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Heavy metals distribution in water and soil of the coastal zone of the Styr River (Ukraine) and its tributaries

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ABSTRACT

Investigation of the peculiarities of chemical contamination of water and soil in the coastal zone of the river Styr and its tributaries in relation to the distance from the source of pollution and the type of landscape, analysis of the general trends in the distribution of chemical elements in comparison with the control site. Statistical processing of parameters of chemical contamination of water and soil; data mining methods; correlation analysis; assessment of ecotope similarity and grouping of chemical elements based on cluster analysis; multidimensional ordination of ecotopes in the space of geochemical parameters based on Principal Component Analysis. Chemical contamination of water and soil in the coastal zone of the Styr River and its tributaries is characterised by significant heterogeneity. The main feature of the increasing intensity of anthropogenic load on the aquatic environment is associated with an increase of Cu, Zn, Pb, Mn content compared to the natural background. The intensity of soil pollution in the coastal zone of the Styr River and its tributaries mainly depends on the presence of Cu, Cd and Ni. The analysis of the relationship between chemical elements concentrations indicates a strong dependence between many parameters. Based on the similarity of chemical elements in terms of their distribution in the water of the river Styr and its tributaries, 4 associations (groups) were identified: I – Cu, Mn; II – Zn, Pb; III – Cd, Cr, Sr; IV – Co, Ni. For the soils in the coastal zone, 3 associations (groups) of chemical elements were identified: I – Cu, Cd; II – Zn, Mn; III – Cr, Co, Ni, Pb. Three groups of sites of the Styr River and its tributaries were identified according to the pollution rate of water and soils of the coastal zone with heavy metals. The multidimensional ordination of the ecotopes of the Styr River and its tributaries on the axes of complex geochemical environmental gradients reflects the gradients of water and soil pollution in the coastal zone compared to the control areas. Geochemical information visualisation based on two-dimensional diagrams with chemical element concentrations or complex environmental gradients as axes can be used to predict the dynamics of ecosystem components as a result of changes in chemical pollution. The practical relevance of the obtained results is that forecasting of dynamic trends, protection and restoration of ecosystem components is impossible without taking into account their interrelationships with environmental conditions, including chemical 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 the complex gradients of the environment of the Styr river and its tributaries, to predict the stability and possible changes in vegetation, fauna and microflora caused by environmental pollution.

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

INTRODUCTION

Excessive content of heavy metals in the river water of large cities leads to irreversible processes in the hydrographic networks throughout the country (Stepova et al., 2020; Konanets and Stepova, 2024). The ingress of heavy metals into aquatic organisms results in a halt to their development and growth, and ultimately in their death (Sysa et al., 2019). When heavy metals enter the human body, they cause dangerous chronic diseases (Serhiyenko et al., 2021; Serhiyenko et al., 2022a). Chronic diseases can be accompanied by hypertension and the development of diabetes mellitus (Nersesyan et al., 2021; Serhiyenko et al., 2022b). Significant research on water quality is being conducted globally, and various models of water management are being established. Some of them will be discussed below. In particular, the study (Mukherjee et al., 2024) focused on the analysis of the quality, treatment and economic feasibility of the Nehora River (India). Pearson correlations showed a positive correlation (0.629) between temperature and total solids (TS), while a negative correlation (-0.23) for dissolved oxygen with other parameters. The study (Adeoti et al., 2024) presents the Predictive Iterative Sustainability Model (PISM), a specialised framework developed to improve the assessment of water infrastructure sustainability in Nigeria.

Surface water samples were collected from 27 sites in the Upper Kebir Sub-basin [North-Eastern (NE) Algeria] in 2020-2021 during both the wet and dry seasons. The analysis revealed that the basin was largely polluted and showed significant seasonal and spatial variations in water quality, which is largely dependent on climatic conditions and human activities (Allia et al., 2024). The scientific paper (Mendivil-García et al., 2024) reported on two-monthly water monitoring conducted from 2013 to 2020 for 23 parameters at 23 sampling sites. This resulted in nine clusters for the rainy and dry seasons, which reduced approximately 50% of the sampling sites and created an optimised network of 11 sampling sites.

The study (Prajapati et al., 2024) presents the Soil and water assessment tool (SWAT), which was used to predict hydrological runoff in the Sunkoshi River Basin (SRB) based on daily rainfall and temperature data for 36 years. It was found (Tran, 2024) that climate change has a significant impact on the irrigation water needs of coffee plants in the Central Highlands of Vietnam. Five CMIP6 models and a method of bias correction and spatial disaggregation were used to improve the resolution for future data (precipitation and temperature).

The river Styr, a major axis of the green zone of the city of Lutsk (Ukraine), forms the main hydrographic network of the investigated area. The river is 11.2 km long within the city of Lutsk. The river valley is predominantly of a well-defined, trapezoidal floodplain type. The riverbed is rather winding, with numerous oxbows and meanders 2–10 m wide. Depths on the riffles vary from 0.4 to 0.6 m, and on the rifts from 0.1 to 0.3 m. Current velocities in low water are 0.2–0.5, increasing during floods to 1.1–2.5 m/s. The river is fed by limestone and marl and chalk deposits of the Upper Cretaceous and Tertiary systems. This determines the hydrocarbonate-calcium composition. The water in the river is colourless and clear.

MATERIALS AND METHODS

The ecological features of water and soil pollution in the coastal zone of the river Styr and its tributaries were examined using data mining methods (Skrobala et al., 2020). Data mining is the process of analytical research of large amounts of information in order to identify certain patterns and dependencies between variables (hidden knowledge) that can be applied to new data sets and to reliably predict processes and phenomena. Unlike traditional statistical methods, data mining procedures are based on the 'black box' principle and are more focused on the practical use of the results (Skrobala et al., 2022). The research included three main stages: studying the structure of the mutual arrangement of elementary sites in the multidimensional space of heavy metal content features, mathematical modelling of the structure, and verification of the mathematical model.

The analysis of literary sources showed that no statistical processing of heavy metals using cluster analysis was found in the Styr River. This technique makes it possible to distribute heavy metals by pollution groups.

The basis of the environmental information is the data on water and soil contamination of the coastal zone of the Styr River and its tributaries at 8 sites with 9 heavy metals: Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr. The mathematical modelling was carried out by establishing systematic relationships between the concentrations of heavy metals. Each site can be represented as a point in a multidimensional feature space, the coordinates of which correspond to the values of chemical element concentrations. In this case, the similarity of the sites in terms of a set of environmental parameters of environmental pollution can be determined based on the distances between the points. The essence of the subsequent mathematical procedure is to identify the axes of maximum variation, determine their number, and estimate the contribution of each environmental parameter to the variation based on principal component analysis. The mathematical model was tested based on a comparative assessment of the position of the sites on the axes of maximum variation (multidimensional ordination) with the results of research on soil, vegetation cover of the coastal zone and organoleptic indicators of water (Skrobala et al., 2020).

Within the regional centre - the city of Lutsk, the Sapalaivka, Omelyanyk and Zhyduvka rivers flow into the main river of the basin, and the Chornohuzka river flows into its southern outskirts (Shepeliuk, 2019). As a result of drainage reclamation works, a large number of main canals have been constructed in the river catchment area, and some small rivers and streams have been converted into canals. Since the river flows in the impact zone of the Lviv-Volyn coal basin, this is an additional factor in the deterioration of water quality due to mine operations (Petlovanyi et al., 2021).

The city of Lutsk is located in the north-west of Ukraine. From west to east, from north to south, it stretches for 10 and 15 km, respectively. The city is located in the polissya forest and forest-steppe physiogeographical zones. The climate of the city of Lutsk is moderately continental, with mild winters and warm summers. The average annual air temperature is +7.4 °C, the lowest in January (-4.9 °C), the highest in July (+18.0 °C). On average, 560 mm of atmospheric precipitation falls in Lutsk per year, the least in March, the most in July. The average annual relative humidity is 78%, the lowest in May (64%), the highest in December (89%) (Zabokrytska et al. 2016).

Surface runoff from the city changes the quality of surface water. Comparison of surface runoff and drainage shows that the daily runoff into the Styr River from the city area increases by 6–11 times with the average maximum amount of precipitation. Surface runoff carries pollutants into the rivers of Lutsk, which partially contributes to the pollution of their waters. The level of water pollution in the Styr River also depends to a large extent on the distance to the probable source of pollution. Considering this, the following 8 sites were selected to study (Fig. 1).

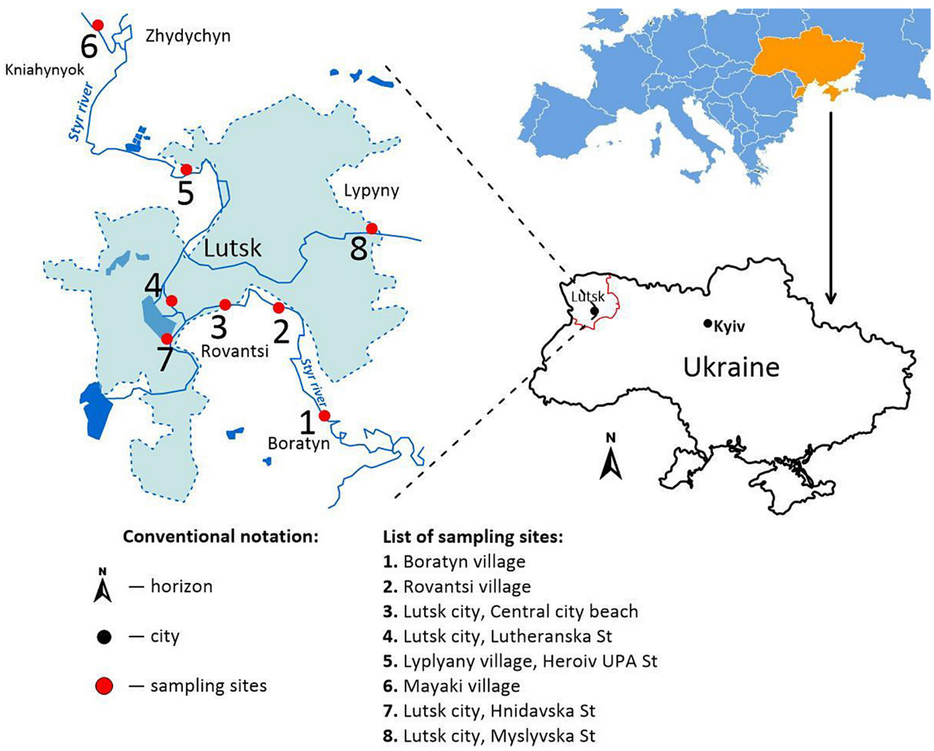

Figure 1. Schematic representation of the research sites

Site 1 is located 9 km from the city of Lutsk, on the outskirts of Boratyn village, Lutsk district (geographical coordinates 50.7089822° N; 25.3747323° E). The intensity of anthropogenic load is low. A potential source of pollution may be household discharges from the territory of Pidhaitsi village and Boratyn village, adjacent to the river Styr. The site is located 400 m from the international motorway M19, which is an integral part of the motorway route E 85. The width of the Styr River in this section is 8–10 m. The water is relatively clean, the current speed is low. According to the organoleptic characteristics of the water, this experimental site can be classified as ‘control’.

Site 2 is located near the intersection of Hlushets Street and Dubnivska Street in Rovantsi village, 3 km from Lutsk city (geographical coordinates 50.7366998° N; 25.3581113° E). The width of the Styr River in this section is 12–14 m, and the current velocity is low. Both banks are densely covered with woody and herbaceous vegetation. In some places, there are destructions of soil cover caused by natural recreation, as well as shifts of the coastline caused by water erosion. Fragments of tree branches are often found in the water.

Site No. 3 is the central city beach, an integral part of the recreational area of the Lesia Ukrainka Park of Culture and Recreation in Lutsk (geographical coordinates 50.7380890° N; 25.3336791° E). The territory is located between the old and new centre of Lutsk and is a traditional place of recreation and leisure for local residents and visitors. Potential sources of pollution of the ecosystem of the Styr River may include the Lutsk Zoo’s wastewater, the beach area and pier, the Lutsk Venice complex with a water cafe and boat rental along the park’s canals, commercial buildings (summer playgrounds, shopping stalls), and small illegal landfills. The width of the river in this section is 12-15 m, and the flow rate is quite high. There is slight waterlogging in the tree plantations along the shoreline.

Site No. 4–9 Lutheranska str., Lutsk, near the territory of the State Historical and Cultural Reserve ‘Old Lutsk’. The width of the riverbed is 9–11 m, and the current speed is low. There is a viewing bridge near the sampling site. The site is often used by urban residents for recreational purposes. The distance to the street carriageway is 12 m, and the intensity of traffic is low. On the shoreline, there are places of damage to vegetation and soil cover caused by spontaneous trampling, minor contamination with household waste, and partial waterlogging.

Site No. 5 – Geroyev UPA street, Lyplyany village (geographical coordinates 50.7719745° N, 25.3189323° E), is located outside the city of Lutsk.

The main anthropogenic source of pollution of the Styr River is the sewage treatment plant of the Lutskvodokanal Municipal Enterprise, which receives wastewater from both the city and a number of united territorial communities. In particular, in 2023, it was planned to remove up to 200,000 tonnes of sludge from the treatment plant’s sludge sites, which poses an environmental hazard and is a source of unpleasant odour, especially in summer. Private household wastewater poses a potential problem in terms of impact on the sanitary condition of the river Styr. At the sampling site, the width of the riverbed is 12–13 m, and the current velocity is low.

Site 6 – Knyahynynok village, Lutsk district (geographical coordinates 50.8069892° N; 25.2842275° E), 8 km from the city boundaries, in the impact area of the Lutsk-Kovel motorway. The width of the Styr river in this section is 11–12 m. The water is rather muddy, yellowish-green and has a low flow rate. The main potential anthropogenic source of river pollution, like in the previous section, is the treatment facilities of the Lutskvodokanal Municipal Enterprise, which receive wastewater from the city as well as from a number of neighbouring united territorial communities, including the village of Kniahynynok. Field surveys revealed areas of vegetation and soil cover degradation, shoreline shifts caused by water erosion, and waterlogging processes.

Site No. 7 – Hnidavska Street, Lutsk (geographical coordinates 50.729680° N, 25.310865° E), general zoological reserve of local value ‘Hnidavske boloto’, located between the central part of the city, the neighbourhood ‘Hnidava’ and Rovantsi village. The reserve is located in the floodplain of the Styr River.

Hydrologically, the bog is connected to the river Styr by a system of canals (Zabokrytska et al. 2016). Peat-bog soils were formed on the territory of the reserve, which contain a large amount of humus and are quite fertile. The peat is 2–6 metres thick. Illegal burning of dry grass occurs almost every year, which only exacerbates the transformation of the research area (Besarabchuk et al. 2017). In 2021, an unauthorised domestic sewage system was discovered here, with sewage flowing directly into the reserve’s water body.

Site No. 8 - Myslyvska Street, Lutsk (geographical coordinates 50.756437° N, 25.392037° E)

– Teremnivski ponds is a hydrological natural monument of local value located within the eastern part of the city. The reservoir was created by damming the Sapalaivka river, a tributary of the Styr River; its area is 6.3 ha and depth is 1.0 m. The shores are clean, sometimes with single trees. Cases of car washing have been reported, resulting in the pollution of the water body with oil products. According to microbiological indicators, the water body is often unsuitable for swimming. The main source of pollution of the Sapalaivka river and Teremnivske ponds is untreated surface runoff from the urban area.

Note that through natural channels from the river Styr combines the Hnidavske marsh massif (Site No. 7) and the Teremnivski ponds (Site No. 8), which requires detailed hydrological studies in connection with its specific ecosystem.

The category of heavy metals includes metals with a specific gravity higher than that of iron. The most common are lead, copper, zinc, and the most dangerous are mercury, lead, cadmium, and arsenic. Heavy metals have a mutagenic and toxic effect, significantly reducing the intensity of biochemical processes in water bodies (Yurasov et al., 2011). The content of chemicals in the water of water bodies or its parts should not exceed the maximum permissible concentrations (MPC). The sanitary and hygienic MPC of a substance (Yurasov et al., 2011) in water is the maximum concentration that does not directly or indirectly affect the health of the current and future generations of humans when exposed to the body and does not affect the sanitary conditions of water use. Therefore, to assess the level of abnormality of a chemical element, a concentration factor (K_c) is determined:

$$K_c = C / MPC \quad (1)$$

where: C is the real content of a certain chemical element in water, mg/dm^3; MPC is the maximum permissible concentration of a chemical element, mg/dm^3.

RESULTS AND DISCUSSION

For most heavy metals (Cu, Zn, Cr, Co, Ni, Sr), their content in the water of the Styr River and its tributaries does not exceed the maximum permissible concentrations (Table 1). The concentration of Pb in the water slightly exceeds the MPC

Table 1. Water pollution levels in the Styr River and its tributaries

Site No.*	Heavy metal content in water								
	Cu	Cd	Zn	Pb	Cr	Co	Mn	Ni	Sr
Concentration of heavy metals, mg/dm^3									
1	0.002	0.003	0.006	0.025	0.004	0.010	0.036	0.036	0.180
2	0.002	0.002	0.006	0.029	0.005	0.010	0.219	0.032	0.230
3	0.002	0.002	0.004	0.027	0.002	0.009	0.050	0.031	0.109
4	0.002	0.002	0.007	0.026	0.004	0.008	0.046	0.020	0.320
5	0.003	0.002	0.015	0.033	0.001	0.012	0.097	0.031	0.242
6	0.003	0.003	0.009	0.032	0.003	0.012	0.022	0.031	0.245
7	0.012	0.003	0.019	0.032	0.003	0.008	0.319	0.027	0.230
8	0.007	0.003	0.006	0.032	0.002	0.008	0.308	0.026	0.260
MPC, mg/dm^3	1.0	0.001	1.0	0.03	0.05	0.1	0.1	0.1	7.0
Exceedance of the maximum permissible concentration, multiplicity									
1	0.002	3.0	0.006	0.83	0.08	0.10	0.36	0.36	0.026
2	0.002	2.0	0.006	0.97	0.10	0.10	2.19	0.32	0.033
3	0.002	2.0	0.004	0.90	0.04	0.09	0.50	0.31	0.016
4	0.002	2.0	0.007	0.87	0.08	0.08	0.46	0.20	0.046
5	0.003	1.6	0.015	1.10	0.02	0.12	0.97	0.31	0.035
6	0.003	3.0	0.009	1.07	0.06	0.12	0.22	0.31	0.035
7	0.012	2.7	0.019	1.07	0.06	0.08	3.19	0.27	0.033
8	0.007	2.5	0.006	1.07	0.04	0.08	3.08	0.26	0.037

Note: * Numerical numbering of the sites: 1 – Boratyn village; 2 – Rovantsi village; 3 – central city beach, Lutsk; 4 – 9 Lutheranska str., Lutsk; 5 – . Lyplyany village; 6 – Knyahynynok village; 7 – Hnidavske marsh, Lutsk; 8 – Teremnivski ponds, Lutsk.

at sites 5–8 (5 – s. Lyplyany; 6 – Knyahynynok village; 7 – Hnidavske marsh, Lutsk; 8 – Teremnivski ponds, Lutsk). At all sites, the MPCs are exceeded by 1.6–3.0 times for Cd. High values of the Mn concentration coefficient were registered in Rovantsi village, Hnidavske marsh and Teremnivski ponds (sites 2, 7 and 8).

Exceeding the MPCs for heavy metals in the soil results in a decrease in the productivity of urban and agricultural phytocoenoses and a decrease in their buffering properties (Shepeliuk, 2019). It should be noted that investigations of temperature effects on soils have shown that high temperatures lead to increased migration of heavy metals (Popovych and Gapalo, 2021).

The concentration of heavy metals in the soils of the coastal zone of the river Styr and its tributaries is also characterised by great heterogeneity. This is proved by the variability of the minimum, maximum and average concentrations and their comparative analysis with the control site (Table 2). Comparing the maximum concentrations of chemical elements, we can conclude that there is a significant increase in the content of certain chemical elements.

Cadmium compounds are extremely toxic even in low concentrations, and therefore are classified as hazard class I. Exceedance of the maximum permissible concentration of cadmium in the soils of the coastal zone is observed in areas 7 (Hnidavske marsh) and 8 (Teremnivski ponds). Zinc is a heavy metal of the first hazard class. Under high humidity conditions, high migration of zinc in the soil is typical. Lead is also considered to be one of the most toxic chemical elements, even in small quantities, and belongs to the first hazard class. Zinc and lead contamination of the soils of the coastal zone of the river Styr and its tributaries is characterised by values below the maximum permissible concentration.

Copper is a chemical element that belongs to heavy metals of the second hazard class. It has low phytotoxicity, but is highly toxic to the human body. In case of excessive intake in humans and animals, it has carcinogenic effects and has a toxic effect on the heart, blood and other organs. The copper content in the soil exceeds the MPC at the site 7 (Hnidavske marsh). Nickel is a hazard class II element that can cause acute and chronic poisoning if it gets on the skin and into the respiratory system. In almost all areas, except Teremnivski ponds, its content exceeds the maximum permissible concentration. The content of chromium, cobalt and manganese in the soils of the

Table 2. Soil pollution in the coastal zone of the Styr River and its tributaries

Site No.*	Heavy metal content in water							
	Cu	Cd	Zn	Pb	Cr	Co	Mn	Ni
Concentration of heavy metals, mg/dm³								
1	0.560	0.900	2.210	8.401	1.500	3.235	134.194	10.077
2	0.770	0.930	4.380	9.605	1.620	3.513	245.980	10.056
3	0.720	0.760	4.390	8.524	1.580	3.207	255.260	10.434
4	0.750	0.680	5.250	9.640	1.582	3.086	267.360	11.827
5	0.630	0.230	6.040	9.595	1.600	2.800	205.970	6.806
6	0.500	0.800	5.850	9.304	0.990	2.583	153.490	5.959
7	3.640	3.100	4.950	4.640	0.650	0.200	177.300	6.670
8	0.460	3.430	5.800	7.420	0.380	0.170	210.000	3.420
MPC, mg/kg	3.00	3.00	23.00	32.00	6.00	5.00	1500.0	4.00
Exceedance of the maximum permissible concentration, multiplicity								
1	0.19	0.30	0.10	0.26	0.25	0.65	0.09	2.52
2	0.26	0.31	0.19	0.30	0.27	0.70	0.16	2.51
3	0.24	0.25	0.19	0.27	0.26	0.64	0.17	2.61
4	0.25	0.23	0.23	0.30	0.26	0.62	0.18	2.96
5	0.21	0.08	0.26	0.30	0.27	0.56	0.14	1.70
6	0.17	0.27	0.25	0.29	0.17	0.52	0.10	1.49
7	1.21	1.03	0.22	0.14	0.11	0.04	0.12	1.67
8	0.15	1.14	0.25	0.23	0.06	0.03	0.14	0.85

Note: * The numerical reference number of the sites is given in Table 1.

coastal zone of the river Styr and its tributaries is characterised by low values.

The location of the site relative to the source of pollution and the type of landscape (agricultural or urban) have a significant impact on the distribution of chemical elements. The similarity of locations in terms of chemical element concentrations was assessed using cluster analysis. The Ward's method was used, in which the minimum variance within clusters is optimised, resulting in clusters of approximately the same size. The Euclidean distances were used as a measure of differences. The main outcome of hierarchical cluster analysis is a dendrogram (Fig. 2–3). Based on the distribution of heavy metals in the water of the Styr River and its tributaries, the similarity of the sites was determined and the following groups were preliminarily identified (Fig. 2, b): I – 1 (Boratyn village), 6 (Knyahynynok village); II – 3 (central city beach, Lutsk), 4 (area of 9 Lutheranska Street, Lutsk), 5 (Lyplyany village); III – 2 (Rovantsi village), 7 (Hnidavske bog, Lutsk), 8 (Teremnivski ponds, Lutsk).

The principle of the similarity dendrogram construction can be explained by calculating group indicators – the sum of concentration

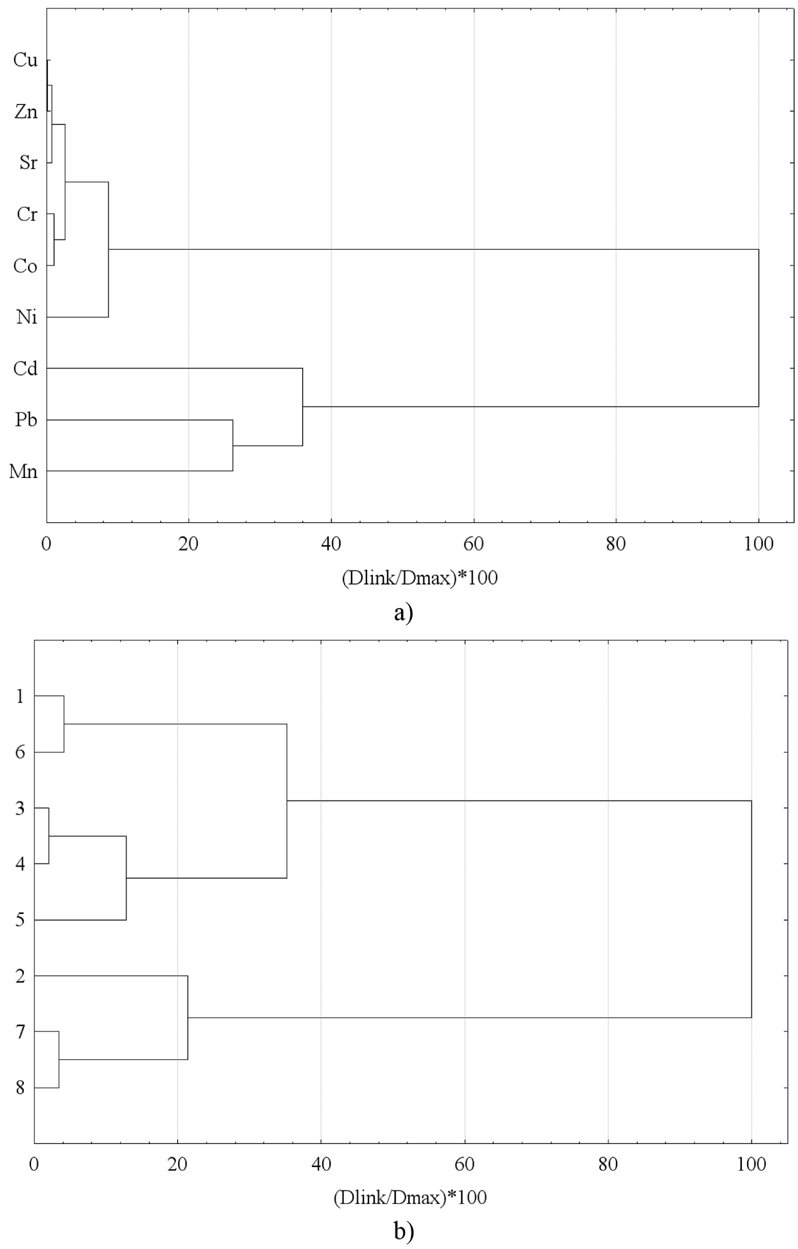

Figure 2. Dendrogram of similarity of chemical elements (a) and sites (b) based on the distribution of pollutants in the water of the Styr River and its tributaries. Conventions: the numerical reference number of the sites is given in Table 1

coefficients (*SCc*) or the average value of concentration coefficients (*MKc*). Thus, the smallest average concentration coefficients are characterised by sites of the second group No. 3, 4, 5 – 0.429, 0.416, 0.464, respectively. The first group is formed by sites No. 1 and 6, with average concentration coefficients of 0.530 and 0.536. For the third group (plots 2, 7, 8), the values of the *MKc* are 0.635, 0.826 and 0.786, respectively.

A typical approach to cluster analysis of chemical element distribution is to use elemental sites as objects. However, an alternative approach can be used when chemical elements can also be used as objects of analysis, the features of which are their concentrations in elemental areas. Using this approach, the similarity of chemical elements was determined according to their distribution in the water of the river Styr and its tributaries, in particular, the following associations (groups) of chemical elements were identified (Fig. 2, a):

- I – Cu, Zn, Sr, Cr, Co, Ni (average values of the *MKc* concentration coefficients for them are 0.004, 0.009, 0.032, 0.060, 0.096, 0.292, respectively).
- II – Pb, Mn, Cd (average values of the *MKc* concentration coefficients for them are 0.983, 1.371, 2.350, respectively).
- According to the nature of the distribution of heavy metals in the soils of the coastal zone of the Styr river and its tributaries, the following groups of sites were identified (Fig. 3, b):
- I – 1 (Boratyn village), 2 (Rovantsi village), 3 (central city beach, Lutsk), 4 (area of 9 Lutheranska Street, Lutsk): the average values of *MKc* concentration coefficients for the sites are 0.530, 0.35, 0.429, 0.416, respectively;
- II – 5 (Lyplyany village), 6 (Knyahynynok village): average values of *MKc* concentration coefficients for these sites are 0.464, 0.536, respectively; III – 7 (Hnidavske bog, Lutsk), 8 (Teremnivski ponds, Lutsk): the average values of the *MKc* coefficients for these sites are 0.826 and 0.786, respectively.

Based on the similarity of the distribution of heavy metals in the soils of the coastal zone of the Styr river and its tributaries in terms of chemical elements, the following associations (groups) were preliminarily identified (Fig. 3a):

- I – Cu, Cd (average values of the concentration coefficients of *MKc* for them are 0.335 and 0.451, respectively); II – Zn, Mn, Pb, Cr, Co (average values of the *MKc* coefficients are 0.211, 0.137, 0.262, 0.206, 0.470, respectively), III – Ni (average value of the coefficient *MKc* is 2.039).

Conventions: the numerical reference number of the sites is given in Table 1. The distribution of heavy metals in the water and soils of the coastal zone of the river Styr and its tributaries is characterized by great heterogeneity. Even within the same area, there is a discrepancy in the level of chemical pollution in water and soil. A significant disadvantage of cluster analysis is the use of Euclid's distance as a metric when there is a large number of parameters under study and a correlation between them. The cluster analysis also fails to take into account the unequal importance of heavy metals belonging to different hazard classes. Therefore, it is advisable to verify the information obtained using different methods of information processing.

The analysis of the relationship between the concentrations of heavy metals in the water of the river Styr and its tributaries indicates that there is a close relationship between individual chemical elements. Thus, for Cu and Mn, the correlation coefficient is $r = 0.80$, for Sr and Ni $r = -0.69$, for Zn and Cu $r = 0.69$, for Zn and Pb $r = 0.63$. The idea of our further research was the mathematical modelling of the location structure in the hyperspace of features. Since it is impossible to visually recognize the structure in a multidimensional space, we focused on multidimensional ordination methods (Skrobala et al., 2020). The task of mathematical modelling was to replace an array of numbers (concentrations of heavy metals) with a scatter of points that would help to identify its structure as a reflection of the environmental features of water pollution in the river Styr and its tributaries.

Since the concentrations of heavy metals in the water of the river Styr and its tributaries are correlated, it can be concluded that the observed 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 (Skrobala et al., 2020). This reduces the dimensionality of the observation space. Graphically, the calculation procedure is reduced to moving the origin to the center of the data and rotating the coordinate axes so that the abscissa goes in the direction of the maximum variance of the data set.

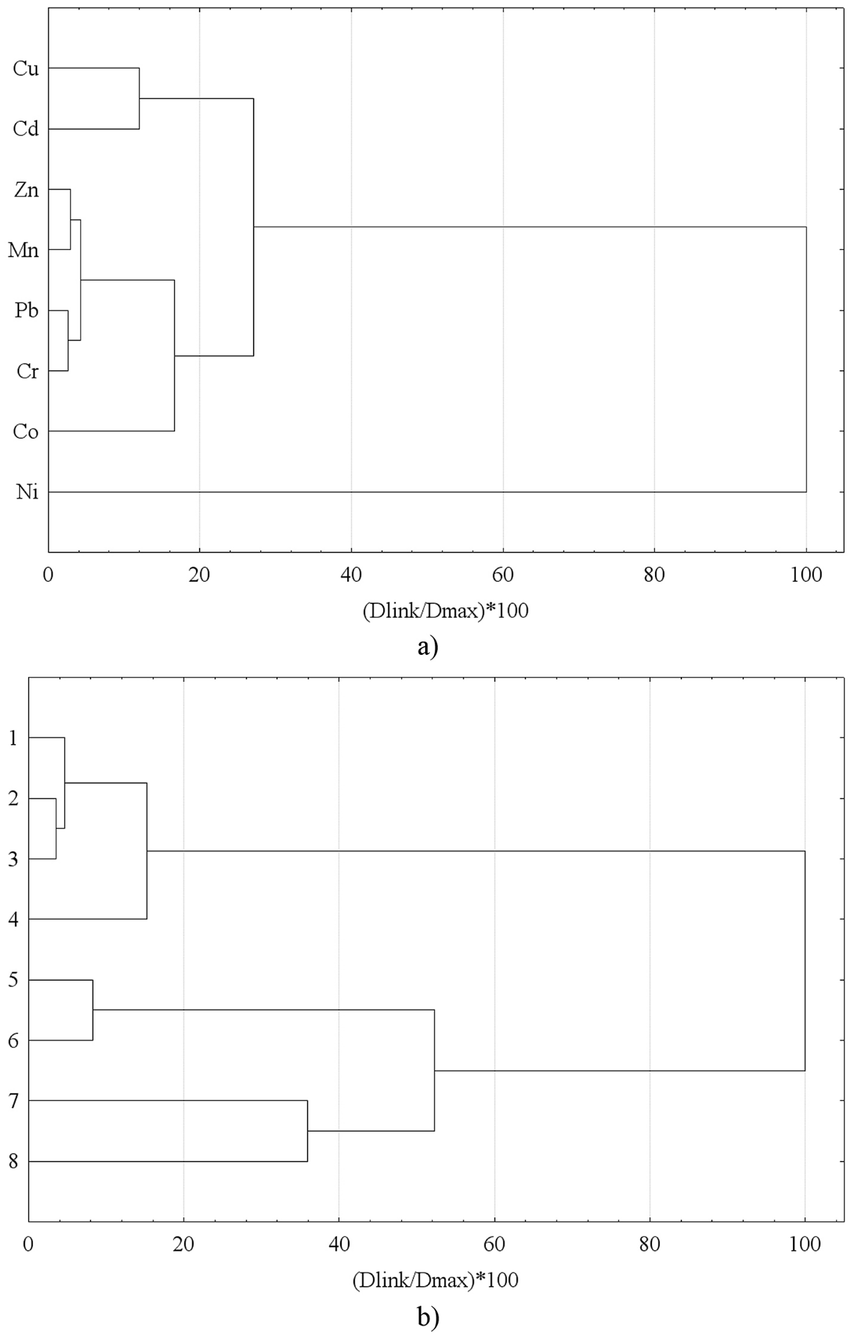

Figure 3. Dendrogram of similarity of chemical elements (a) and sites (b) based on the distribution of pollutants in the soils of the coastal zone of the river Styr and its tributaries

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

$$Factor_1 = 0.506\times Cu + 0.011\times Cd + 0.408\times Zn + 0.399\times Pb - 0.174\times Cr - 0.208\times Co + 0.448\times Mn - 0.285\times Ni + 0.251\times Sr,\ \lambda_1=3.20 \quad (1)$$

$$Factor_2 = -0.001\times Cu + 0.011\times Cd - 0.279\times Zn - 0.405\times Pb + 0.430\times Cr - 0.549\times Co + 0.101\times Mn - 0.438\times Ni + 0.263\times Sr,\ \lambda_2=2.07 \quad (2)$$

$$Factor_3 = 0.325\times Cu + 0.638\times Cd - 0.008\times Zn - 0.117\times Pb + 0.259\times Cr - 0.166\times Co + 0.235\times Mn + 0.406\times Ni - 0.399\times Sr,\ \lambda_3=1.50 \quad (3)$$

where $Factor_i$ – component coordinates, complex gradients of the environment; ·Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni, Sr – standardised concentrations of heavy metals in water; λ_i – eigenvalues of the vectors.

An analysis of the characteristics of the eigenvalues λ_i shows that the three principal components account for 75.2% of the total variance, so for many analysis purposes it is sufficient to use a three-dimensional projection of the original data matrix (Skrobala et al., 2020). The eigenvectors of the correlation matrix (1)–(3) allow to identify combinations of environmental factors that determine the axes of maximum variation in the sections of the Styr River and its tributaries. The main pattern of water quality formation in the river Styr and its tributaries (the first principal component of $Factor_1$) is based on the following structure of relationships between chemical elements (Fig. 4, a): with an increase in the concentration of Cu (correlation coefficient r = 0.90), the concentrations of Zn (r = 0.73), Pb (r = 0.71), Mn (r = 0.80) and Sr (r = 0.45) increase. The first principal component explains only 35.5% of the total variance, but its values clearly show the main pattern of formation of ecotopes of the aquatic environment of the river Styr and its tributaries. Thus, the low values of the first principal component $Factor_1$ are characterised by sites 1 (Boratyn

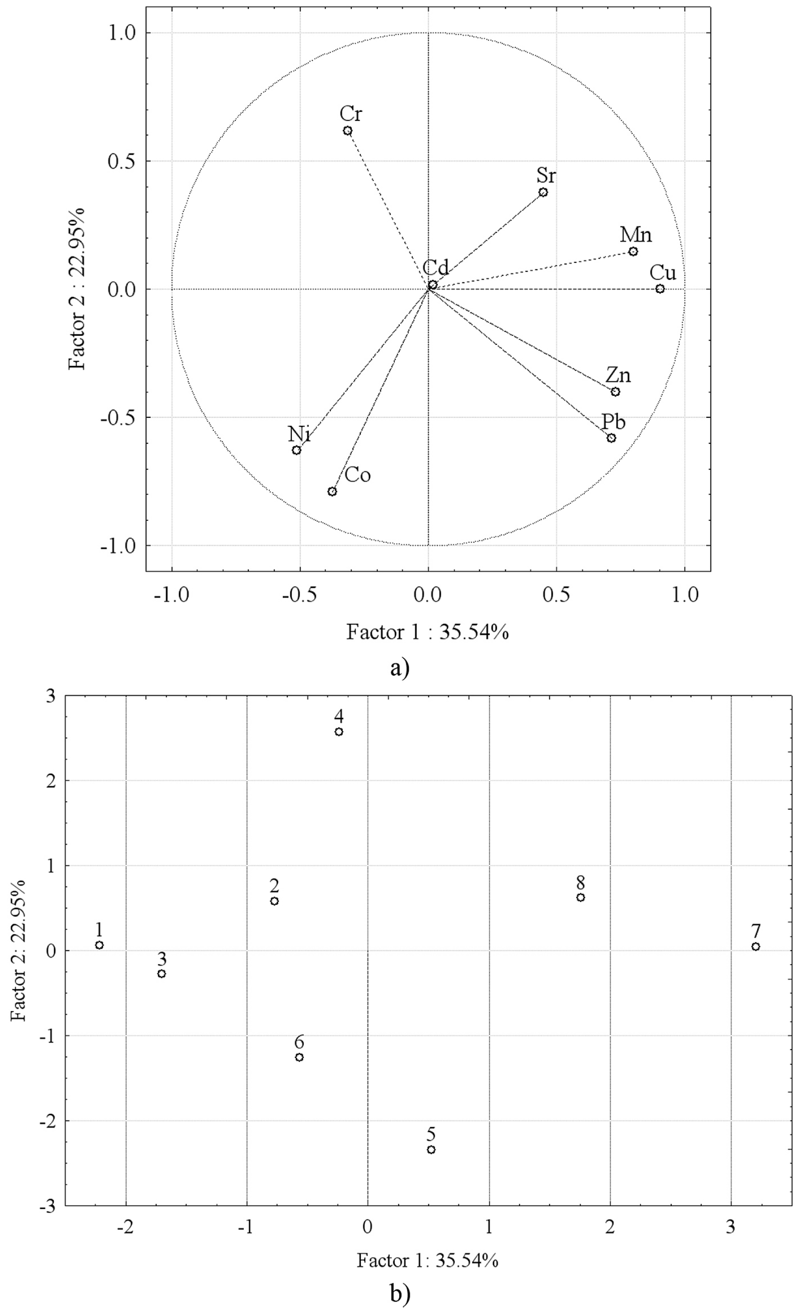

Figure 4. Results of the analysis of the main components of heavy metal content in the water of the river Styr and its tributaries: (a) the system of relationships between the concentrations of chemical elements and complex environmental gradients; (b) location of sites in the coordinate system of complex environmental gradients

village) and 3 (central city beach, Lutsk), which are distinguished by low average values of the coefficients of concentration K_c of heavy metals Cu, Zn, Pb, Mn and Sr (Table 1). The maximum values of the first principal component are distinguished by sites 7 (Hnidavske bog, Lutsk) and 8 (Teremnivski ponds, Lutsk), where these chemical elements have high values of the K_c concentration coefficients.

The second axis of maximum variation, Factor$_2$, additionally explains 23.0% of the total variance of the data. The value of the Factor$_2$ function mainly depends on the content of Co (r = -0.79), Ni (r = -0.63), Pb (r = -0.58) and Cr (r = 0.62). Thus, site 4 (Lutheranska Street, 9, Lutsk), which has the maximum value of the second principal component, can claim to be the cleanest water environment, as it has the lowest average value of the heavy metal concentration coefficient K_c. The minimum value of the second principal component is recorded in site 5 (Lyplyany village), which is characterised by high average concentrations of Co, Ni and Pb and low Cr. The third axis of maximum variation, Factor$_3$, which additionally explains 16.7 % of the total variance of the data, mainly depends on the Cd content (r = 0.78). According to the location of the sites of the river Styr and its tributaries on the axes of complex gradients of the aquatic environment (Fig. 4, b), the following groups can be distinguished (Fig. 3, b):

I – 1 (Boratyn village), 2 (Rovantsi village), 3 (central city beach, Lutsk), 4 (area of Lutheranska street, 9, Lutsk); II – 5 (Lyplyany village), 6 (Knyahynynok village); III – 7 (Hnidavske bog, Lutsk), 8 (Teremnivski ponds, Lutsk).

The most distant in the hyperspace of complex gradients of the aquatic environment by the content of heavy metals (Fig. 4, b) are sites 1 and 7 (Euclid's distance is 5.51) and sites 3 and 7 (Euclid's distance is 5.50).

Conventions: Factor$_{1\text{-}2}$ – main components, complex gradients of the environment; the numerical reference number of the sites is given in Table 1.

Based on the correlation between the content of heavy metals and complex gradients of the aquatic environment (Fig. 4, a), the following associations (groups) of chemical elements can be distinguished:

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

Alternatively, groups I and II can be combined.

The most distant chemical elements in the hyperspace of complex gradients of the aquatic environment are Ni and Sr (Euclidean distance 1.84), Pb and Cr (Euclidean distance 1.76), Co and Mn (Euclidean distance 1.73), and Cu and Co (Euclidean distance 1.71).

The presence of a close relationship between individual chemical elements is also characteristic of the soils of the coastal zone of the Styr River and its tributaries. Thus, for Cr and Co, the correlation coefficient is r = 0.94, for Cr and Cd r = -0.91, for Pb and Cu r = -0.85, for Pb and Co r = 0.82. The results of the principal component analysis based on the correlation matrix are as follows (Fig. 4):

$$\text{Factor}_1 = 0.290\times\text{Cu} + 0.428\times\text{Cd} + 0.143\times\text{Zn} - 0.398\times\text{Pb} - 0.438\times\text{Cr} - 0.453\times\text{Co} - 0.168\times\text{Mn} - 0.359\times\text{Ni},\ \lambda_1=4.70 \quad (4)$$

$$\text{Factor}_2 = 0.405\times\text{Cu} + 0.041\times\text{Cd} - 0.679\times\text{Zn} - 0.361\times\text{Pb} + 0.136\times\text{Cr} + 0.072\times\text{Co} - 0.277\times\text{Mn} + 0.378\times\text{Ni},\ \lambda_2=1.56 \quad (5)$$

$$\text{Factor}_3 = 0.399\times\text{Cu} + 0.122\times\text{Cd} + 0.229\times\text{Zn} - 0.174\times\text{Pb} + 0.118\times\text{Cr} - 0.081\times\text{Co} + 0.776\times\text{Mn} + 0.346\times\text{Ni},\ \lambda_3=1.12 \quad (6)$$

where: factor$_i$ – component coordinates, complex gradients of the environment;×Cu, Cd, Zn, Pb, Cr, Co, Mn, Ni – standardised concentrations of heavy metals in the soils of the coastal zone of the Styr river and its tributaries; λ_i – eigenvalues of the vectors.

The analysis of the characteristics of the eigenvalues λ_i shows that the two principal components account for 78.3 % of the total variance, so for many analysis purposes it is sufficient to use a two-dimensional projection of the original data matrix (Skrobala et al., 2020). The eigenvectors of the correlation matrix (4)-(6) allow us to identify combinations of environmental factors that determine the axes of maximum variation in the sections of the river Styr and its tributaries. The main regularity of soil quality formation in the coastal zone of the river Styr and its tributaries (the first principal component of Factor1) is the following structure of relationships between chemical elements (Fig. 4, a): with an increase in the concentration of Cd (correlation coefficient r = 0.93), the concentrations of Pb (r = -0.86), Cr (r= -0.95), Co (r = -0.98) and Ni (r = -0.78) decrease, and the concentrations of Cu (r = 0.63) increase. The first principal component explains 58.8 % of the total variance, and its values clearly show the main pattern of formation of the edaphototopes of the coastal zone of the river Styr and its tributaries. Thus, the low values of the first principal component Factor1 are characterised by sites 4 (Lutheranska Street, 9, Lutsk), 2 (Rovantsi village) and 3 (central city beach, Lutsk), which are distinguished by low average values of the concentration coefficients K_c of heavy metals Cu and Cd (Table 2). The maximum values of the first principal component are distinguished by sites 7 (Hnidavske bog, Lutsk) and 8 (Teremnivski ponds, Lutsk), in which the mentioned chemical elements have high values of the K_c concentration coefficients.

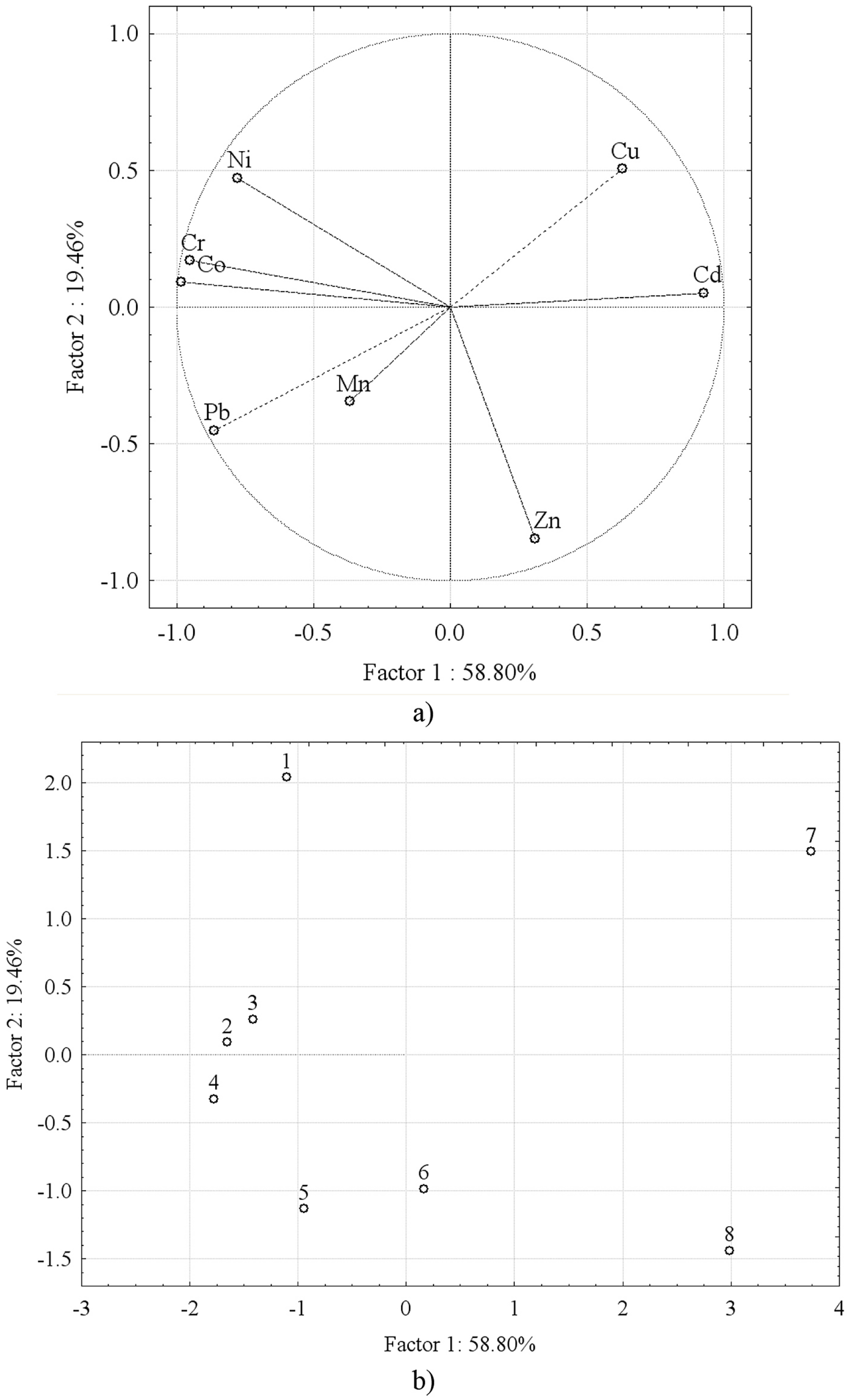

Figure 5. Results of the analysis of the main components of heavy metal content in the soils of the coastal zone of the river Styr and its tributaries: (a) the system of relationships between the concentrations of chemical elements and complex environmental gradients; (b) location of sites in the coordinate system of complex environmental gradients.

Conventions: $Factor_{1-2}$ – main components, complex gradients of the environment; the numerical reference number of the sites is given in Table 1. The second axis of maximum variation, $Factor_2$, additionally explains 19.5% of the total variance in the data. The value of the $Factor_2$ function mainly depends on the content of Zn (r = -0.85), and less on Cu (r = 0.50), Ni (r = 0.47), Pb (r = -0.45) and Mn (r = -0.35). Thus, site 1 (Boratyn village) is characterised by the maximum values of Factor2 due to low concentrations of Zn and Pb. The minimum values of the second principal component are characterised by sites 8 (Teremnivski ponds, Lutsk), 5 – (Lyplyany village) and 6 (Knyahynynok village), where the soils of the coastal zone are characterised by high average values of Pb and Zn concentrations.

The third axis of maximum variation, $Factor_3$, which additionally explains 14.0 % of the total variance of the data, mainly depends on the Mn content (r = 0.82). The low values of the Factor3 function are characterised by sites 1 (Boratyn village) and 6 (Kniahynynok village), where Mn concentration was minimal. According to the nature of the location of the sites of the river Styr and its tributaries on the axes of complex gradients of the aquatic environment (Fig. 5, b), the following groups can be distinguished (Fig. 2, b):

I – 1 (Boratyn village); II – 5 (Lyplyany village), 6 (Knyahynynok village); III – 2 (Rovantsi village), 3 (central city beach, Lutsk), 4 (area of 9 Lutheranska Street, Lutsk); IV – 7 (Hnidavske marsh, Lutsk), 8 (Teremnivski ponds, Lutsk).

Alternatively, groups I and II can be combined. The most distant in the hyperspace of complex gradients of the edaphic environment of the coastal zone of the river Styr and its tributaries in terms of heavy metals (Fig. 5, b) are sites 4 and 7 (Euclidean distance 5.89), sites 2 and 7 (Euclidean distance 5.68), sites 1 and 7 (Euclidean distance 5.60) and sites 1 and 8 (Euclidean distance 5.57).

Based on the correlation between the content of heavy metals and complex gradients of the edaphic environment (Fig. 5, a), the following associations (groups) of chemical elements can be identified:

- I – Cu, Cd; II – Zn, Mn; III – Cr, Co, Ni, Pb.
- Alternatively, groups I and II can be combined.

The most distant in the hyperspace of complex gradients of the edaphic environment are the chemical elements Cd and Co (Euclidean distance is 1.97), Cd and Cr (Euclidean distance is 1.95), Cu and Pb (Euclidean distance is 1.93), Cd and Ni (Euclidean distance is 1.81).

CONCLUSIONS

The distribution of heavy metals in the water and soils of the coastal zone of the river Styr and its tributaries is characterised by significant heterogeneity. The mosaic of chemical element concentrations depends on the distance to the source of pollution, the type of landscape (agricultural or urban), and the intensity of polluted surface runoff from the surrounding area. Even within the same polluted area, water and soil can differ greatly in their nature and level (rank) of chemical contamination.

The multidimensional ordination of the ecotopes of the river Styr and its tributaries by the concentration of chemical elements is characterised by an ordered structure. The analysis of the dependence between the concentrations of chemical elements indicates a close relationship between many parameters. The main feature of the increase in the intensity of anthropogenic load on the aquatic environment is associated with an increase in the concentration of Cu, Zn, Pb, Mn compared to the natural background. The intensity of soil pollution in the coastal zone of the Styr river and its tributaries mainly depends on the concentration of Cu, Cd and Ni. Based on the similarity of chemical elements with regard to their distribution in the water of the river Styr and its tributaries, 4 associations (groups) were defined: I – Cu, Mn; II – Zn, Pb; III – Cd, Cr, Sr; IV – Co, Ni. For the soils of the coastal zone, 3 associations (groups) of chemical elements were identified: I – Cu, Cd; II – Zn, Mn; III – Cr, Co, Ni, Pb. According to the nature of the location of the sections of the river Styr and its tributaries on the axes of complex gradients of the ecotope, 3 groups were identified (Fig. 2, b):

I – 1 (Boratyn village), 2 (Rovantsi village), 3 (central city beach, Lutsk), 4 (Lutheranska street, 9, Lutsk); II – 5 (Lyplyany village), 6 (Knyahynynok village); III – 7 (Hnidavske bog, Lutsk), 8 (Teremnivski ponds, Lutsk).

Graphical visualisation of geochemical information based on typological schemes, where the axes are concentrations of chemical elements or complex environmental gradients, can be used to predict the ecological state of objects and monitor the environment.

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