

Evaluation of the ecological and geochemical condition of geosystems of subregions of Northern Bukovyna

Halyna Khodan¹ 

¹ Yuriy Fedkovych Chernivtsi National University, Department of Physical Geography, Geomorphology and Paleogeography, Chernivtsi, Ukraine.

*Correspondence: g.hodan@chnu.edu.ua

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Abstract: The study assessed the ecological and geochemical state of geosystems of the subregions of Northern Bukovyna: Prut-Dniester, Prut-Siret, and Bukovynian Carpathians. In the Prut-Dniester interfluvium, the ecological condition of rural geosystems can be assessed as moderately favorable and low-favorable. Bukovynian Subcarpathians, in the middle part of Northern Bukovyna, are distinguished by favorable ecological conditions for both human life and rural tourism. The predominance of the leaching soil water regime of geosystems (sufficient rainfall) and notable wooded areas contributed to the sanitation of these landscapes from various artificial pollutions. The Carpathian subregion is the most distinct and unusual in terms of geocological evaluation. There is a more complex set of natural conditions (vertical differentiation of landscape complexes). Fluvial terrace landscape complexes (with a chain or mosaic-scattered settlements) have highly favorable ecological and geochemical conditions. This subregion is the most optimal regarding the recreational and tourist trend. Among the geocological factors of its development, it is worth noting the high quality of groundwater (drinking water), which, despite the excess precipitation, is sufficiently saturated with biologically essential macro- and micronutrients and have mostly medium hardness (Ca + Mg) and mineralization.

1. Introduction

A significant level of anthropogenic pressure on the environment requires a quick solution to most environmental problems, which are the fundamental tasks of modern society. As a result of long-term anthropogenic impact, almost all geosystems have undergone significant changes (Gutsulyak, 1995; Valchuk, 2002; Khodan, 2011). For further rational use and improvement of the living conditions of the population, detailed studies and environmental assessment are needed both at the regional and global levels (Blokhin and Hysmatullin, 1997; Blokhin et al., 2000; Kyrlyuk, 2021). One of the main indicators of the ecological properties of geosystems is their geochemical characteristics. Therefore, landscape-geochemical analysis and assessment of geosystems is a special type of purposeful integrated ecological-geographical research (Ratas et al., 2013; Yu et al., 2014, 2020). The main purpose of the study is to determine the landscape-geochemical features and assess the ecological state of the geosystems of the territory of Northern Bukovina.

2. Materials and Methods

During field surveys and laboratory testing, the following methods were used:

1. The method of conjugate analysis. This is a specific research method for studying the geochemistry of landscapes. The main principle is the simultaneous study of the chemical composition of all components of the landscape (rocks, weathering crust, surface and ground waters, soils, vegetation) and the specifics of geochemical relationships between landscapes (Rollinson, 1993; Gałuszka and Migaszewski, 2011).

2. Method of radial geochemical structures. We also used it, since the radial geochemical structures well reflect the migration of elements within the elementary geochemical landscape, and are also characterized by a number of landscape-geochemical coefficients (Stepanova and Mironycheva-Tokareva, 2021).

3. Results and Discussion

3.1. Study area

Prut-Dniester subregion (Figure 1). In terms of geochemical landscape, this subregion is represented by mainly eluvial, neoluvial, transeluvial, and super-aquatic geochemical landscapes of calcium and acid-calcium classes.

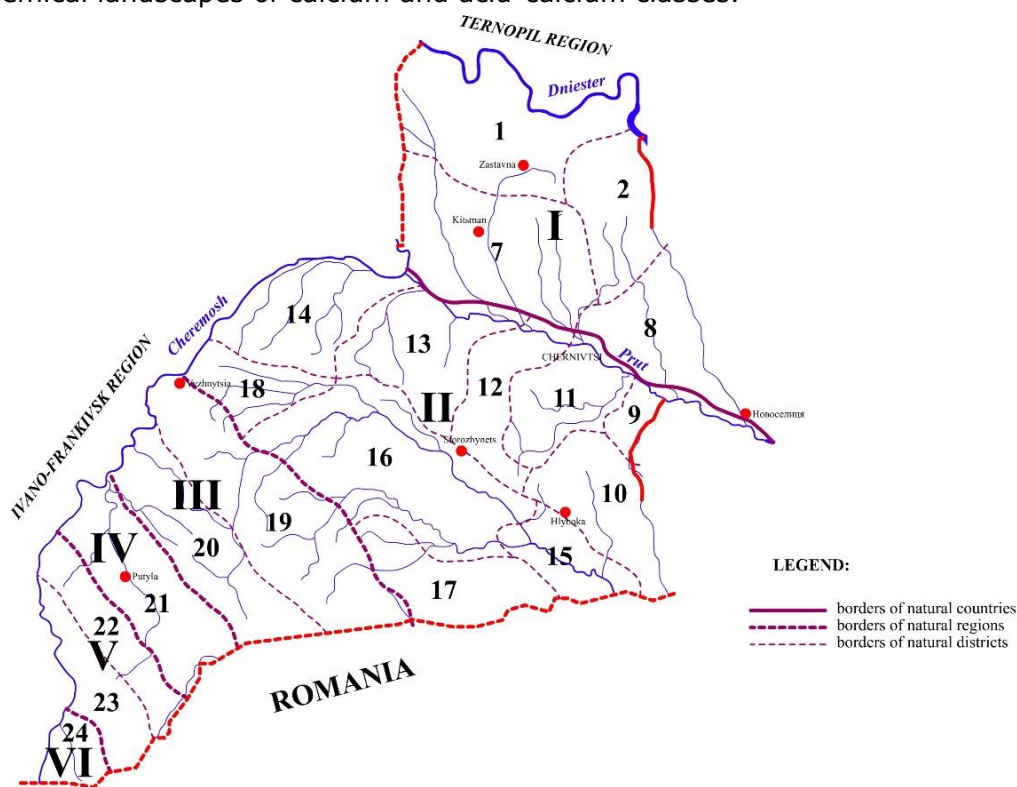


Figure 1. I – Prut-Dniester elevated plain forest steppe region: 1 – Zaxtavna karst, steppe area; 2 – Khotyn upland rolling country, forest area; 7 – Kitsman step-terraced, forest steppe area; 8 – Novoselytsia basin, step-terraced, forest steppe area. II – Prut-Siret elevated hilly silvopasture region: 9 – Hertsa step-terraced, forest steppe area; 10 – Tarashany watershed, basin-rolling, silvopasture area; 11 – Derelui basin, valley-slip, forest steppe area; 12 – Chernivtsi watershed rolling country, forest area; 13 – Brusnytsia rolling-basin, silvopasture area; 14 – Cheremosh-Vashkivtsi rolling country, terraced silvopasture area; 15 – Hlyboka step-terraced, forest steppe area; 16 – Intersiret rolling-hilly, terraced, transitional meadow area; 17 – Krasnoilsk upland, flat-hilly, forest area; 18 – Bahnenska valley flat-wavy, uphill, waterlogged, transitional meadow area. III – Bukovynian Carpathians region: 19 – Berehomet low-mountain, silvopasture area; 20 – Shuryn mid-mountain, forest area; 21 – Putyla low-mountain, silvopasture area; 22 – Maximets, high-mountain, forest area; 23 – Yarovytsia high-mountain, forest area. IV – Maramures Carpathians region: 24 – Chornodilskyi high-mountain subalpine-forest region.

The key sections of rural landscapes in this subregion are the geosystems of villages Prylypche, Verenchanka, and Yurkivtsi in Zastavna raion, Toporivtsi in Novoselytsia raion, and Dubivtsi in Kitsman raion.

Prut-Siret silvopasture subregion (Figure 1) of North Bukovyna region. Geochemically it differs from the previous one (Prut-Dniester forest-steppe). The geochemical landscape structure of this territory is mainly eluvial, eluvial-accumulative, transeluvial, transeluvial-super-aquatic (swamps) geochemical landscapes of acid-calcium, acid-calcium-gley, and acid-gley classes (Buggle et al., 2008).

Bukovynian Carpathians subregion (Figure 1). Geochemical properties of this subregion differ from the previous two subregions. The existing vertical differentiation of landscape complexes (vertical zonation of mountains) has led to a more complex set of EGL (elementary geochemical landscape). Under the conditions of migration, transeluvial, transeluvial-super-aquatic (swamps), neoaccumulative, and transaccumulative are predominant. Acidic, weakly acidic, and even acid-calcium (azonal) classes of EGL are distinguished relative to typomorphic elements of the environment.

3.2. Prut-Dniester subregion

Primarily we analyzed hydrochemical characteristics (groundwater) of the subregion. It is known that natural water is the primary geochemical agent of migration and redistribution of elements in the landscape. It interacts between all its components, and the main role in this interaction lies in the upper horizon of groundwater.

Various natural and anthropogenic factors influence the formation of the appropriate geochemical composition and groundwater properties of rural geosystems. This applies to both individual macrocomponents (cations, anions) and trace elements (heavy metals).

Studies show that the quantitative characteristics of many elements (including heavy metals) in groundwater are directly dependent on the total content of these elements in soils. Weakly acidic (and acidic) waters promote migration of Zinc, Copper, Cadmium, and with weaker effect – Lead (Khodan, 2011).

The groundwater of the subregion is characterized by the following properties: alkaline-acid conditions – neutral and slightly alkaline; hardness – quite hard (due to the presence of carbonate rocks); the degree of mineralization – fresh (0.6-0.8 gm/dm³). The hydrocarbon-calcium type of water predominates, although there are also sulfate-hydrocarbon-calcium, hydrocarbon-sulfate-calcium, sulfate-calcium, and others.

The pH ranges from 6.6 to 7.1. The total hardness is from 12.0 to 13.7 mg/dm³. In terms of hardness, the water exceeds the national sanitary-chemical standard (10 mg/dm³), its maximum values are typical for super-aquatic elementary landscapes. The concentration of chlorides ranges from 35.0 to 75.0 mg/dm³ and does not exceed the established norms. The content of nitrites is 0.01 mg / dm³ and less, nitrates – less than 0.2 mg/dm³, ammonium 0.08 mg/dm³, and less, which does not exceed the standards. The concentration of HM (heavy metals) in groundwater is weak and varies within the following limits (mg/dm³): for lead 0.007 – 0.010, zinc – 0.042-0.046, copper - 0.011-0.019, cadmium <0.001 mg/dm³. The change in hydro-geochemical parameters can be traced in the graph below (Figure 2).

Soil cover (chornozems podzolic, dark gray, gray, and light gray forest, as well as meadow) by pH value is characterized by weakly acidic and neutral reaction, the humus content in soils ranges from 3.2% (rolling country deciduous forest landscapes) to 4.5% (meadow-steppe). Podzolic chornozems and dark gray forest soils of the northern areas of the subregion are richer in micronutrients, but their content does not exceed the maximum allowable norms and does not pose an ecological threat.

The content of the 4 main microelements – Lead, Zinc, Copper, Cadmium, which belong to 1-2 classes of ecological danger, was determined in the soil samples of key areas (Figure 8).

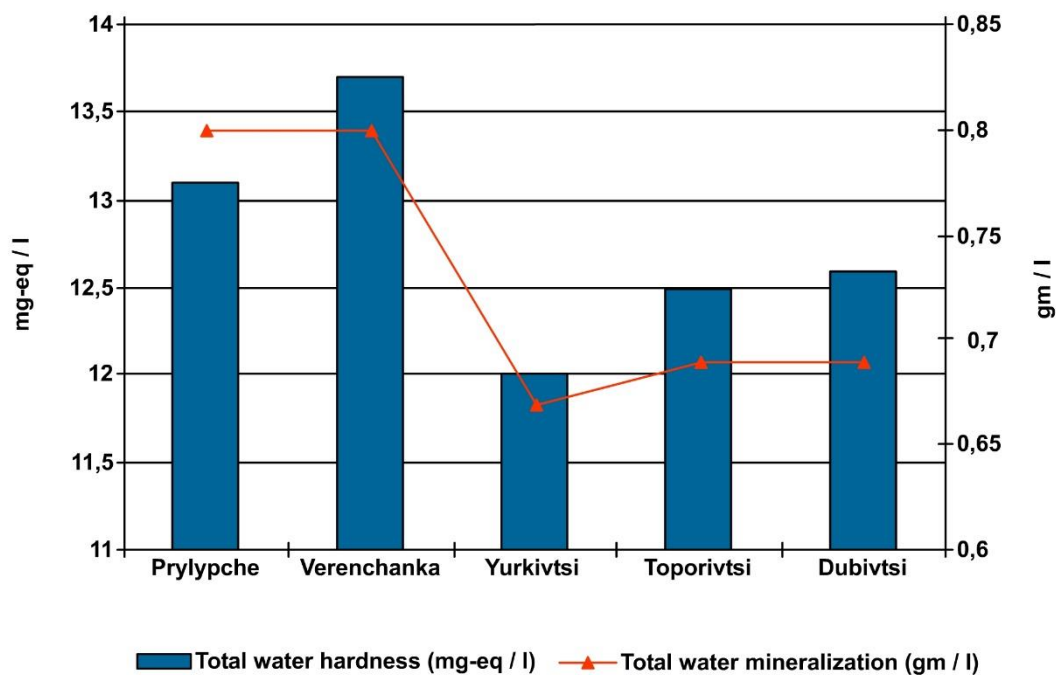


Figure 1. Hydrogeochemical indicators of groundwater of the Prut-Dniester subregion (by key areas).

The analysis of HM content shows that their highest values are observed in meadow-steppe (calcium, eluvial-accumulative) landscapes (Yurkivtsi) and partially meadow (acid-calcium-gley, neoluvial LGS) (Dubivtsi village). This is due to the landscape structure of these areas and their proximity to the roads of the regional and territorial network. The lowest indicators of HM content were found in meadow-steppe calcium neoluvial (Prylypche), meadow-steppe (calcium), and middle forest-steppe (acid-calcium) neoluvial (Toporivtsi) landscapes (Figure 3).

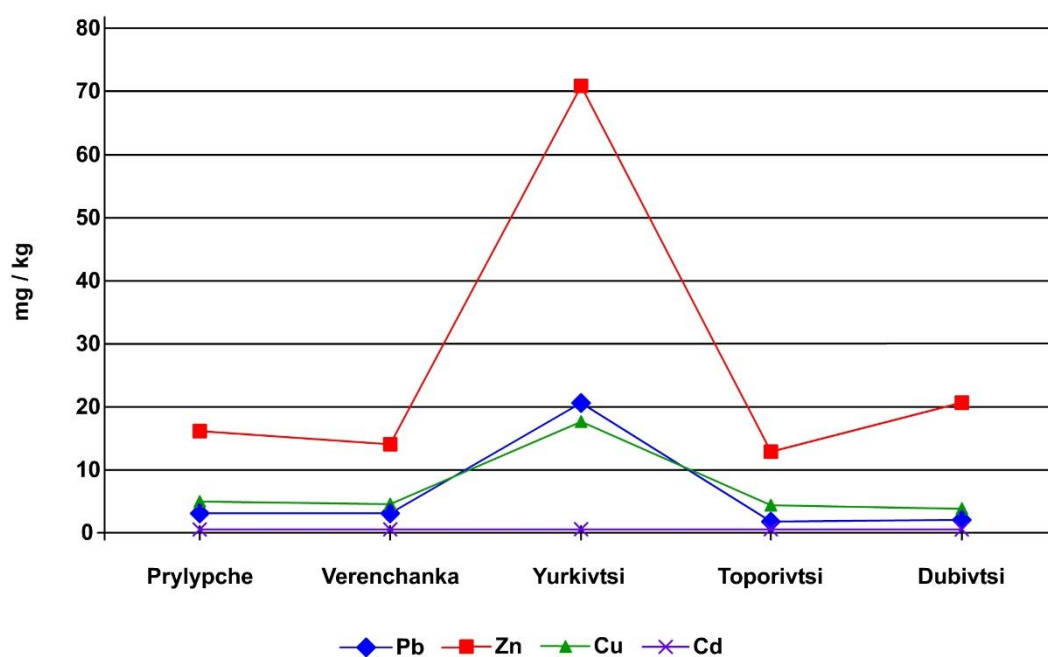


Figure 3. Indicators of gross content of HM in the soils of the Prut-Dniester subregion (by key areas).

The average values of HM content in the soils of the subregion are as follows (mg / kg): lead 1.6–36.5, copper 2.2–22.4, cadmium 0.01–0.1, zinc 4.4–86.3. The saturation index of the soil cover of HM varies from 0.82 (eluvial landscapes) to 1.31 (super-aquatic), i.e. there is a scattering of HM in eluvial EGL and their accumulation in super-aquatic EGL. The coefficients of lateral migration are highest for lead, copper, and cadmium in super-aquatic EGL, and zinc in eluvial and transeluvial. Coefficients of radial differentiation and migration indices indicate the migration of HM from the upper horizons to the parent rock. The concentration coefficient of lead is 0.41–2.80, copper and cadmium 0.72–2.62 and 0.2–7.5, zinc 0.40–5.52. The intensity of soil pollution (Pj) varies from 11.96 to 71.50. The highest rate is observed in super-aquatic EGL, which corresponds to the category of “moderately contaminated” soil. The total pollution rate here is in the range of 1.20–3.0 (Figure 4).

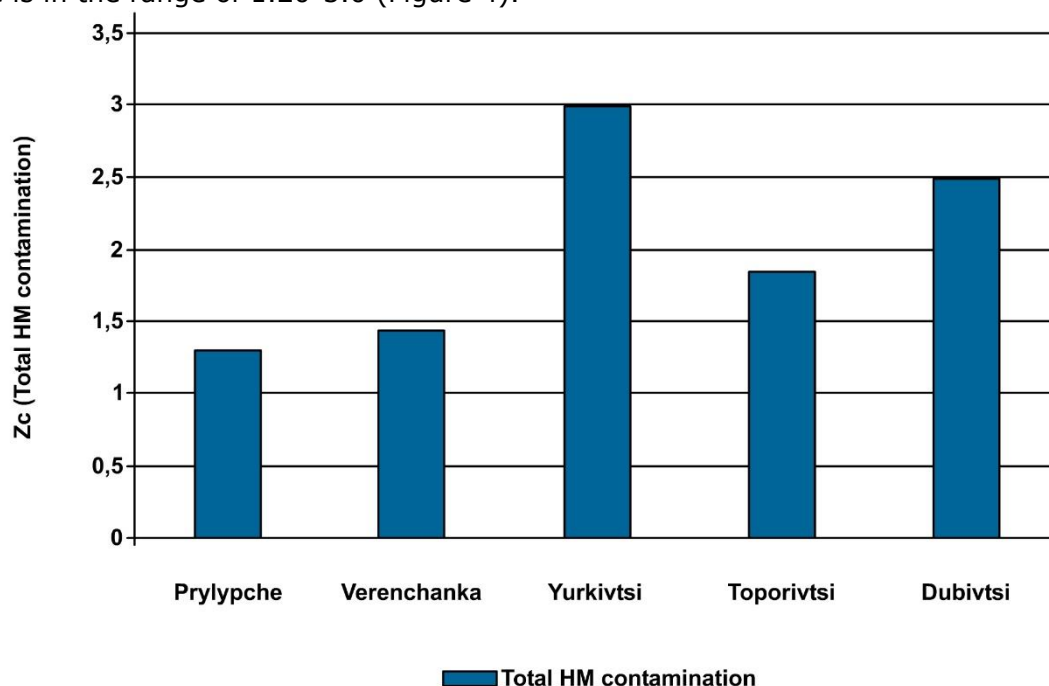


Figure 4. Total HM contamination of soils in the Prut-Dniester sub-region (by key areas).

The coefficient of environmental hazard (relative to the maximum permissible concentration MPC) for the content of lead varies from 0.02 to 1.2, cadmium ranges from 0.01 to 0.14, copper 0.04 to 0.40, and zinc 0.04 – 0,86.

According to the results of chemical analysis of biomass (herbaceous-cereal association), the following predominant indicators of content (mg/kg) were established: Lead – 0.09; Zinc – 20.0; Copper – 10.8; Cadmium – 0.02, which indicates mainly the absence of man-made pollution.

In general, in the Prut-Dniester subregion, following the specified geochemical parameters, significant exceedances of background concentration and maximum permissible concentrations of elements, as well as total indicators of their pollution were not detected. There is only a noticeable excess of groundwater hardness standards and some slight increase in the intensity of soil pollution of the HM (super-aquatic elementary geochemical landscapes). All this indicates that the study area in ecological terms as a whole has very favorable conditions for the rational use of nature and human life.

3.3. Prut-Siret silvopasture subregion

Geochemically, this subregion differs from the previous one (Dniester-Prut forest-steppe). The landscape-geochemical structure of this territory is characterized by eluvial, eluvial-accumulative, transeluvial, transeluvial-super-aquatic (swamp) geochemical landscapes of acid-calcium, acid-calcium-gley, and acid-gley classes.

The research was conducted in key areas of settlements: Drachyntsi in Kitsman raion, Ispas, and Myhove in Vyzhnytsia raion, Petrashivka in Hertsa raion, Kupka and Korchivtsi in Hlyboka raion (Figure 9). These geosystems relate to the transitional meadow and mixed forest landscapes.

The groundwater alkaline-acid conditions of the subregion range from 6.0 to 7.3 (there are weakly acidic and neutral waters).

Value of total hardness ranges here is from 5.8 to 9.3 mg/dm³, moderately (about 6) and moderately-hard (7-9) waters prevail. According to the degree of mineralization, groundwater belongs to medium- and strongly mineralized. In some EGL mineralization increases to 0.6 gm/dm³. The minimum values are 0.14 gm/dm³, the maximum is 0.6 (Figure 5).

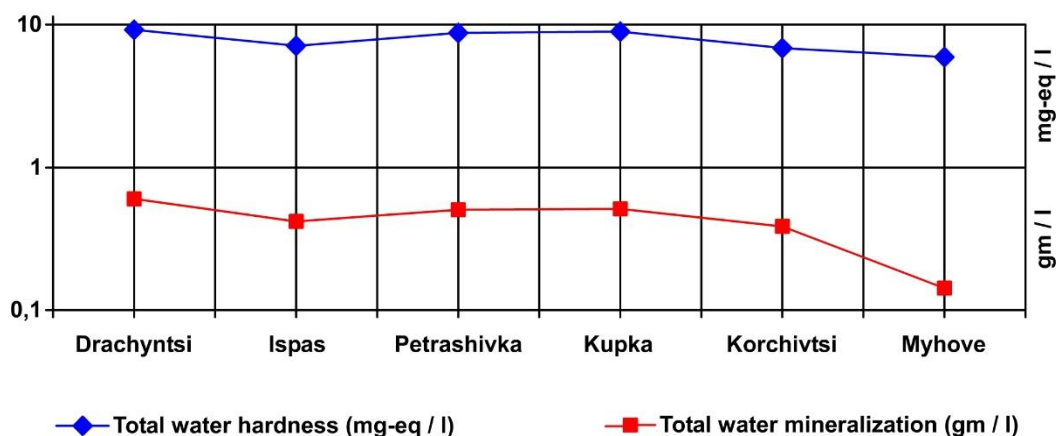


Figure 5. Hydrogeochemical indicators of groundwater of the Prut-Siret subregion (by key areas).

The predominant type of water is hydrocarbon-calcium, but there are other types. In the water samples analyzed, no exceedances of the normative content of macro and microelements were detected.

The indicators of the content of heavy metals are as follows (mg/dm³): lead 0.001-0.031 (average value is 0.016), zinc 0.024 – 0.354 (average 0.113), copper ranges from 0.007 to 0.059 (average value 0.022), the value of cadmium in all water samples subregion ranges from 0.001 to 0.002 mg/dm³. This content indicates that the maximum concentration limits of these trace elements in the groundwater of the study area were not detected.

The soils of the subregion are pH acidic and slightly acidic. The humus content in gray and dark gray forest soils varies between 3.2 – 4.0%, in sod-podzolic 2.8 – 3.2%. In terms of heavy metals, soils are generally slightly poorer than in forest-steppe landscapes, and the content of these elements (including lead and zinc) in vegetation (herbaceous-cereal association) is slightly higher than in the Prut-Dniester physical-geographical region.

In the soil cover the content of HM (mg/kg) varies: lead from 0.86 to 3.26, zinc 4.01 – 41.01, copper 12.91 – 16.54, cadmium from 0.01 to 0.06 mg/kg.

The coefficients of HM concentration in the soil are as follows: lead 0.61 – 1.81 (average 1.07), zinc 0.56 – 14.7 (average 0.9), copper 0.48 – 1.47 (average 1.0), cadmium 1.24 – 2.7 (average 1.9).

The coefficient of environmental hazard for lead varies from 0.02 to 0.06, cadmium from 0.06 to 0.08, copper from 0.10 to 0.32, and zinc from 0.17 to 0.45. The intensity of soil pollution varies from 8.6 to 21.9. The total pollution rate here is in the range of 1.3-2.5 (Figure 6).

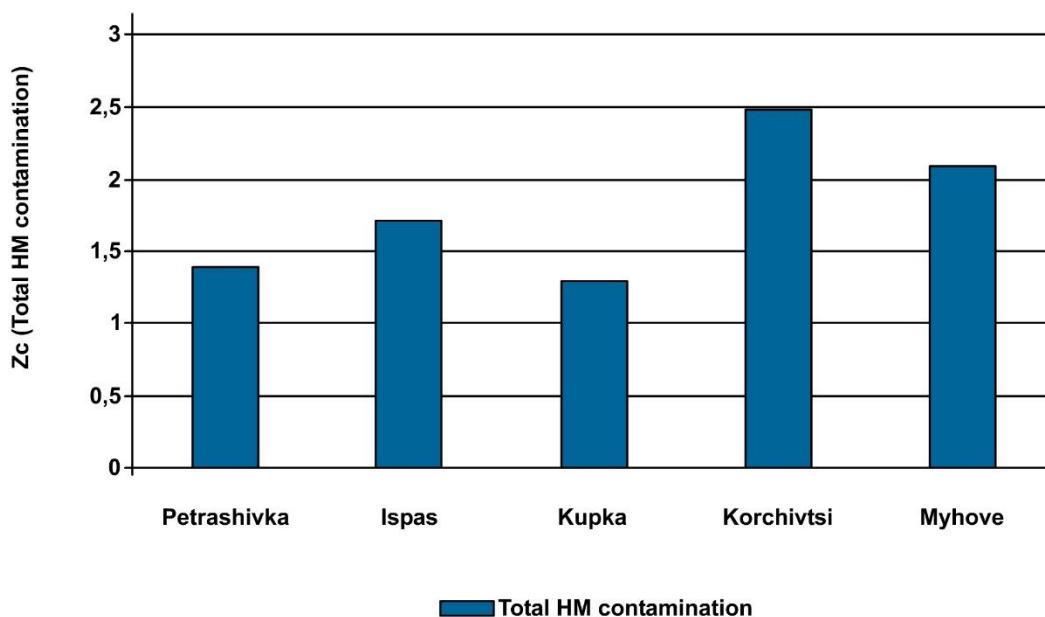


Figure 6. Total indicators of HM soil contamination of the Prut-Siret subregion (by key areas).

Coefficients of lateral differentiation and saturation indices of the soils with HM showed that the accumulation of chemical elements occurs in super-aquatic EGL. Scattering and background values are characteristic of eluvial and transeluvial geochemical landscapes. The values of the saturation index vary within the following limits: minimum 0.50 (for eluvial) and maximum 2.3 (for super-aquatic EGL).

Migration indices and coefficients of radial differentiation showed that in soil horizon of elementary geochemical landscapes, HM accumulate in the upper horizon and their active migration along the profile, zinc, and copper migrate well in soils, lead and cadmium migrate slightly slower. The largest accumulation in the upper soil horizons is accounted for by lead and zinc, slightly weaker for copper and cadmium.

For biomass (herbaceous-cereal association), the indicators of HM content vary within the following limits (mg/kg): lead 0.02 – 0.12, zinc 20.9 – 34.1, copper 11.3 – 14.2, cadmium 0,01 – 0.02. The maximum content of lead and cadmium characteristic for super-aquatic EGL, while zinc and copper are characteristic for eluvial EGL. The concentration coefficient of lead in plants of rural geosystems varies from 0.26 to 1.42, copper from 0.92 to 1.15, zinc 0.08 – 1.32, cadmium – 0.95 – 1.17. The intensity of vegetation pollution in some cases can reach 21.8.

Consequently, the landscape structure of the Prut-Siret subregion is dominated by fluvial terrace, slope, and watershed landscape complexes. In geochemical terms, the territory is represented by eluvial, neoalluvial, transeluvial, and super-aquatic elementary geochemical landscapes – acid-calcium, acid-calcium-gley, and acid-gley classes. Heavy metals migrate from eluvial and accumulate in super-aquatic locations. In general, the content of HM in the components of the landscape does not exceed the MPC.

3.3. Bukovynian Carpathians subregion

Landscape and geochemical studies were conducted in key areas around Putyla urban-type settlement, the villages of Selyatyn, Ust-Putyla, in Putyla raion. These key areas are related to mountain silvopasture, acid, transeluvial-super-aquatic landscape-geochemical systems (Figure 9).

Groundwater, in general for the studied areas, by pH – neutral and slightly acidic; hardness – soft and moderately hard; by the level of mineralization – fresh and ultra-

fresh. Hydrocarbonate-calcium, hydrocarbon-calcium-sodium, hydrocarbon-sodium-calcium, sodium chloride waters are common.

Soils of the subregion (light brown mountain-forest, dark-brown mountain-forest, sod-brown-earth) have mainly acidic and weakly acidic reaction, humus content – up to 3-4%. According to the analysis of the gross content of HM, there is a different migration capacity in different EGL vertical profiles. A more pronounced accumulation of all studied elements (lead, zinc, copper, cadmium) is observed in the background of brown mountain-forest soils of transeluvial (slightly sloping) locations. In general, zinc, copper, cadmium, and lead to a less extent, are heavy metals characterized by the highest migration capacity.

The content of HM, in general for key areas, varies (mg/kg): lead – in the range of 1.5 – 3.7, zinc – from 28.1 to 71.0 (analysis of the content of lead shows that its highest content is typical for super-aquatic EGL, where it accumulates). The content of copper varies from 12.4 to 34.9, the value of cadmium – from 0.017 to 0.077 mg / kg.

The index of soil saturation with heavy metals varies from 0.76 to 1.52. Their accumulation occurs mainly in super-aquatic EGL, and scattering and background values are most characteristic of eluvial and transeluvial.

In general, according to the coefficients of radial migration and indicators of migration indices of heavy metals in soil sections, we can talk about their accumulation in the transition horizons and migration from the upper humus horizons. This radial differentiation of HM is characteristic of both eluvial and super-aquatic EGL.

According to the analysis of the concentration coefficients (Kc) of HM in the soil cover of the study area, it was found that the highest values of lead Kc are characteristic of super-aquatic EGL, where it accumulates. Copper Kc varies from 0.69 (transeluvial) to 1.94 (super-aquatic), cadmium values range from 0.57 (in eluvial) to 2.58 (in super-aquatic EGL).

The intensity of soil pollution in key areas varies from 11.0 to 23.2. The total pollution rate here is in the range of 1.2 – 2.7. The coefficient of ecological danger based on the content of lead varies from 0.05 to 0.12, cadmium – from 0.01 to 0.07, copper – 0.20-0.62, and zinc – 0.28-0.71.

Analysis of biomass (herbaceous plants) of the studied area showed low concentrations of HM. Indicators of HM content are poorly differentiated and vary within the following limits (mg/kg): lead 0.06 – 0.08, zinc 9.3 – 26.8, copper 6.07 – 9.97, cadmium 0.01 – 0.02. The maximum content of zinc, copper, and cadmium is typical of eluvial EGL. For transeluvial and super-aquatic EGL – lead. In general, there are no biogeochemical anomalies, except for the EGL of highways, where the excess of the average values of Kc is denoted primarily for lead and zinc (1.5 – 3 times or more); while in other artificial landscapes (for example, Chernivtsi) indicators of anomalies increase tenfold. At this stage, no significant geochemically man-caused pollution has been identified for the Carpathian LC, which serves as an indicator of their favorable ecological status. This should be taken into account in the development of tourism in the region.

The general regional plan based on ecological and geochemical indicators established a rather evident regional differentiation of living conditions of the population of the region (Table 1). Favorable environmental conditions are improving in the direction from the Prut-Dniester subregion through the Precarpathians to the Carpathians. Such a change in optimal ecological conditions corresponds to a change in ecological and geochemical parameters (state of drinking water, soil, biomass).

In the Prut-Dniester subregion, the ecological condition can be assessed as “reduced favorable” and “weakly favorable” (in certain areas of the Dniester valley, where groundwater hardness exceeds standards, as well as in plakor agroecosystems, which are geochemically contaminated through the surplus of chemical fertilizers in the soil). Here the total pollution rate (TPR) is the highest in the region.

Table 1. Indicators of the ecological and geochemical condition of rural geosystems of subregions of Northern Bukovyna.

Nº	Subregion	Value	Zc (TPR)	Pj*	I _H	Condition
1	Prut-Dniester	Min.	3,69	17,67	52,47	reduced favorable
		Max.	17,32	93,34	252,2	
		Avg.	5,54	36,08	117,16	
2	Prut-Siret	Min.	2,23	19,44	74,88	favorable
		Max.	6,81	48,52	165,23	
		Avg.	4,13	32,80	116,45	
3	Bukovynian Carpathians	Min.	2,07	18,19	68,96	increased favorable
		Max.	9,06	54,82	167,54	
		Avg.	3,85	32,43	113,88	

*Pj – The intensity of soil pollution; I_H – The integral pollution index.

In the subregion of Bukovynian Precarpathians, environmental conditions are relatively more favorable. The predominance of the leaching soil water regime of geosystems (sufficient rainfall) and notable wooded areas contributed to the sanitation of these landscapes (from various artificial pollutions). In addition, there are favorable conditions for the formation of high-quality groundwater (drinking water), which should be taken into account (as an important factor) in the medical and geographical evaluation of the territory. Hydro- and pedogeochemical parameters are the most favorable (Figure 7).

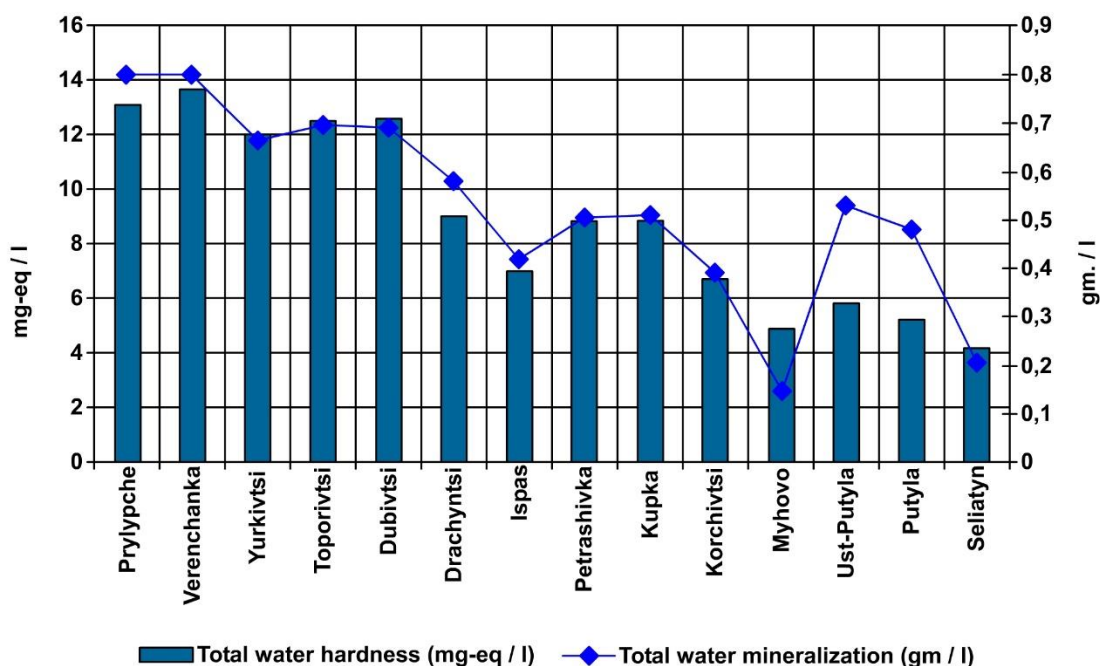


Figure 7. Hydrochemical parameters of groundwater (by key areas).

The Carpathian subregion within the study area in terms of geo-ecological assessment is the most specific and original, as it is necessary to take into account a more complex set of natural conditions. Our research covers mainly Fluvial terrace landscape complexes, with a chain or settlements. Hydrogeochemical parameters do not exceed the standards, concentration coefficients, and total pollution rate relative to the Prut-Siret subregion is slightly higher (Figure 8, 9, 10).

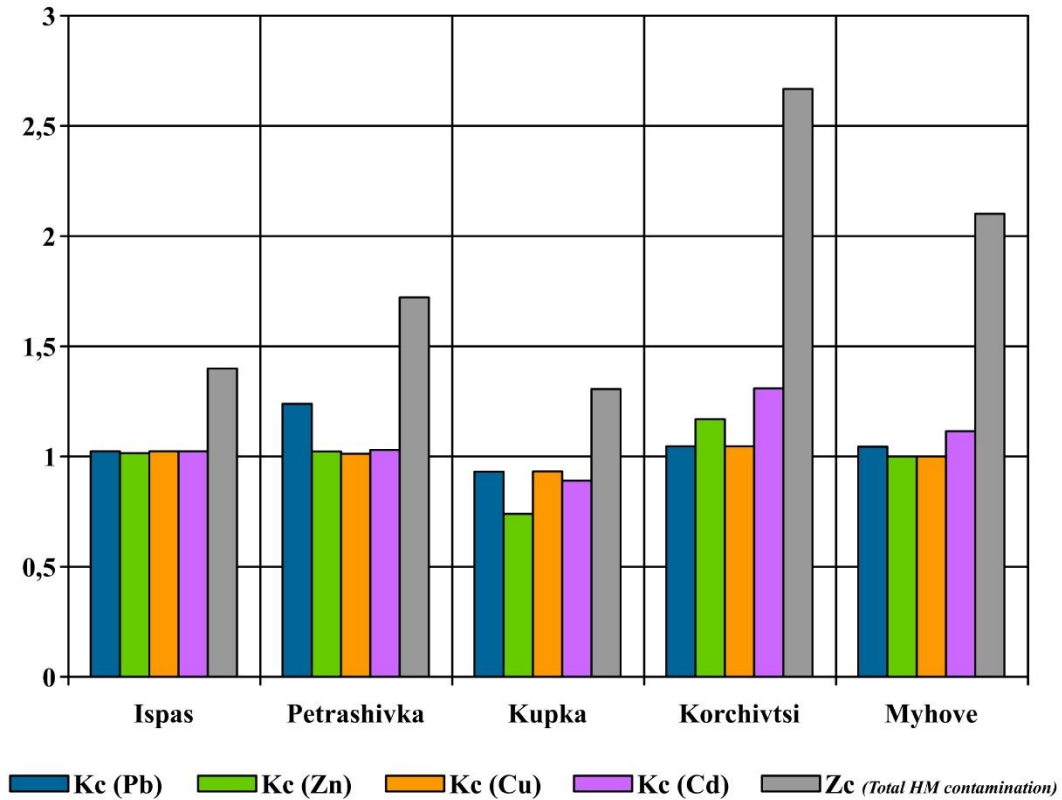


Figure 8. Total pollution indicators and soil concentration coefficients of heavy metals of the Bukovynian Carpathians Subregion (by key areas).

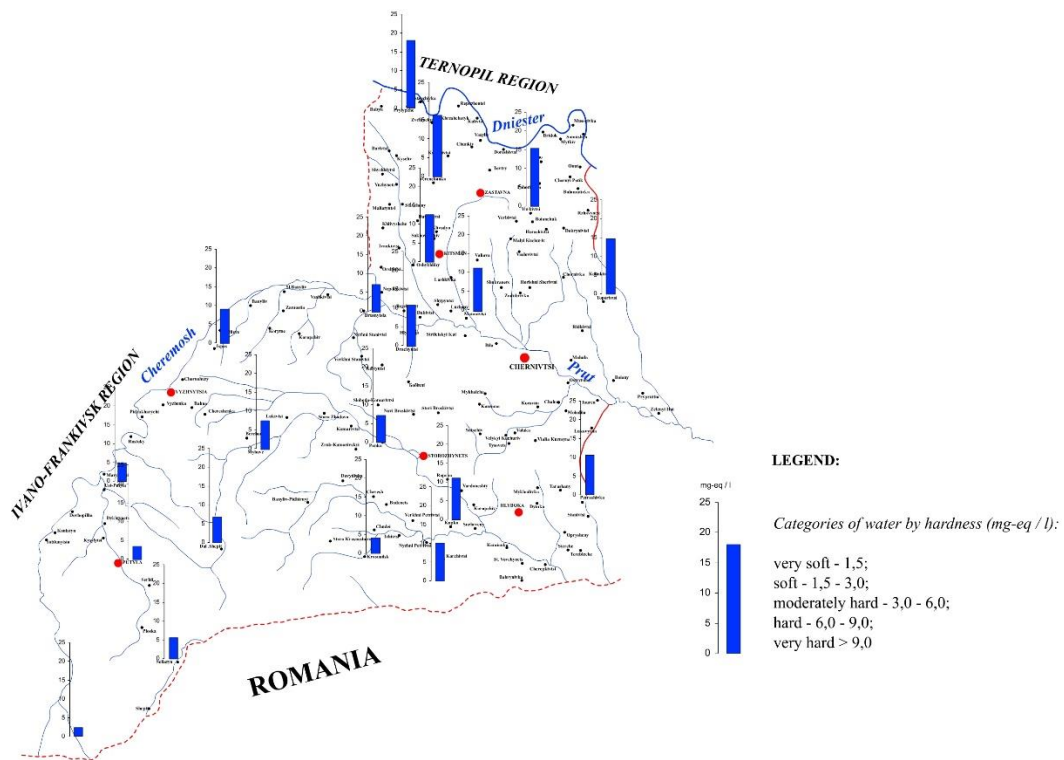


Figure 9. Indicators of groundwater hardness of rural geosystems of Northern Bukovina.

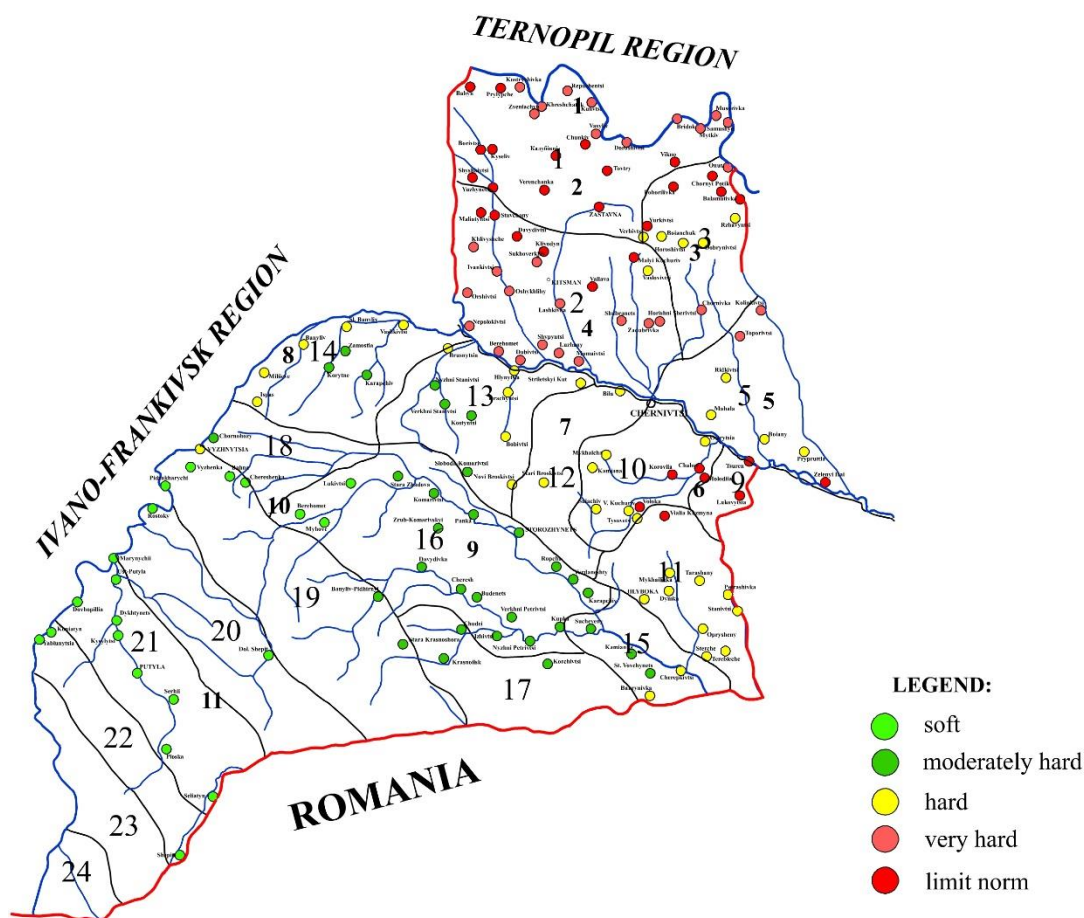


Figure 10. Estimation of groundwater quality of rural geosystems of Northern Bukovina (by hardness).

4. Conclusions

In general, the geosystems of Northern Bukovyna are characterized by significant geochemical diversity, as they are located in different types and classes of landscapes and therefore differ in features that affect the migration processes in them. The geochemical indicators obtained during the study allow us to state that the level of total hardness and mineralization of groundwater (drinking water) of forest-steppe rural landscapes of the Prut-Dniester subregion has higher values, which often exceed the standards. Waters of silvopasture areas and forests of the Pre-Carpathian and Carpathian subregions are noted to have better hydrochemical parameters.

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