – intergroup and intragroup sums of squares of deviations; MS Effect and MS Error – mean value of intergroup (factor) and intragroup (residual) squared deviations; df - degrees of freedom; F – Fisher's test; p – significance level.

Table 5. Results of mathematical modelling of spatial and temporal features of water pollution by heavy metals

Object*	Date**	Position of water bodies on the axes of complex environmental gradients					
		Model I (spatial features)		Model II (time dynamics)		Model III (spatial features and time dynamics)	
		Root 1	Root 2	Root 1	Root 2	Factor 1	Factor 2
1	VI	-5.75	0.46	3.58	6.23	-4.38	-0.65
	XI	-6.13	0.50	-9.71	-0.10	-0.64	-1.91
	II	-5.41	0.79	1.63	-1.44	0.91	0.37
	IV	-4.75	-0.98	4.36	-3.67	-4.38	2.53
2	VI	0.77	-0.04	3.10	5.02	0.86	0.32
	XI	-0.37	-3.11	-10.09	-0.09	-2.07	-4.52
	II	0.39	-0.18	2.82	-2.59	1.13	0.63
	IV	-2.52	-0.71	3.35	-5.21	-3.08	1.65
3	VI	0.21	0.50	3.37	7.04	0.81	0.38
	XI	1.85	2.42	-11.40	-0.61	1.46	-1.25
	II	0.86	-0.40	3.07	-3.43	1.15	0.53
	IV	0.59	1.02	3.63	-3.58	0.82	0.97
4	VI	1.39	0.51	4.35	4.74	0.86	0.66
	XI	2.62	-0.62	-10.08	0.04	0.24	-1.56
	II	1.67	-0.40	2.67	0.82	1.15	0.37
	IV	3.86	0.00	4.24	-4.01	0.79	0.95
5	VI	3.67	-0.56	1.73	6.06	0.86	0.10
	XI	1.57	0.95	-7.01	0.20	1.40	-0.92
	II	2.56	-0.73	2.70	-1.81	1.24	0.46
	IV	2.91	0.58	3.69	-3.62	0.87	0.91

Conventions. * Numbering of sites: 1 - a small reservoir located at the foot of the spoil pile, near Chervonohrad; 2 - anthropogenic reservoir at the foot of the spoil pile, near Chervonohrad; 3 - the Rata River, Silets village; 4 - the Western Bug River, Horodyshche village; 5 - the Rata River, Velyki Mosty town. ** Date of sampling for chemical analysis: VI - 07.06.2022; XI - 01.11.2022; II - 24.02.2023; IV - 25.04.2023.

ments of the second hazard class (Cd, Pb, Co, Sr), the minimum value of the significance level p=0.146 according to the least significant difference test (LSD test) is observed only for the April and February. The maximum value of Fisher's criterion and the highest significance of differences in the average values of heavy metals in water is characteristic of Pb, Cr and Sr, which are the main factors of seasonal differentiation of chemical pollution of water in rivers and reservoirs of Male Polissia (see **Table 4**). The June version differs most from other periods by Pb concentration, the April version by Cr concentration, and the November version by Sr concentration.

3.2. Mathematical modelling of the typological scheme of water bodies of Male Polissia

Although the one-dimensional statistical analysis provides a lot of information for understanding the peculiarities of heavy metal pollution of rivers and water bodies, its results should be considered preliminary. The idea of our further research was to mathematically model the typological scheme of water bodies in Male Polissia in the coordinate system of chemical element concentrations, taking into account the available information on the belonging of temporal variants of data to a specific area of space. Therefore, we calculated the optimal combinations of parameters of chemical water pollution, which can be used to determine the boundaries of sites in the multidimensional space of chemical element concentrations Model I (see **Table 5**).

The results of mathematical modelling (see **Figure 3**) are presented in the following equations:

$$Root_1 = 17.683\times Cu + 1495.010\times Cd + 0.244\times Zn - 43.759\times Pb - 134.126\times Cr - 337.796\times Co - 0.336\times Mn + 13.806\times Ni - 1.414\times Sr + 5.459,\ l_1 = 11.78 \quad (3)$$

$$Root_2 = -51.381\times Cu - 312.511\times Cd - 0.554\times Zn + 27.903\times Pb - 19.101\times Cr + 64.522\times Co + 0.088\times Mn - 3.952\times Ni + 5.563\times Sr - 0.886,\ \lambda_2 = 0.50 \quad (4)$$

Where:

$Root_i$ – canonical discriminant functions, axes of the typological scheme of water bodies; Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – values of heavy metal concentrations in water; l_i – eigenvalues of vectors.

The values of the first discriminant function $Root_1$ explain 91.2 % of the total variance. They mainly depend on the concentration of Cd (r = -0.68), Co (r = -0.86), Mn (r = -0.51), and Ni (r = -0.45). The same chemical elements were distinguished by relatively higher values of Fisher's index F in the univariate analysis of variance. The minimum values of the discriminant function Root1 are characterized by 4 time variants of site No. 1 (a small reservoir located at the foot of the spoil pile, near Chervonohrad), where the highest rates of total heavy metal contamination of water and high concentrations of Cd, Co, Mn, and Ni were observed. The maximum values of the discriminant function $Root_1$ are characteristic of the April variant of site No. 4 (the Western Bug River, the village of Horodyshche), the June and April variants of site No. 5 (the Rata River, the city of Velyki Mosty).

The values of the second discriminant function Root1 explain only 3.8% of the total variance and have a low differential ability. They depend mainly on the Zn concentration (r = -0.49). Discriminant functions explain 95.0% of the total variance. They allow to correctly identify 70% of the objects. For example, the June version of site No. 2 in terms of chemical contamination with a probability of 49.2% tends to site No. 3, and the February and April versions of site No. 4 – to site No. 5 (with a probability of 55.4% and 59.9%, respectively). The most distant in the space of discriminant functions are sites No. 1 and No. 5 (the Mahalanobis distance in the D_M^2 Squared Mahalanobis Distances is 90.3). If site No. 1 is considered to be an example of the highest water pollution (a small water body located at the foot of the spoil pile near Chervonohrad), then the following hierarchy of sites for improving the ecological state of water bodies can be obtained based on D_M^2 distance No. 1 → No. 2 (D_M^2 = 37.2) → No. 3 (D_M^2 = 56.1) → No. 4 (D_M^2 = 84.3) → No. 5 (D_M^2 = 90.3). The most distant in the space of discriminant functions are sites No. 4 and No. 5 (D_M^2 = 3.8), No. 3 and No. 4 (D_M^2 = 6.8), No. 2 and No. 3 (D_M^2 = 7.1). Thus, model I characterizes the spatial features of water pollution with heavy metals. The shorter the distance to the source of pollution, the worse the water quality indicators.

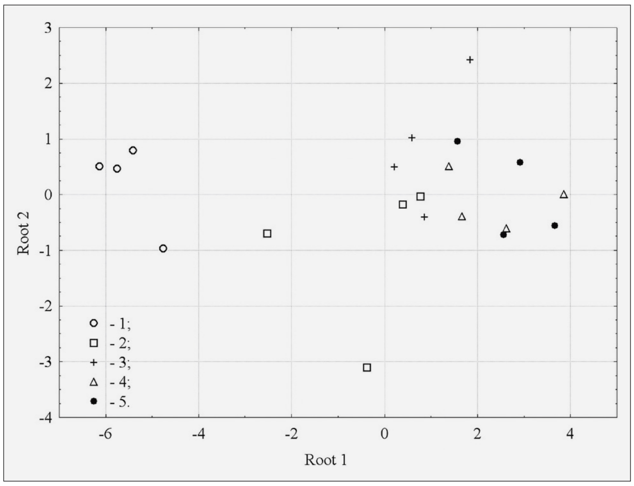

Figure 3. Typological scheme of reservoirs and rivers of Male Polissia: aspects of spatial features (Conventions. Numbering of sites: 1 – a small reservoir located at the foot of the spoil pile, near Chervonohrad; 2 – a man-made reservoir at the foot of the spoil pile, near Chervonohrad; 3 – the Rata River, Silets village; 4 – the Western Bug River, Horodyshche village; 5 – the Rata River, Velyki Mosty town).

Model II characterizes the peculiarities of the temporal (seasonal) dynamics of chemical elements concentration. The results of mathematical modelling are represented by the following equations:

$$Root_1 = 12.258\times Cu - 333.988\times Cd - 0.014\times Zn + 23.774\times Pb - 181.461\times Cr + 4.669\times Co - 0.091\times Mn + 5.227\times Ni - 15.494\times Sr + 4.961,\ l_1 = 39.11 \quad (5)$$

$$Root_2 = -5.127\times Cu - 289.622\times Cd + 0.594\times Zn + 139.702\times Pb + 399.521\times Cr - 94.009\times Co + 0.017\times Mn + 0.402\times Ni - 4.177\times Sr - 7.311,\ \lambda_2 = 16.52 \quad (6)$$

Where:

$Root_i$ – canonical discriminant functions, axes of the typological scheme of water bodies; Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – values of heavy metal concentrations in water; l_i – eigenvalues of vectors.

The values of the first discriminant function $Root_1$ explain 65. % of the total variance. They mainly depend on the concentration of Cr (correlation coefficient r=-0.83), Sr (r=-0.75) and Zn (r =-0.60). However, these chemical elements were mainly characterized by relatively low concentrations, and only the Zn content in the November variants of sites No. 1 and No. 2 exceeded the maximum permissible concentration. The minimum values of the

$Root_1$ discriminant function are characterized by the November variant of the sites, where relatively higher levels of Cr, Sr and Zn concentrations were observed in the water of sites No. 1-5. The maximum values of the $Root_1$ discriminant function are characteristic of the April variant of sites No. 1-5.

The values of the second discriminant function $Root_1$ explain an additional 27.7% of the total variance. They mainly depend on the Pb concentration (r=0.54). The minimum values of the discriminant function $Root_2$ are typical for the April variant of sites No. 1-5, where the average value of the total water pollution index by 9 chemical elements has the maximum value (Z_c=1111.3). The maximum values of the $Root_2$ discriminant function are typical for the June version of sites No. 1-5, where the average total water pollution index has a minimum value (Z= 29.2). The most distant in the space of discriminant functions are the June and November variants (Mahalanobis squared distance D_M^2 = 251.6 Squared Mahalanobis Distances), as well as the April and November variants (D_M^2=251.4). The variants April and February (D_M^2=40.1) are the least distant in the space of discriminant functions (see **Figure 4**). Thus, model II characterizes the temporal (seasonal) peculiarities of water pollution by heavy metals. The worst water quality indicators were observed in April 2023.

The analysis of the relation between the concentrations of heavy metals in the water of rivers and reservoirs of Male Polissia indicates a close relationship between many chemical elements. Thus, for the entire set of time variants of sites No. 1-5, the correlation coefficient for Mn and Ni concentrations is r=0.98, for Co and Cd – r=0.93, for Zn and Cr – r=0.72, for Pb and Co – r=0.64. The results of the principal component analysis based on the correlation matrix:

$$Factor_1=-0.349\times Cu - 0.502\times Cd - 0.160\times Zn - 0.299\times Pb + 0.017\times Cr - 0.470\times Co - 0.366\times Mn - 0.388\times Ni + 0.072\times Sr, l1=3.58; \quad (7)$$

$$Factor_2 = -0.095\times Cu - 0.162\times Cd - 0.525\times Zn + 0.078\times Pb - 0.627\times Cr - 0.179\times Co + 0.298\times Mn + 0.311\times Ni - 0.269\times Sr, l2=2.26; \quad (8)$$

$$Factor3 = 0.103\times Cu - 0.038\times Cd + 0.020\times Zn - 0.574\times Pb +0.120\times Cr - 0.219\times Co + 0.413\times Mn + 0.373\times Ni + 0.535\times Sr, l3=1.47. \quad (9)$$

Where:

$Factor_i$ – component coordinates, complex gradients of the environment; Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – standardized values of heavy metal concentrations in water; li – eigenvalues of the vectors.

3.3. Concentration of heavy metals in the water of rivers and reservoirs

The analysis of the characteristics of the eigenvalues of l_i shows that two principal components provide 64.9% of the total variance. The eigenvectors of the correlation matrix (7)-(9) enable the identification of combinations of environmental factors that determine the axes of maximum variation in the seasonal dynamics of chemical water pollution. The main regularity of the water quality of the sites (the first principal component of $Factor_1$) is the following structure of correlations between chemical elements (see **Figure 5**): with a decrease in the concentration of Cd (correlation coefficient r = 0.95), the concentrations of Co (r = 0.89), Ni (r = 0.73), Mn (r = 0.69), Cu (r = 0.66), Pb (r = 0.57) decrease.

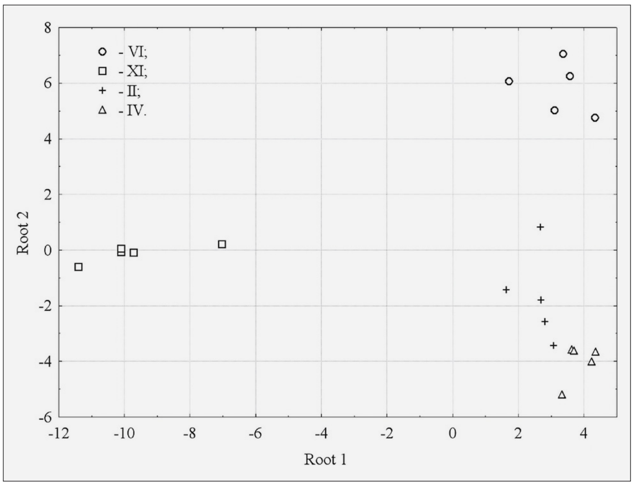

Figure 4. Typological scheme of reservoirs and rivers of Male Polissia: aspects of temporal dynamics (Conventions. Date of sampling for chemical analysis: VI – 07.06.2022; XI – 01.11.2022; II – 24.02.2023; IV – 25.04.2023).

The first principal component explains only 39.8% of the total variance, but its values clearly show the main regularity of the temporal dynamics of water quality in the studied sites. Thus, the low values of the first principal component $Factor_1$ are characterized by the April 1.IV and June 1.VI time variants of site 1, April 2.IV and November 2.XI time variants of site No. 2, which are characterized by high concentrations of Cd and other chemical elements. The maximum values of the first principal component are characterized by the November 3.XI and 5.XI time variants of sites No. 3 and No. 5, as well as the February 1-5.II time variants of all sites No. 1-5, which were characterized by low rates of water pollution by heavy metals.

The second axis of maximum variation, $Factor_2$, additionally explains 25.1% of the total variance in the data. The values of the $Factor_2$ function mainly depend on the content of Cr (correlation coefficient r=-0.94), Zn (r=-0.79), Ni (r=0.47), and Mn (r=0.45). Thus, the low values of the second principal component $Factor_2$ are characterized by the November 1-5.XI time variants of plots 1-5, which are characterized by increased concentrations of Cr and Zn. The maximum values of the second principal component of $Factor_2$ are characterized by the April variants 1.IV and 2.IV of plots 1 and 2.

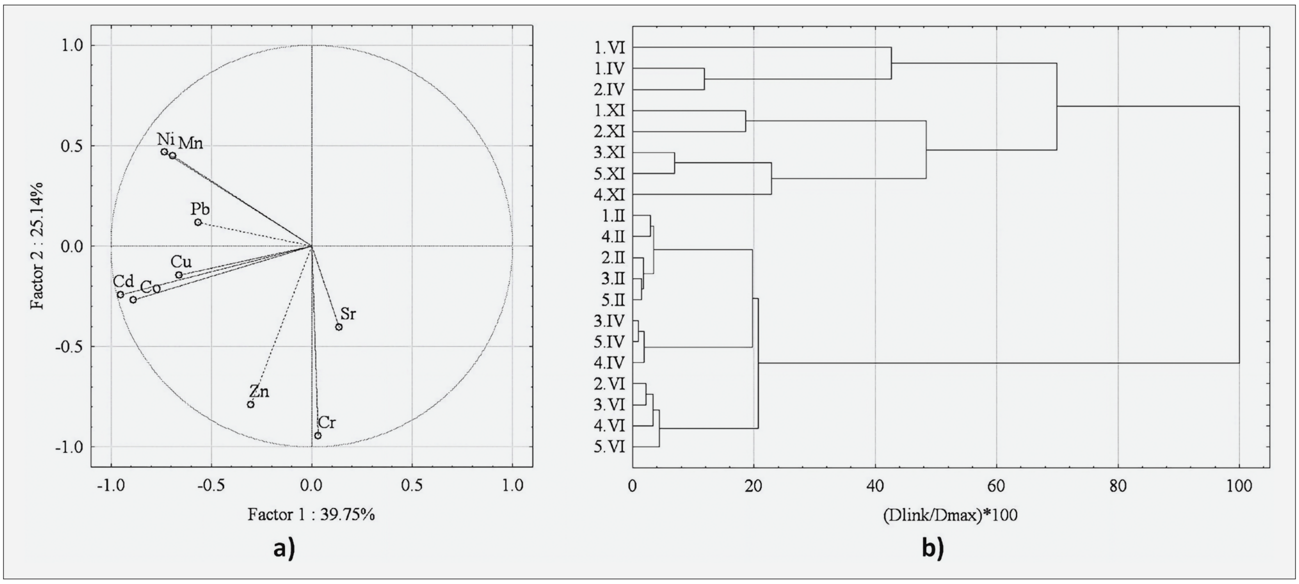

Figure 5. Results of the analysis of the main components of heavy metal content in water: spatial and temporal aspects: a) system of relations between concentrations of chemical elements and complex environmental gradients; b) dendrogram of similarity of temporal variants of water bodies (Conventions: Factor1-2 – the main components, complex gradients of the environment; Arabic numerals indicate the numbers of plots, Roman numerals – the serial number of the month).

The third axis of maximum variation, $Factor_3$, additionally explains 16.3 % of the total variance of the data. The values of the $Factor_3$ function mainly depend on the content of Pb (correlation coefficient r=-0.70), to a certain extent Sr (r=0.65), Mn (r=0.50), and Ni (r=0.45). The low values of the third principal component of $Factor_3$ are characterized by June 1.VI time variant of site No. 1, which was characterized by increased Pb concentrations. The maximum values of the third principal component of $Factor_3$ are characterized by April 1.IV and 2.IV variants of sites No. 1 and No. 2, and the November 3.XI, 4.XI, and 5.XI variants of sites No. 3-5.

4. Discussion

The multidimensional ordination of temporal variants of sites on the axes of complex pollution gradients $Factor_{1-3}$ is primarily used to identify abnormal cases of exceeding the maximum permissible concentrations. For the classification of water bodies, we additionally used cluster analysis, which resulted in a dendrogram of similarity of temporal variants of sites. Based on the dendrogram of similarity, 2 groups and 6 subgroups of objects were identified (numbering of objects see **Table 1**):

1. Group of sites with high concentrations of heavy metals in water:

subgroup 1.1: 1.IV, 2.IV, 1.VI; (exceeding the maximum permissible concentration for Cd by 16-23 times, for Pb by 1.4-6.3 times, for Ni by 6.5-67.5 times, for Mn by 46-3267 times; the total water pollution level Z_c for 4 chemical elements (Cd, Pb, Co, Sr) belonging to the second hazard class has a maximum value of Z_c = 23.3);

subgroup 1.2: 1.XI, 2.XI; (exceeding the maximum permissible concentration for Cd by 14-20 times, for Zn – by 1.6-2.2 times; Z_c = 18.2);

2. A group of sites with relatively low concentrations of heavy metals in water:

subgroup 2.1: 1.II, 2.II, 3.II, 4.II, 5.II; (Cd concentration within the maximum permissible concentration, Zc=1.6);

subgroup 2.2: 3.IV, 4.IV, 5.IV; (exceeding the maximum permissible concentration for Cd by 2.0-3.0 times, for Pb by 1.2-1.3 times, for Mn by 1.2-83.5 times, for Ni by 0.9-1.7 times, Zc=3.7);

subgroup 2.3: 2.VI, 3.VI, 4.VI, 5.VI; (exceeding the maximum permissible concentration for Cd – by 1.0-3.0 times, for Pb – by 1.7-2.2 times, for Mn – by 1.9-25.3 times, Z_c = 3.5);

subgroup 2.4: 3.XI, 4.XI, 5.XI; (exceeding the maximum permissible concentration for Cd by 1.4-1.9 times, Z_c = 2.0).

The most distant in the hyperspace of complex gradients of the aquatic environment by the content of heavy metals are time variants 1.IV and 2.XI (Euclidean distance D_E = 7.85), 1.VI and 3.XI (D_E = 7.77), 1.VI and 5.XI (D_E = 7.39), 1.IV and 4.XI (D_E = 7.33).

Based on the correlation between the content of heavy metals and complex gradients of the aquatic environment, the following associations (groups) of chemical elements can be identified: I – Cu, Pb, Co, Cd; II – Mn, Ni; III – Zn, Cr, Sr. The most distant in the hyperspace of complex gradients of the aquatic environment are the chemical elements Cr and Ni (Euclidean distance D_E = 1.65), Cr and Mn (D_E = 1.64), Co and Sr (D_E = 1.51), Zn and Pb (D_E = 1.50), Cd and Sr (D_E = 1.50).

The above analysis of scientific literature sources allows us to state that in world practice there is a huge number of different studies on the state of ecosystems in mining regions. Such studies can be divided into separate blocks: study of environmental pollutants; study of geomechanical consequences of mining; impact of pollutants on living organisms and human organisms; establishment of species composition of biota in the zone of influence of coal mining; environmental monitoring. Establishment of the content of heavy metals in water bodies is a component of comprehensive environmental monitoring of the environment.

5. Conclusions

Water pollution in the water bodies of the Chervonograd Mining District with heavy metals during the year 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, Pb, compared to the maximum permissible concentration. The highest level of heavy metal pollution during the entire monitoring season was observed in the water bodies at the foot of the Mezhyrichanska mine spoil pile, which is located near the city of Chervonohrad. Among the river bodies, the worst water condition, in terms of heavy metal pollution, was found for the Rata River (Silets Village), which is located in the zone of influence of mining enterprises. The maximum excess of heavy metals in water in the seasonal dynamics at all sites was characterized by the April version of water bodies. Based on the similarity of chemical elements in terms of their distribution in water, the following associations (groups) were identified: I – Cu, Pb, Co, Cd; II – Mn, Ni; III – Zn, Cr, Sr.

Prediction of dynamic trends, protection and restoration of ecosystem components are impossible without taking into account their interrelationships with environmental conditions, including the level of chemical pollution of water. 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 environmental gradients, to predict the stability and possible changes in all ecosystem components due to environmental pollution.

6. References

Abraham, M.R. and Susan, T.B. (2017). Water contamination with heavy metals and trace elements from Kilembe copper mine and tailing sites in Western Uganda; implications for domestic water quality. Chemosphere, 169, 281-287. https://doi.org/10.1016/j.chemosphere.2016.11.077

Aggarwal, C.C. (2015). Data Mining: The Textbook. Springer International Publishing Switzerland, 746 p. https://doi.org/10.1007/978-3-319-14142-8

Bhardwaj, S., Soni, R., Gupta, S.K. and Shukla, D.P. (2020). Mercury, arsenic, lead and cadmium in waters of the Singrauli coal mining and power plants industrial zone, Central East India. Environmental Monitoring and Assessment, 192, 251. https://doi.org/10.1007/s10661-020-8225-2

Bogolyubov, V.M., Klymenko, M.O., Mokin, V.B. and et al. (2018). Environmental monitoring: a textbook. Edition 2, revised and supplemented, Kyiv, NUBiPU, 435 p.

Bosak, P., Popovych, V., Stepova, K. and Marutyak, S. (2020). Features of seasonal dynamics of hazardous constituents in wastewater from colliery spoil heaps of Novovolynsk mining area. News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences, 5, 443, 39-46. https://doi.org/10.32014/2020.2518-170X.102

Cobbina, S.J., Myilla, M. and Michael, K. (2013). Small scale gold mining and heavy metal pollution: Assessment of drinking water sources in Datuku in the Talensi-Nabdam District. International Journal of Scientific & Technology Research, 2, 1, 96-100.

Hadzi, G.Y., Essumang, D.K. and Ayoko, G.A. (2018). Assessment of contamination and health risk of heavy metals in selected water bodies around gold mining areas in Ghana. Environmental Monitoring and Assessment, 190, 406. https://doi.org/10.1007/s10661-018-6750-z

Igwe, E.O., Ede, C.O., Nnabo, P.N. and Ukpai, S.N. (2021). Impact of heavy metals dispersion on water supplies around Oshiri and Ishiagu mine districts of Southern Benue Trough, Nigeria. Modeling Earth Systems and Environment, 7, 2015-2030. https://doi.org/10.1007/s40808-020-00950-3

Jara, C., Gaete, H., Lobos, G. and Hidalgo M.E. (2014). Oxidative stress in the mollusk Echinolittorina peruviana (Gasteropoda: Littorinidae, Lamarck, 1822) and trace metals in coastal sectors with mining activity. Ecotoxicology 23, 1099-1108. https://doi.org/10.1007/s10646-014-1253-3

Jiménez-Oyola, S., Chavez, E., García-Martínez, M.J., Ortega, M.F., Bolonio, D., Guzmán-Martínez, F., García-Garizabal I. and Romero, P. (2021). Probabilistic multi-pathway human health risk assessment due to heavy metal (loid) s in a traditional gold mining area in Ecuador. Ecotoxicology and Environmental Safety, 224, 112629. https://doi.org/10.1016/j.ecoenv.2021.112629

Jonjev, M., Miletić, Z., Pavlović, D., Matić, M., Čakmak, D., Mitrović, M. and Pavlović, P. (2024). Health risk assessment of potentially toxic elements in the riparian zone of the Sava River (southeastern Europe): effects of high and low water events. Environmental Sciences Europe, 36, 133. https://doi.org/10.1186/s12302-024-00952-3

Kantardzic, M. (2020). Data Mining. Concepts, Models, Methods, and Algorithms. 3rd ed. Wiley: IEEE press, 639 p.

Kapoor, D. and Singh, M.P. (2021). 10 - Heavy metal contamination in water and its possible sources. Heavy Metals in the Environment, Impact, Assessment and Remediation. 179-189. https://doi.org/10.1016/B978-0-12-821656-9.00010-9

Khilchevskyi, V.K. and Zabokrytska, M.R. (2022). Features of normative assessment of water quality of water bodies for recreational purposes in Ukraine. Hydrology, Hydrochemistry and Hydroecology, 1, 638, 40-53. https://doi.org/10.17721/2306-5680.2022.1.4.

Lermi, A. and Sunkari, E.D. (2023). Pollution and probabilistic human health risk assessment of potentially toxic elements in the soil-water-plant system in the Bolkar mining district, Niğde, south-central Turkey. Environmental Science and Pollution Research, 30, 25080-25092. https://doi.org/10.1007/s11356-021-15398-w

Modoi, O.C., Roba, C., Török, Z. and Ozunu, A. (2014). Environmental risks due to heavy metal pollution of water resulted from mining wastes in NW Romania. Environmental Engineering and Management Journal, 13, 9, 2325-2336

Moldovan, A., Török, A.I., Kovacs, E., Cadar, O., Mirea, I. C. and Micle, V. (2022). Metal contents and pollution indices assessment of surface water, soil, and sediment from the Arieș River Basin Mining Area, Romania. Sustainability, 14, 13, 8024. https://doi.org/10.3390/su14138024

Nanda, S.P., Panda, B.P., Panigrahi, K.C.S. and Pradhan, A. (2024). Ecological risk assessment of heavy metals contaminated mining sites of eastern india using soil and moss. Environmental Monitoring and Assessment, 196, 1029. https://doi.org/10.1007/s10661-024-13166-0

Nersesyan, A., Mišík, M., Cherkas, A., Serhiyenko, V., Staudinger, M., Holota, S., Yatskevych, O., Melnyk, S., Holzmann, K. and Knasmüller, S. (2021). Use of micronucleus experiments for the detection of human cancer risks: a brief overview. Proceeding of the Shevchenko Scientific Society. Medical Sciences, 65, 2, 50-58. https://doi.org/10.25040/ntsh2021.02.05

Obasi, P.N. and Akudinobi, B.B. (2020). Potential health risk and levels of heavy metals in water resources of lead–zinc mining communities of Abakaliki, southeast Nigeria. Applied Water Science, 10, 184, 1-23. https://doi.org/10.1007/s13201-020-01233-z

Ojekunle, O.Z., Awolokun, G.S., Olatunde, A.K., Adegoke, K.A., Maxakato, N.W., Balogun, M.A. and Afolabi, T.A. (2023). Environmental and health hazards of heavy metal concentrations in Ota and Agbara industrial areas, Ogun State, Nigeria. Environmental Earth Sciences, 82, 79. https://doi.org/10.1007/s12665-022-10742-w

Othmani, M.A., Souissi, F., Durães, N., Abdelkader, M. and Ferreira da Silva, E. (2015). Assessment of metal pollution in a former mining area in the NW Tunisia: spatial distribution and fraction of Cd, Pb and Zn in soil. Environmental Monitoring and Assessment, 187, 523. https://doi.org/10.1007/s10661-015-4734-9

Petlovanyi, M., Medianyk, V., Sai, K., Malashkevych, D. and Popovych, V. (2021). Geomechanical substantiation of the parameters for coal auger mining in the protecting pillars of mine workings during thin seams development. ARPN Journal of Engineering and Applied Sciences, 16, 15, 1572-1582.

Petlovanyi, M., Sai, K., Malashkevych, D., Popovych, V. and Khorolskyi, A. (2022). Influence of waste rock dump placement on the geomechanical state of underground mine workings. 4th International Conference on Essays of Mining Science and Practice, RMGET, 187693. https://doi.org/10.1088/1755-1315/1156/1/012007

Popovych, V. and Gapalo, A. (2021a). Monitoring of ground forest fire impact on heavy metals content in edafic horizons. Journal of Ecological Engineering, 22, 5, 96-103. https://doi.org/10.12911/22998993/135872

Popovych, V. and Voloshchyshyn, A. (2019). Features of temperature and humidity conditions of extinguishing waste heaps of coal mines in spring. News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences, 4, 436, 230-237. https://doi.org/10.32014/2019.2518-170X.118

Popovych, V., Voloshchyshyn, A., Bosak, P. and Popovych, N. (2021b). Waste heaps in the urban environment as negative factors of urbanization. IOP Conference Series: Earth and Environmental Science, 915, 012001. https://doi:10.1088/1755-1315/915/1/012001

Prasad, B., Kumari, P., Bano, S. and Kumari, S. (2014). Ground water quality evaluation near mining area and development of heavy metal pollution index. Applied Water Science, 4, 11-17. https://doi.org/10.1007/s13201-013-0126-x

Punia, A. (2021). Role of temperature, wind, and precipitation in heavy metal contamination at copper mines: a review. Environmental Science and Pollution Research, 28, 4056-4072. https://doi.org/10.1007/s11356-020-11580-8

Razo, I., Carrizales, L., Castro, J., Díaz-Barriga, F. and Monroy, M. (2004). Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. Water, Air, and Soil Pollution, 152, 129-152. https://doi.org/10.1023/B:WATE.0000015350.14520.c1

Sankhla, M.S., Kumari, M., Nandan, M., Kumar, R. and Agrawal, P. (2016). Heavy metals contamination in water and their hazardous effect on human health-a review. International Journal of Current Microbiology and Applied Sciences, 5, 10, 759-766. https://dx.doi.org/10.2139/ssrn.3428216

Serhiyenko, V. and Serhiyenko, A. (2022a). Ezetimibe and diabetes mellitus: a new strategy for lowering cholesterol. International Journal of Endocrinology (Ukraine), 18, 5, 302-314. https://doi.org/10.22141/2224-0721.18.5.2022.1190

Serhiyenko, V. and Serhiyenko, O. (2021). Diabetes mellitus and arterial hypertension. International Journal of Endocrinology (Ukraine), 17, 2, 175-188. https://doi.org/10.22141/2224-0721.17.2.2021.230573

Serhiyenko, V., Holzmann, K., Holota, S., Derkach, Z., Nersesyan, A., Melnyk, S., Chernysh, O., Yatskevych, O., Mišík, M., Bubalo, V., Strilbytska, O., Vatseba, B., Lushchak, O., Knasmüller, S. and Cherkas, A. (2022b). An exploratory study of physiological and biochemical parameters to identify simple, robust and relevant biomarkers for therapeutic interventions for PTSD: study rationale, key elements of design and a context of war in Ukraine. Proceeding of the Shevchenko Scientific Society. Medical Sciences, 69, 2. https://doi.org/10.25040/ntsh2022.02.14

Singh, A., Sharma, A., Verma, R.K., Chopade, R.L., Pandit, P.P., Nagar, V., Aseri, V., Choudhary, K.S., Awasthi, G., Awasthi K.K. and Sankhla, M.S. (2022). Heavy metal contamination of water and their toxic effect on living organisms. The Toxicity of Environmental Pollutants. IntechOpen. https://doi.org/10.5772/intechopen.105075

Skrobala, V., Popovych, V. and Pinder, V. (2020). Ecological patterns for vegetation cover formation in the mining waste dumps of the Lviv-Volyn coal basin. Mining of Mineral Deposits, 14, 2, 119-127. https://doi.org/10.33271/mining14.02.119

Skrobala, V., Popovych, V., Tyndyk, O. and Voloshchyshyn, A. (2022). Chemical pollution peculiarities of the Nadiya mine rock dumps in the Chervonohrad Mining District, Ukraine. Mining of Mineral Deposits, 16, 4, 71-79. https://doi.org/10.33271/mining16.04.071

Tiwari, A.K., Singh, P.K. and Mahato, M.K. (2017). Assessment of metal contamination in the mine water of the West Bokaro Coalfield, India. Mine Water and the Environment, 36, 532-541 (2017). https://doi.org/10.1007/s10230-017-0440-x

Zhang, Q. and Wang, C. (2020). Natural and human factors affect the distribution of soil heavy metal pollution: a review. Water, Air, & Soil Pollution, 231, 350. https://doi.org/10.1007/s11270-020-04728-2

SAŽETAK

Modeliranje sezonske dinamike onečišćenja vodnih tijela s teškim metalima unutar rudarskoga područja

Odlagališta otpada iz rudnika ugljena zagađuju okoliš spontanim izgaranjem otpada i onečišćenom otpadnom vodom koja curi u podzemne i površinske vodonosnike. Zajedno sa zagađenjima u vodu dospijeva velika koncentracija teških metala. Predmet su ovoga istraživanja vodna tijela u zoni utjecaja Červonogradskoga rudarskog okruga, dijela Ljvivsko-volinskoga ugljenog bazena (Ukrajina). Razina kemijske kontaminacije vode antropogenih rezervoara u rudarskome okrugu mjerila se pokazateljima razvijenim na temelju geokemijskih i higijenskih istraživanja okoliša. U istraživanju su korištene metode statističke obrade parametara kemijskoga onečišćenja vode i tla, korelacijska analiza, metode rudarenja podataka, procjena sličnosti ekotopa i grupiranje kemijskih elemenata na temelju klasterske analize te višedimenzionalna ordinacija ekotopa u prostoru geokemijskih indikatora, a grafička vizualizacija temeljena je na metodi *Principle Component Analysis*. Za područje Male Polisja karakteristična je znatna heterogenost kemijskoga onečišćenja rijeka i akumulacije teških metala tijekom sezone. Glavni razlog pogoršanja ekološkoga stanja vodnih tijela povezan je s povećanjem sadržaja Mn, Ni, Cd, Pb u odnosu na maksimalno dopuštene koncentracije. Najviša razina onečišćenja tijekom cijele sezone praćenja zabilježena je u vodnim tijelima u podnožju odlagališta rudnika Mežiričanska, u blizini grada Červonograda. Na temelju korelacije između sadržaja teških metala i gradijenta složenosti vodnoga okoliša identificirane su sljedeće skupine kemijskih elemenata: I. – Cu, Pb, Co, Cd; II. – Mn, Ni; III. – Zn, Cr, Sr. Višedimenzionalni raspored vodnih tijela na osi geokemijskoga gradijenta složenosti okoliša odražava sezonsku dinamiku onečišćenja vode i njezinih prostornih značajki. Praktična važnost dobivenih rezultata leži u činjenici da su predviđanje dinamičkih trendova, zaštita i obnova komponenti ekosustava nemogući bez uzimanja u obzir njihovih odnosa s uvjetima u okolišu, a posebno s razinom kemijskoga onečišćenja vode.

Ključne riječi:
teški metali, kemijsko onečišćenje, ekotop, gradijent složenosti okoliša, višedimenzionalna percepcija ekotopa, matematičko modeliranje, sigurnost okoliša

Author's contribution

Vasyl Popovych (Dr. Sci. (Engin.), Professor, Vice-rector for research Lviv State University of Life Safety) proposed and defined the idea of the scientific article, led the field research, provided suggestions for interpreting the results and graphical presentation of the data, and developed an algorithm for measuring the content of heavy metals in water bodies within mining areas. **Viktor Skrobala** (PhD (Agricul.), Associate Professor at the Department of Landscape Architecture, Gardening and Urban Ecology, Ukrainian National Forestry University) data collection and modelling, participation in field research and analysis, mathematical modelling of the typological scheme of water bodies, graphical representation of data. **Oleh Tyndyk** (Postgraduate student of the Department of environmental safety Lviv State University of Life Safety) analysed the parametric data, prepared the modelling results and the presentation of the article. **Mykhailo Petlovanyi** (PhD (Engin.), Associate Professor at the Department of mining engineering and education, National Technical University "Dnipro Polytechnic"), **Kateryna Sai** (PhD (Engin.), Associate Professor at the Department of mining engineering and education, National Technical University "Dnipro Polytechnic") and also **Natalya Popovych** (PhD (Engin.), Lviv Department of the National Ecological Center of Ukraine) evaluated and edited the manuscript and analysed the results of the analysis of the main components of heavy metals in water. **Roman Konanets** (PhD, Deputy head at the Department of fire tactics and rescue operations Lviv State University of Life Safety) participated in the field research, provided funding for the fieldwork, and contributed to the discussion and formulation of the findings. **Bohdan Ilkiv** (Specialist, International cooperation department Lviv State University of Life Safety) assisted with the modelling analysis and participated in the discussion and formulation of conclusions.
All authors have read and approved the final version of the manuscript.