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## Biogeochemical peculiarities of accumulation of chemical elements by plants of the Svydovets Massif of the Ukrainian Carpathians

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**Abstract.** The objective of the paper was determining biogeochemical peculiarities of accumulation of chemical elements (Mn, Ni, Co, V, Cr, Zr, Cu, Pb, Zn, Ba, P) by wild-growing shrubs (stems and leaves) – bog bilberry (*Vaccinium uliginosum*), European blueberry (*Vaccinium myrtillus* L.), alpine juniper (*J. communis* subsp. *alpina*); perennial herbaceous plants (flowers and leaves) – common tormentil (*Potentilla erecta* (L.) Hampe), willow

gentian (*Gentiana asclepiadea*), true sedges (*Carex*); and trees (needles) of European silver fir (*Abies alba*) on nine plots in the Svydovets Massif of the Ukrainian Carpathians. The results we obtained based on field surveys (selection of samples of soil and vegetation) and interpretation of their analysis allowed us to determine the total regional background of chemical elements in soils and ash of plants using emission spectral analysis. We assessed the total concentration of chemical elements in soils of the plots (least to highest): the Apshynets Ridge – the Herashaska Polonyna – Drahobratske Lake – the Svydovets stream – Apshynets Lake – Herashaska Lake – the Zhuravlyne Bog – Vorozheske Lake (group of small lakes) – Vorozheske Lake (large) and determined the dependence on type of soil and pH. We determined that for wild-growing herbaceous plants the biogeochemical activity of species increases in the following sequence: true sedges - willow gentian - common tormentil; for wild-growing shrubs (bog bilberry, European blueberry, alpine juniper) such a sequence is impossible to determine due to the great difference between the values on different plots. We determined the role of each plant as medicinal for treating microelement deficiency in Cu, Zn, Co. We determined that in the plot of the Herashaska Polonyna, the needles of alpine juniper contain a maximum amount of Zn and Co, the needles and leaves of bog bilberry – Cu, Zn, Co; the flowers and leaves of common tormentil by Apshynets Lake and European silver fir near the area of the Svydovets stream – Cu. We calculated the daily dose of each element according to species of plants to overcome microelementosis. The results of biogeochemical surveys may be the basis for determining and recommending plants as medicinal, and also of geochemical and biogeochemical monitoring studies.

**Key words:** biogeochemical peculiarities. The Svydovets Massif of the Ukrainian Carpathians, accumulation of chemical elements, soils, vegetation, microelementosis

## Біогеохімічні особливості накопичення хімічних елементів рослинністю Свидовецького масиву Українських Карпат

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**Анотація.** Метою роботи є виявлення біогеохімічних особливостей накопичення хімічних елементів (Mn, Ni, Co, V, Cr, Zr, Cu, Pb, Zn, Ba, P) дикорослою рослинністю: кущі (стебла та листя) – лохина (*Vaccinium uliginosum*), чорниця (*Vaccinium myrtillus* L.), ялівець сибірський (*Juniperus communis* subsp. *alpina*); багаторічні трав'янисті рослини (квіти та листя) – перстач прямостоячий, калган (*Potentilla erecta* (L.) Hampe), тирлич ваточниковий (*Gentiana asclepiadea*), осока (*Carex*); та дерев (хвоя) ялиці білої (*Abies alba*) на дев'яти ділянках Свидовецького масиву Українських Карпат. Результати отримані авторами на основі польових робіт (відбору зразків ґрунту та рослинності), та інтерпретаційної їх обробки дозволили визначити валовий регіональний фон хімічних елементів у ґрунтах та золі рослинності за допомогою емісійного спектрального аналізу. Оцінено сумарну концентрацію хімічних елементів у ґрунтах ділянок (від меншого до більшого): хребет Апшинець – полонина

Герашаська – озеро Драгобращьке – потік Свидовець – озеро Апшинець – озеро Герашаська – болото Журавлина – озеро Ворожеське (група малих озер) – озеро Ворожеське (велике) та з'ясовано залежність від виду ґрунтів та pH. Встановлено, що для дикорослих трав'янистих рослин біогеохімічна активність виду зростає в ряду: осока – тирлич – перстач; для дикорослих кушів (лохина, чорниця, ялівець сибірський) такий ряд неможливо визначити, зважаючи на великий перепад значень на різних ділянках. Визначена роль кожної рослини, як лікарської в якості подолання мікроелементозного дефіциту Cu, Zn, Co. Встановлено, що на ділянці полонина Герашаська гілки ялівця сибірського вміщують максимальну кількість Zn та Co, гілки та листя лохини – Cu, Zn, Co; квіти та листя перстача оз. Апшинець і ялиця біла ділянки потік Свидовець – Cu. Розрахована добова доза кожного елементу за видами рослини для подолання мікроелементозу. Результати біогеохімічних робіт можуть стати базою при визначенні та рекомендації рослин як лікарських, а також моніторингових геохімічних та біогеохімічних досліджень.

*Ключові слова:* біогеохімічні особливості, масив Свидовець Українських Карпат, накопичення хімічних елементів, ґрунти, рослинність, мікроелементоз

## Introduction.

Biogeochemical studies of the highland belt of the Svydovets Massif of the Ukrainian Carpathians are especially valuable as the gold standard for the region. The remoteness of the Massif from the industrial centers gives us reasons to suggest the ecologically pristine states of the flora.

Among well-known studies on determining the geochemical constituent of environmental objects, we have to note the following research (Kabata-Pendias, Pendias, 1989), (Alekseenko, 2000), (Samofalova, 2009), (Lang, Kruger, Chmara, 2017), (Kryuchenko, Zhovinsky, Paparyga, 2019) which is of high precision due to use of more advanced analytical methods.

For the territory of Ukraine, an important issue is assessing natural or technogenic geochemical anomalies, and in order to do so in the first place it is necessary to determine the regional background content of chemical elements in soils and vegetation. The studies (Klos, Birke, Zhovinsky, 2012), (Zhovinsky, Kryuchenko, 2014), (Zhovinsky, Kuraeva, 2002) devoted to determining sources of anomalous content of chemical elements in soils and vegetation gave a new sense to the aspects concerning assessment of the anomalies.

Currently, there are very few studies on the biogeochemical condition of the Ukrainian Carpathians. The first studies on determining the chemical content of soils and vegetation of the Ukrainian Carpathians concerned the use of secondary aureoles and flows of diffusion of metallogenic provinces (Sushik, 1978). After these studies, materials on geochemical composition of the regions' environmental objects have not been presented for quite a while. As a result of complex study of geochemistry of the territory of the Carpathian Biosphere Reserve (CBR), the results were published of research (Zhovinsky, Kryuchenko, 2014) which included analyses of geochemical content of environmental objects, and results were presented of research on patterns of chemical elements and their mobile forms in soils, ground water and surface wa-

ters, vegetation, mushrooms and atmospheric precipitations (Zhovinsky, Kryuchenko, Paparyga, 2013). Further studies (Kryuchenko, Zhovinsky, Paparyga, 2018) performed in these regions focused on ore and technogenic geochemical anomalies (lithochemical, hydrochemical, atmochemical, biogeochemical) in the protected territories of the Ukrainian Carpathians.

Biochemical studies with ecological purpose are broadly conducted in different regions of the world. Recent studies (2017-2020), presented to the scientific community, concern different species of plants (Kudrevatykh, Kalinin, Alekseev, 2019) as bioindicators for assessment and monitoring of environmental contamination with heavy metals (Kryuchenko, Zhovinsky, Paparyga, 2019), their accumulation in agricultural plants (Hazrat., Ezzat, Ikram, 2019), ecological toxicology of microelements (Wang, Wu, Liu, Liao, Hu, 2017), ecological resistance, toxicity and bioaccumulation of heavy metals in the environmental objects (Buts, 2018), (Palutoglu, Akgul, Suyarko, Yakovenko, Kryuchenko, Sasmaz, 2018).

The biogeochemical research conducted by us has practical importance. In spite of the fact that most plants of the Svydovets Massif are medicinal ones used not only as raw material for the pharmaceutical industry, but also by the locals as tinctures, decoctions, it has become necessary to determine the properties of these plants in solving the problems of microelement deficiency, which we emphasized in our work.

**The objectives of the study** were peculiarities of accumulation of chemical elements (Mn, Ni, Co, V, Cr, Zr, Cu, Pb, Zn, Ba, P) by wild-growing vegetation (shrubs – bog bilberry (*Vaccinium uliginosum*), European blueberry (*Vaccinium myrtillus* L.), alpine juniper (*J. communis* subsp. *alpina*); perennial herbaceous plants – common tormentil (*Potentilla erecta* (L.) Hampe), willow gentian (*Gentiana asclepiadea*), true sedges (*Carex*) and trees (coniferous) European silver fir (*Abies alba*)) in nine plots in the Svydovets Massif of the Ukrainian Carpathians.



## Materials and methods.

Materials for the studies were the samples of surface deposits (soils) and wild-growing plants (the stems and leaves) and trees (the needles) in nine plots of the Herashaska Polonyna (montane meadow) (hereinafter – the Herashaska Pol.), the Apshynets Range (hereinafter – the Apshynets R.), Apshynets Lake (hereinafter – Apshynets L.), Herashaska Lake (hereinafter – Herashaska L.), the Zhuravlyne Bog (hereinafter – the Zhuravlyna B.), Drahobratske Lake (hereinafter – Drahobratske L.), Vorozheske Lake – large (hereinafter – Vorozheske L.), Vorozheske Lake – a group of small lakes (hereinafter – Vorozheske L. s.), the Svydovets stream (hereinafter – Svydovets s.).

The authors of the article collected the samples of soils and vegetation during the period of August–September of 2019. The criteria for selection of phyto-objects for geochemical testing were their ubiquitousness in the places of complex geochemical sampling (samples of vegetation were taken in the places of sampling the surface deposits). In total, 120 samples of soil and 150 samples of vegetation (around 25 samples of each species) were collected. The species of plants the samples were collected from are presented in Fig. 1.

Quantitative general chemical analysis of soils and ash was performed on a Saturn-3 spectrograph with graphite furnace in the Chemical-Analytic Center of the M.P. Semenenko Institute of Geochemistry, Mineralogy and Ore Formation of the National Academy of Sciences of Ukraine (analysts – V. I. Kolomiets, O. A. Zhuk). Sensitivity of analyses for different elements equaled  $0.01 \mu\text{g}/\text{dm}^3$  to  $0.0001 \mu\text{g}/\text{dm}^3$ .

*Analytic studies.* Due to the absence of anthropogenic contamination of the studied territory, which is thanks to most of its area being under protected status, we used the following parameters to assess the soils (Alekseenko, 2000): coefficient of concentration (Kc) – ratio of actual content of chemical element to background content and total indicator of concentration ( $\Sigma\text{Kc}$ ) which equals the total of coefficients of concentrations of separate elements.

During the study of vegetation, we used such a parameter as coefficient of biological absorption (Ax) which equals the ratio of the content of the element in the ash of plants to its content in soil the plant lives in. To quantitatively express the general ability of species to concentrate microelements, we used the parameter of biogeochemical activity of species (BCA) which is



Fig. 1. Species of plants of the Svydovets Massif, from which we took the samples

the total amount of coefficients of biological absorption ( $A_x$ ) of separate microelements (Kudrevatykh, Kalinin, Alekseev, 2019). Statistical data analysis was performed using Statistica 10 software.

### Characteristics of the areas of studies.

All sites were located within the Svydovets Mountain Massif – between the Teresva River (in the west) and the Chorna Tysa (in the east). This structure is one of the system-forming elements of the Ancient-Glacial high polonynas (montane meadow) of flysch landscapes of the Ukrainian Carpathians (Gerenchuk, 1981). It is characterized by slightly wavy lines of the mountains without sharp transitions between the saddles and peaks. According to the altitude level, it is the highland of the Ukrainian Carpathians located above the natural upper border of the forest (1,300–2,061 m above sea level), covered by Alpine and Sub-Alpine vegetation on mountain alkaline-brown and mountain peat-brown soil (Vovk, Orlov, 2014).

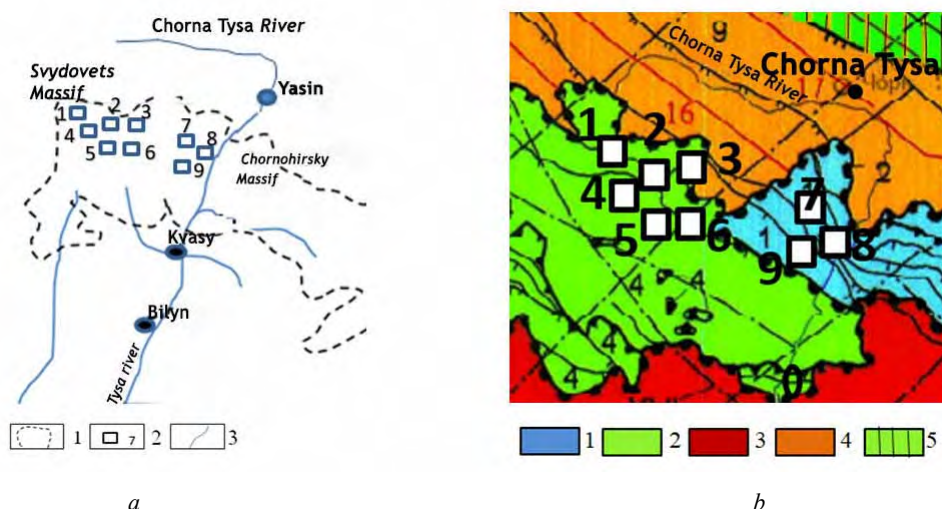
According to the tectonic division, the surveyed sites belong to the Chornohirsky and Dukliansky nappes (Suschik, 1978) composed of Cretaceous and Paleogenic flysch and are different from each other in the structures of flysch deposits and some morphological peculiarities of the folded and rupture dislocations. Sites 1–6 are located within the Chornohirsky nappe, sites 7–9 – the Dukliansky nappe (Fig. 2).

The surveyed plots were identified as belonging to the high-mountain (1,400–1,700 m) altitude belt of the Ukrainian Carpathians. The high altitude zone of the mountains, located above 1,400 m, with its cold excessively humid climate and shrub-meadow

vegetation is distinct in its highly idiosyncratic soil processes. The influence of rich herbaceous vegetation has resulted in the development of a peat type of soil formation, but biological life of the soil in such severe climatic conditions is less active than in the plains. Specific mountain-meadow-brown soils have been formed, the soil-forming rocks for which were the deposits sedimented over the period from the Lower Cretaceous to the Eocene. The soils are represented by rough-rhythmic flysch – with dominance of sandstones and fine- or average-rhythmic flysch – distinctive alternation of sandstones and clayey schists (Gerenchuk, 1981). In the process of weathering of these rocks, mostly loamy deposits form. The genetic profile of brown mountain-meadow soils is as follows: the layer of dead dry semi-humid 2–6 cm-deep meadow litter, humus horizon measuring 8–12 cm, of grey-brown colour, with well manifested grainy-fine nut structure, which together with debris of the parent rocks conditions the dryness and favourable aqua-air regime of brown earths (Zhovinsky, Kryuchenko, Paparyga, 2013). The rocks on which the brown mountain-meadow soils form are extremely poor in calcium compounds. Thus, they are poorly saturated with cations of two-valent metals and highly acid. Furthermore, the type of soil (sandy, sandy-loamy, loamy and clayey) corresponds to migratory properties of chemical elements (Table 1).

### Results and discussion.

To determine peculiarities of uptake of chemical elements by plants, one needs to know their content in the soil. We determined the content of Mn, Ni, Co,



**Fig. 2.** Scheme of locations of the plots in the study on the plan a): 1 – borders of the protected massifs of the Carpathian Biosphere Zapovednik, 2 – study plots and their numbers: 1 – Apshynets L., 2 – Vorozheske L. 1., 3 – Vorozheske L. s., 4 – Herashaska L., 5 – the Apshynets R., 6 – the Herashaska Pol., 7 – the Svydovets s.; 8 – Drahobratske L., 9 – the Zhuravlyna B.; b) the tectonic scheme (Matskiv, Pukach, Vorobkanych, Pastukhanova, Hnylko, 2009): 1 – the Chornohirsky nappe; 2 – the Dukliansky nappe; 3 – the Porkuletsky nappe 4 – the Krosnenska zone, 5 – Ivano-Frankivsk Oblast.



**Table 1.** Characteristics of survey plots in the Svydovets Massif

Number (according to Fig.1)	Name of the plot	Height (m a.s.l.)	Type of soil, pH	Samples of vegetation
1	Apshynets L.	1495	Clayey, pH 5.5–6.5	common tormentil, willow gentian
2	Vorozheske Lake L. l.	1450	Sandy-loamy and loamy, pH 4.5–6	alpine juniper
3	Vorozheske L. s.	1524	Sandy-loamy and loamy, pH 3.7–4.5	bog bilberry
4	Herashaska L.	1583	Sandy-loamy, pH 4.5–6	true sedges
5	Apshynets R.	1659	Sandy-loamy, pH 5.3–6.5	European blueberry
6	Herashaska Pol.	1633	Sandy-loamy, pH 4.9–6	bog bilberry, alpine juniper
7	Svydovets s.	1133	Loamy, pH 6.5–7	European silver fir
8	Drahobratske L.	1400	Loamy, pH 5.5–6	willow gentian, true sedges
9	Zhuravlyna B.	1470	Loamy, pH 3.7–4.5	alpine juniper

Ti, V, Cr, Mo, W, Zr, Hf, Rb, Ta, Cu, Pb, Ag, Sb, Bi, Zn, Cd, Sn, Ge, Ga, Be, Sc, Ce, La, Y, Yb, Th, As, Ba, Li, P, but only the group comprising Mn, Ni, Co, V, Cr, Zr, Cu, Pb, Zn, Ba, P was analyzed, because the content of other elements in ash of plants was lower than analysis sensitivity. For each plot, we determined the average content of the abovementioned elements, and determined the average content for all the plots (Table 2).

Comparing the average content of chemical elements with Clarke number of soils around the world, we determined: Ba, Pb – concentration in soils of the Massif exceeded average values 1.7–1.9; Co, Cr, Ni was 10 times lower; Mn, V, Cu, Zr – twice as low; Zn, P – almost the same. Such content of the elements is related to the regional geochemical background of Ca-poor soils.

To assess the soils of the Svydovets Massif, we determined the background content of chemical elements, making further calculations according to this parameter. We determined that concentrations of Mn, Ba, P were twice as low as the background regional content in all the plots, whereas in the plots of Vorozheske L. l. and Vorozheske L. s. the concentrations exceeded it by two times. This is related to the fact that the soils in the plots of Vorozheske Lake are sandy-loamy and loamy, significantly moistened, i.e. as the level of hydromorphism heightens, the amount of microelements in them increases as well. At the same time, in the conditions of regular outwash regime, metals are driven away from the profile of soils (the Apshynets R.), leading to decrease in their total content. Having calculated the concentration coefficient (Kc), we determined the distribution of chemical elements in the surveyed soils concerning the back-

ground content: the Apshynets R.  $(\text{Pb, Zn, Ba, Cr})_{0.5}$ ; the Herashaska Pol.  $(\text{V, Cr, Zn, Ba, P})_{0.5}$ ; Drahobratske L.  $\text{Zn}_{1.5} > \text{Cu}_1$ , Apshynets L.  $(\text{Pb, Zr, Co, V, Cr})_1$ , the Svydovets s.  $(\text{Pb, Zn, Ba, Cr})_{1.5} > (\text{Cu, P})_1$ , Herashaska L.  $(\text{Pb, Zr, Cr, V, Co})_1$ , the Zhuravlyna B.  $(\text{P, Co, Ni})_2 > \text{Cu}_1$ , Vorozheske L. l.  $(\text{Mn, Ba, Cr, Zr, Cu, Ni, Co})_2 > (\text{Pb, Zn, P})_1$ , Vorozheske L. s.  $(\text{Mn, Ba, Cr, Zr, Cu, Ni, Co})_2 > (\text{Pb, Zn, P})_{1.5}$ . This allowed us to determine that maximum concentration of all chemical elements is characteristic of the plots of Vorozheske L.

The optimum indicator for comparing geochemical peculiarities of non-contaminated soils is the total concentration coefficient ( $\Sigma Kc$ ). Calculation of this parameter allows us to calculate the total concentration of chemical elements in soils of the plots (from lower to highest): the Apshynets R. – the Herashaska Pol. – Drahobratske L. – Svydovets s. – Apshynets L. – Herashaska L. – the Zhuravlyna B. – Vorozheske L. s. – Vorozheske Lake L. (Fig. 3).

We determined that with increase in pH from 4 to 7, the total concentration of chemical elements decreased (23 to 4). When the plots were identical according to the type of soil – brown mountain earth, it was related to the type of soil – in case of loamy types (the Vorozheske lakes l. and s.), there occurred concentration of chemical elements, while in sandy-loamy ones (the Apshynets R. and the Herashaska Pol.) – dispersion.

**Biogeochemical survey.** Biogeochemical surveys were made according to chemical composition of parts of plants (Table 2), and their interpretation by calculating coefficients of biological absorption ( $A_x$ ) and biogeochemical activity of species, allowed us to determine the overall effect of accumulation of microelements in the plants and determine the

**Table 2.** Total content of microelements in soils and ash of vegetation of the Svydovets Massif, mg/kg

Chemical elements	Numbers of the plots (according to Fig.1, Table. 1)									Back-ground in the region	Clarke number of soils around the world [1]
	1	2	3	4	5	6	7	8	9		
	soils										
Mn	100	500	600	200	80	100	100	150	60	210	850
Ni	10	40	60	10	5	8	10	5	40	21	40
Co	3	5	6	3	1	1	2	1	5	3	8
V	30	80	80	40	20	10	30	10	20	36	100
Cr	30	80	100	40	20	10	30	10	10	37	200
Zr	200	400	400	300	80	100	100	100	60	193	300
Cu	10	80	80	10	10	10	40	20	30	32	20
Pb	20	25	18	18	15	18	12	8	12	16	10
Zn	20	50	50	20	20	20	20	50	20	30	50
Ba	100	300	200	100	90	90	100	100	100	131	500
P	200	500	500	200	200	200	400	200	500	322	800
	vegetation										
Mn	600	400	5000	5000	5000	4000	5000	500	5000	3389	7500
Ni	10	50	5	6	50	80	80	4	30	35	50
Co	2	6	2	1	6	10	8	1	4	4	15
V	3	3	2	3	5	6	2	5	4	4	61
Cr	3	6	5	2	5	5	5	5	5	5	250
Zr	10	20	20	30	30	20	40	20	30	24	5
Cu	30	80	80	20	50	60	100	30	60	57	200
Pb	1	10	10	4	6	20	5	5	6	7	10
Zn	50	100	100	50	100	400	100	100	100	122	900
Ba	100	500	600	300	100	300	400	100	100	278	100
P	10000	10000	8000	3000	10000	8000	10000	8000	10000	8556	70000

Note. Species of plants (plots – numbers of the columns, according to Table 1.): 1– willow gentian, 2– alpine juniper, 3 – bog bilberry, 4 – true sedges, 5 – European blueberry, 6 – alpine juniper, 7 – European silver fir, 8 – true sedges, 9– alpine juniper

main differences in intensity of involvement of microelements in biological circulation by different species of plants (Table 3).

We determined that wild-growing shrubs (bog bilberry, European blueberry, alpine juniper) actively absorb Mn, P (and intensely absorb Co, Cu, Zn, Ba from the soils (except the plots of Vorozheske L. l. and the Vorozheske L. s., which is explained by presence of loamy soils, where it is hard for the roots of plants to adjust the element into available form. Herbaceous plants actively and intensely accumulated Mn P Cu. It is noteworthy that only in the Herashaska Pol. did the wild-growing shrubs - bog bilberry and alpine juniper concentrate Mn P Zn Ni, Co, Cu. On that plot, there are sandy-loamy moistened soils. In such conditions, chemical elements turn into a form which is available to plants.

We may draw a general conclusion that all the plants (regardless of growing location) actively and

intensely absorb P and Mn, and furthermore the element which common tormentil accumulated was Cu, alpine juniper concentrated Zn, European silver fir – Ni, and for bog bilberry, European blueberry, willow gentian and true sedges the crucial role was played particularly by the growing location (composition of soils, pH).

It was important to determine the extent of uptake of metals Ni, Co, Cu, Zn, Ba, Pb by one type of vegetation at different plots, and therefore we compared and developed graphs for visual evidences (Fig. 4).

The obtained data indicate that wild-growing shrubs (bog bilberry, European blueberry, alpine juniper) are characteristic of intense biological uptake of Ni, Co, Cu, Zn, Ba, Pb, though in the plot of the Herashaska Pol., Zn was the element of active consumption (Ax equaling 20–25) by bog bilberry and alpine juniper. As for herbaceous plants, Ax value for all the

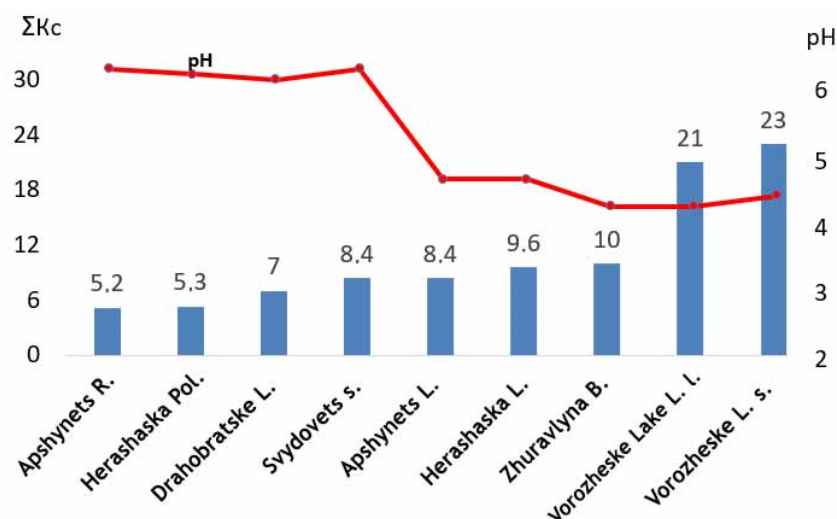
**Table 3.** Coefficients of biological accumulation in (Ax) and biogeochemical activity (BCA) of different species of plants in the Svydovets Massif

Name of the plot	Elements of biological accumulation (Ax)		Elements of biological absorption (Ax)	BCA
	active	intense	average	P Mn, Cu, Zn, Ba, Ni, Co, V, Cr, Zr, Pb, Bi
	10n і більше	10– n	0, n	
Wild-growing shrubs				
bog bilberry				
The Herashaska Pol.	Mn <sub>50</sub> >P <sub>40</sub> > Zn <sub>25</sub> > (Ni, Co, Cu) <sub>10</sub>	Cr, Pb, Ba	V, Zr	153,1
Vorozheske L. s.	P <sub>16</sub>	Mn, Cu, Zn, Ba	Ni, Co, V, Cr, Zr, Pb	31,1
European blueberry				
The Apshynets R.	Mn <sub>60</sub> > P <sub>50</sub> > Ni <sub>10</sub>	Co, Cu, Zn, Ba	V, Cr, Zr, Pb	141,2
The Svydovets s.	(Mn, P) <sub>20</sub>	Zn, Ba	Cu, Ni, Co, V, Cr, Zr, Pb	47,7
alpine juniper				
The Zhyravlyne B.	Mn <sub>83</sub> > P <sub>20</sub>	Cu, Zn, Ba	Ni, Co, Pb, V, Cr, Zr	114,2
Vorozheske L. l.	P <sub>20</sub>	Ni, Co, Cu Zn, Ba	Mn, V, Cr, Pb	28,4
The Herashaska Pol.	(Mn, P) <sub>40</sub> > Zn <sub>25</sub> > (Ni, Co) <sub>10</sub>	Cu, Pb, Ba	V, Cr, Zr	132,5
Herbaceous plants				
common tormentil				
Apshynets L.	Mn <sub>50</sub> > P <sub>50</sub> > Cu <sub>10</sub>	Zn, Ba	Ni, Co, V, Cr, Zr, Pb, Bi	115,7
willow gentian				
Drahobratske L.	P <sub>50</sub>	Mn, Ni, Co, Cu, Bi, Zn, Ba	V, Cr, Zr, Pb	71,1
Apshynets L.	P <sub>50</sub>	Mn, Ni, Cu, Zn, Ba	Co, Pb	64,5
true sedges				
Herashaske L.	Mn <sub>25</sub> >P <sub>15</sub>	Cu, Zn, Ba	Ni, Co, Pb, V, Cr, Zr, Bi	48,8
Drahobratske L.	P <sub>40</sub>	Mn, Co, Cu, Bi, Zn, Ba	Ni, V, Cr, Zr, Pb	51
Trees				
European silver fir				
Svydovets s.	Mn <sub>50</sub> > P <sub>20</sub>	Cu, Zn, Ba	Ni, Co, V, Cr, Zr, Pb, Bi	99,5

elements equaled 1–5, the exception being common tormentil in the plot of Apshynets L., where consumption of Cu equaled 10. The extent of uptake of chemical elements by European silver fir in the plot of the Svydovets s. was 1–8:  $Ni > Zn > Ba > Co > Cu > Pb$ . We should take into account that this chemical element composition of plants which grow in the protected territories may be an etalon for comparison with other plants.

Regardless of the growing location, herbaceous plants - true sedges (Herashaska L., pH 4.5, Drahobratske L., pH 6.3) and willow gentian (Apshynets L., 4.5 and Drahobratske L., pH 6.3) have close values of BCA: true sedges – 47–49, willow gentian – 64–71, common tormentil – 115. For wild-growing

shrubs (bog bilberry, European blueberry, alpine juniper), BCA significantly varied. Therefore, BCA of alpine juniper was 28.4 at the Vorozheske L. (l), whereas in the Herashaska Pol. it was 132.5, i.e. 4 times greater. Bog bilberry of Vorozheske L. (s.) was seen to have BCA of 31.1, whereas in the Herashaska Pol. it equaled 153.1; for European blueberry it was 47.7 in the Svydovets s., and 141.2 in the Apshynets R.; BCAs of alpine juniper were similar in the Zhyravlyna B. and the Herashaska Pol. equaling 114.2 and 132.5 respectively, while accounting for 28.4 at Vorozheske L.(l). As for the trees, BCA of European silver fir was 99.5. We can see that for herbaceous plants, there is a BCA sequence of true sedges–willow gentian– common tormentil. For wild-grow-

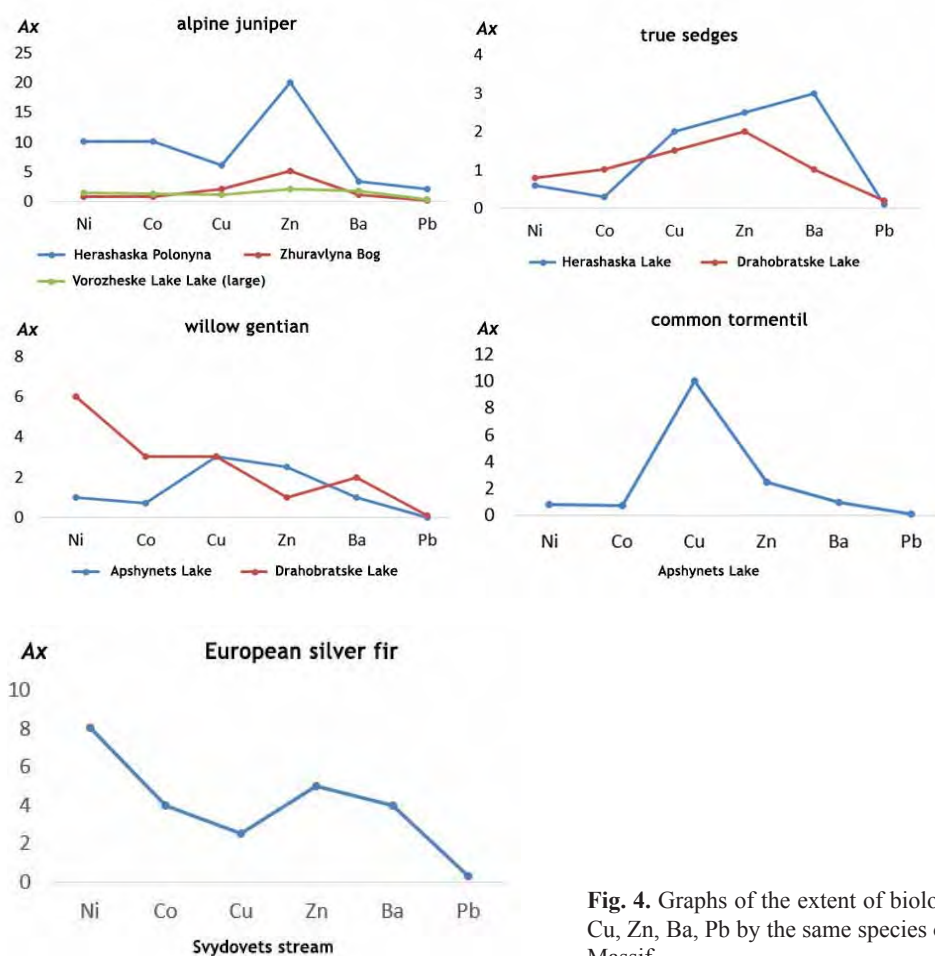


**Fig. 3.** Diagram of values of the total concentrations coefficient ( $\Sigma K_c$ ) of chemical elements (Mn, Ni, Co, V, Cr, Zr, Cu, Pb, Zn, Ba, P) and pH of soils in the study plots

ing shrubs, the sequence is impossible to determine according to BCA due to large differences between the values for various plots.

*Microelements.* Specificity of the element composition of plants determines the possibility of their use as medicinal raw material. The plants we examined are used in folk medicine (Yakovlev, 2015). For

example, one of the most important properties of bog bilberry (berries, leaves) is the ability to mitigate allergy, it has anti-atherosclerotic and anti-ulcer effects; European blueberry (berries and leaves) has antioxidants which affect malignant tumours, cleanses the intestines from salts and metals; common tormentil is used for treatment of dysentery, abscess, hemorrhoids,



**Fig. 4.** Graphs of the extent of biological uptake (Ax) of Ni, Co, Cu, Zn, Ba, Pb by the same species on the plots of the Svydovets Massif



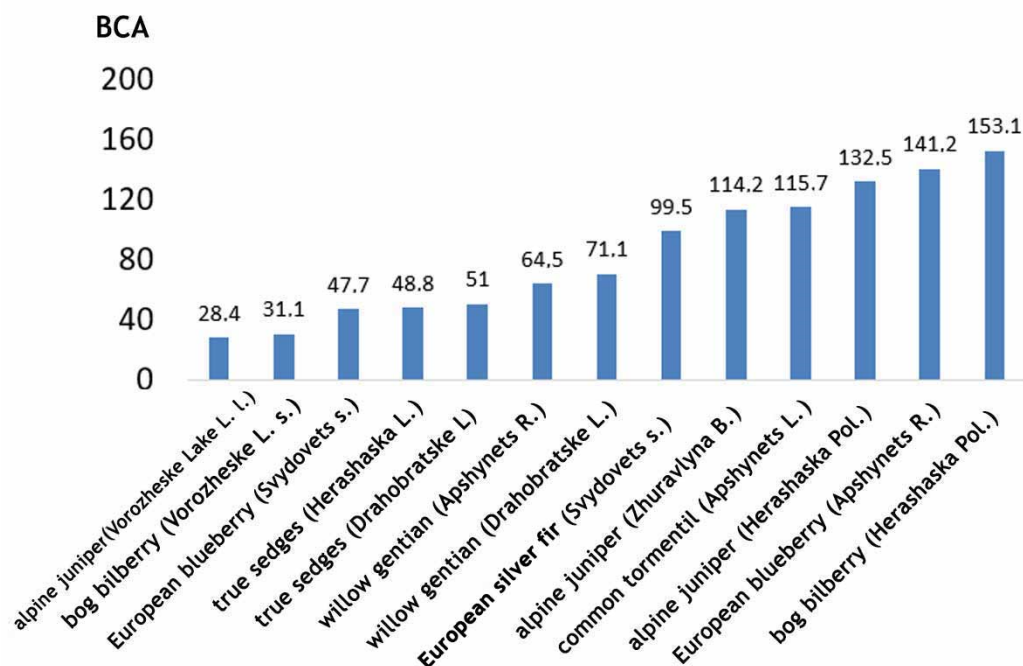


Fig. 5. Diagrams of biogeochemical activity of plants (BCA) in the plots of the Svydovets Massif

has bactericidal, binding and blood-stopping properties, because it reduces penetrability of the capillaries and narrows the vessels; willow gentian has antiseptic, anti-parasitic, diuretic properties; alpine juniper is used to obtain essential oil from the fruits, branches and needles, has toning, generally strengthening, anti-inflammatory, expectorant effect; true sedges are used as diuretic, anesthetic, anti-inflammatory preparation; European silver fir – tincture of needles removes accumulated harmful substances from the organism, is used to treat diseases of the respiratory tracts, strengthening the immune system.

However, a special role in the normal functioning of all physiological systems of the organism belongs to microelements contained in at least 2,000 enzymes which catalyze many chemical reactions in the organism. Deficiency, excess or dysbalance of microelements is called microelementosis (Bardov, 2006). Microelement correction in contemporary practical medicine is becoming more and more popular among people who are convinced of the vital necessity of replenishing deficiency in microelements for successful treatment of patients.

We analyzed the content of microelements – Zn, Cu, Co in plants of surveyed plots for possibility of recommendations concerning their balance in the organism.

**Zinc.** The daily need of a human for zinc is 12–16 mg for adults and 4–6 mg for children (3). The largest amount of zinc among food products is seen in groats: buckwheat – 14.9 mg/kg, wheat groats – 13.7 mg/kg; in vegetables: garlic – 6.7 mg/kg, beet – 3.9 mg/kg

(Ivanov, 1994). Deficiency of zinc is accompanied by growth retardation, over excitement of the nervous system and rapid onset of fatigue.

We determined that the zinc concentrators are the plants in the Herashaska Pol. – alpine juniper and bog bilberry – 400–500 mg/kg (at background – 60 mg/kg), whereas the amount of zinc in these plants in the plots of the Vorozheske L. l. and the Vorozheske L. s. was equal – 70 mg/kg (Fig. 6 a).

We calculated the conditionally sufficient norm for supply of the zinc balance (plants of the Svydovets) for one adult per day: 30 g of bog bilberry would be needed from the Herashaska Pol., and 160 g from Vorozheske L.; as for alpine juniper – 40 g of the plant from the Herashaska Pol., while 160 g of the ones from the Vorozheske L.

**Copper.** Daily copper requirement of the adult organism is 1.5 mg (Bardov, 2006). In plant products the content of copper is 1–10 mg/kg: buckwheat groats – 6.4 mg/kg, oat groats – 5 mg/kg, walnuts – 7.5 mg/kg, beans – 6.8 mg/kg (Ivanov, 1994).

Copper content in plants of the Svydovets Massif varied insignificantly: lowest was seen in true sedges and European blueberry – 20–30 mg/kg, in willow gentian and alpine juniper it accounted for 30–60 mg/kg; maximum – in bog bilberry, common tormentil and European silver fir, equaling 80–100 mg/kg (Fig. 6 b). Thus, the main role belongs to selectivity of plants regarding copper, while growing location is not significant. We estimated that for support of daily balance of copper of one adult, 20 g of bog bilberry, common tormentil and European silver fir, collected

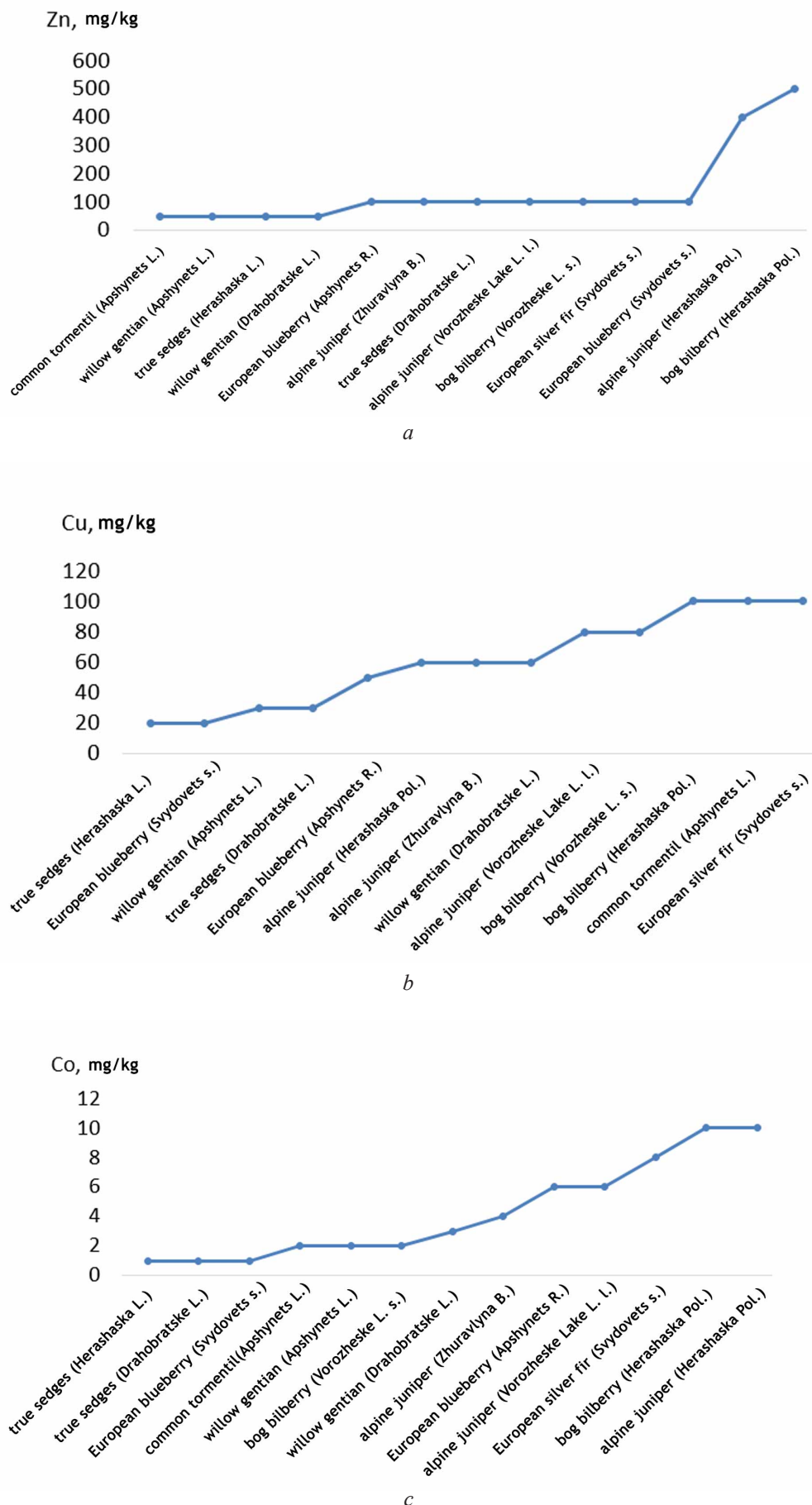


Fig. 6. Graphs of content of Zn, Cu, Co metals in plants of the plots of the Svydovets Massif

from any plots on the Svydovets Massif are needed, whereas other plants would be needed in amount of 70–100 g.

**Cobalt.** The content of cobalt in plants of the Svydovets Massif slowly increased from true sedges (Herashaske and Drahobratske lakes) – 2 mg/kg to alpine juniper and bog bilberry of the Herashaska Pol. – 10 mg/kg (Fig. 6c). For the Heraska Pol., sandy-loamy soil was typical, pH 4–6, and these conditions were optimum for accumulation of cobalt by plants.

Cobalt is a constituent of vitamin B12, the content of which in the human organism reaches 5 mg. The daily requirement for cobalt is 0.1–0.8 mg (Bardov, 2006). Cobalt content in plant products, mg/kg: walnut – 0.15; beet – 0.12 mg/kg; strawberry – 0.9 mg/kg (Ivanov, 1994). By calculating the norm of cobalt for one adult, we determined that 30 g of alpine juniper and bog bilberry from the plot of the Herashaska Pol. would be needed, while other plants would be needed in the amount of 100–300 g.

Finally, we would like to note that correction of microelement deficiency using plant supplements needs to be performed individually, considering specifics of the organism.

## Conclusions.

The research allowed us to find biogeochemical properties of uptake of chemical elements (Mn, Ni, Co, V, Cr, Zr, Cu, Pb, Zn, Ba, P) by wild-growing vegetation (shrubs, herbaceous plants and trees – European silver fir) on nine plots of the Svydovets Massif of the Ukrainian Carpathians. We determined the background content of chemical elements and estimated the total concentration of chemical elements in soil plots (from lowest to highest): the Apshynets R. – the Herashaska Pol. – Drahobratske L. – the Svydovets s. – Apshynets L. – Herashaske L. – the Zhuravlyna B. – Vorozheske L. I. – Vorozheske L.s. The soils in the plots of Vorozheske L were found to be sandy-loamy and loamy, highly moistened, i.e. their reserves of microelements increase following increase in the level of hydromorphism. At the same time, in the conditions of periodic wash-out regime, the metals are driven away from the soil profile (the Apshynets R.), and thus their overall content decreases. We determined that the extent of the influx of the elements to plants depends on the overall content of the elements in the soil. Using the coefficient of biological absorption, we determined that all the plants (regardless of their growing location) actively and intensely absorbed P and Mn from the soils, for common tormentil the element of accumulation was Cu, alpine juniper – Zn, European silver fir – Ni; for

bog bilberry, European blueberry, willow gentian and true sedges the important factor was growing location (composition of soils, pH of environment). We determined that for wild-growing herbaceous plants the biogenic activity of species increases in the sequence: true sedges– willow gentian– common tormentil; for wild-growing shrubs (bog bilberry, European blueberry, alpine juniper) such a sequence is impossible to determine in spite of great differences between different plots. We determined the medicinal role of each plant to treat microelement deficiency in Cu, Zn, Co. We determined that on the plot of the Herashaska Pol. the branches of alpine juniper contain maximum amount of Zn and Co, the branches and leaves of bog bilberry – Cu, Zn, Co; the flowers and leaves of common tormentil from Apshynets L. and European silver fir near the Svydovets s. – Cu. We determined the daily dose of each element according to species of plants to overcome microelementosis. The results of the studies on biogeochemical peculiarities of accumulation of chemical elements by vegetation of the Svydovets Massif of the Ukrainian Carpathians may be the basis for identification and recommendation of plants as medicinal, and also monitoring geochemical surveys to predict the use of plants to overcome microelementosis among the population.

## References

- Alekseenko, V.A., 2000. *Ekologicheskaya geohimiya* [Ecological geochemistry]. Moscow: Logos, 626. ISBN 5-88439-001-7 (in Russian).
- Buts, Yu., 2018. Features of Geochemical Migration of Chemical Elements after Technogenic Loading of Pyrogenic Nature. *Journal of Engineering Sciences*. 5(2), 1–4. Doi:10.21272/jes.2018.5(2).h1
- Bardov, V.H., 2006. *Hihiiena ta ekolohiia* [Hygiene and ecology]. Vinnytsia: New Book, 719 (in Ukrainian).
- Ivanov, V.V., 1994. *Ekologicheskaya geohimiya elementov* [Ecological geochemistry of elements]. Moscow: Bosom, 4, 409. ISBN 5-7120-0647-2 (in Russian).
- Gerenchuk, K.I., 1981. *Pryroda Zakarpatskoi oblasti* [Nature of Transcarpathian region]. Lviv: High school, 156 (in Ukrainian).
- Hazrat, A., Ezzat, K., Ikram, I., 2019. Environmental Chemistry and Ecotoxicology of Hazardous Heavy Metals: Environmental Persistence, Toxicity, and Bioaccumulation. *Journal of Chemistry*. 1–14. Doi: 10.1155/2019/6730305
- Kabata-Pendias, A., Pendias, H., 1989. *Mikroehlementy v pochvakh i rastenyakh* [Trace elements in soils



- and plants]. Moscow: World, 439 (in Russian).
- Klos, V.R., Birke, M., Zhovinsky, E.Ya., 2012. Rehionalni heokhimichni doslidzhennia gruntiv Ukrainy v ramkakh mizhnarodnoho proektu z heokhimichnoho kartuvannia silskohospodarskykh ta pasovyshchnykh zemel Yevropy (GEMAS) [Regional geochemical studies of soils of Ukraine within the framework of the international project on geochemical mapping of agricultural and pasture lands of Europe (GEMAS)]. Exploration and Ecological Geochemistry. 1, 51–67 (in Ukrainian).
- Kryuchenko, N.O., Zhovinsky, E.Ya., Paparyga, P.S., 2018. Rudni ta texnogeni heoximični anomaliji zapovidnyx terytorij Ukraïns'kyx Karpat (na prykladi Karpats'koho biosfernoho zapovidnyka) [Ore and technogenic geochemical anomalies of the nature reserves territories of the Ukrainian Carpathians (on the example of the Carpathian Biosphere Reserve)]. Kyiv: Interservice, 148. ISBN 978-966-02-8453-1 (in Ukrainian).
- Kryuchenko, N.O., Zhovinsky, E.Ya., Paparyga, P.S., 2019. Tekhnohenne zabrudnennia (mikroelementnyi sklad) snihovoho pokryvu hirs'kykh vershyn Karpatskoho biosfernoho zapovidnyka [Technogenic pollution (microelement composition) of snow cover of mountain peaks of the Carpathian Biosphere Reserve]. Geochemistry and Ore Formation. 40, 6–14. Doi: 10.15407/gof. 2019.40.006 (in Ukrainian).
- Kryuchenko, N.O., Zhovinsky, E.Ya., Paparyga, P.S., 2019. Heokhimiia gruntiv Dolyny nartsysiv ta urochyscha Spivakove (Zakarpattia) [Geochemistry of Soils of Narcissus Valley and Spivakovo (Transcarpathia) Tract]. Mineralogical Journal. 41(4), 50–60.. Doi: 10.15407/mineraljournal.41.04.050 (in Ukrainian).
- Kudrevatykh, I., Kalinin, P., Alekseev, A., 2019. Biogenoe nakoplenie himicheskikh elementov rasteniyami rodov *Poaceae* Barnhart i *Artemisia* L. v suhostepnoj i polupustynnoj zonah yuga Russkoj ravniny [Biogenic Accumulation of Chemical Elements by Plants of Genus *Poaceae* Barnhart and Genus *Artemisia* L. in the Dry Steppe and Semi-desert Zones of the South of the Russian Plain]. Siberian Ecological Journal, 12(4), 466–478. Doi:10.1134/S1995425519040061 (in Russian).
- Lang, F., Kruger, J., Chmara, I., 2017. Soil phosphorus supply controls P nutrition strategies of beech forest ecosystems in Central Europe. Biogeochemistry. 136, 5–29. Doi:10.1007/s10533–017–0375–0
- Matskiv, B.V., Pukach, B.D., Vorobkanych, V.M., Pas-tukhanova, S.V., Hnylko, O.M., 2009. Derzhavna heolohichna karta Ukrainy masshtabu 1:200 000, Karpatska seriia. [State Geological Map of Ukraine scale 1: 200 000. Carpathian series]. Kyiv: UkrDHRI, 1 (in Ukrainian).
- Palutoglu, M., Akgul, B., Suyarko, V., Yakovenko, M., Kryuchenko, N., Sasmaz, A., 2018. Phytoremediation of Cadmium by Native Plants Grown on Mining Soil. Bulletin of Environmental Contamination and Toxicology, 100(2), 293–297. Doi: 10.1007/s00128–017–2220–5.
- Samofalova I.A., 2009. Himicheskij sostav pochv i pochvoobrazuyushchih porod [The chemical composition of soils and parent rocks]. Perm: Perm State Agricultural Academy, 132 (in Russian).
- Suschik, Yu.Ya., 1978. Geochemistry of the hypergenesis zone of the Ukrainian Carpathians [Geochemistry of the hypergenesis zone of the Ukrainian Carpathians]. Kiev: Scientific Thought, 210 (in Russian).
- Vovk, O., Orlov, O., 2014. Gruntove riznomanittia oselyshch (habitats) ukrains'kykh Karpat i perspektyvy yoho okhorony [Soil diversity of habitats of Ukrainian Carpathians and prospects for its protection]. Biological Studies. 8(3–4), 157–168 (in Ukrainian).
- Wang, S., Wu, W., Liu, F., Liao, R., Hu, Y., 2017. Accumulation of heavy metals in soil-crop systems: a review for wheat and corn. Environmental Science and Pollution Research, 24(18), 15209–15225. DOI: 10.1007/s11356-017-8909-5
- Yakovlev, G.P. (Ed.), 2015. Bol'shoj enciklopedicheskij slovar' lekarstvennykh rastenij [Great Encyclopedic Dictionary of Medicinal Plants]. St. Petersburg: SpecLit, 762 (in Russian).
- Zhovinsky, E.Ya., Kryuchenko, N.O., 2014. Osnovy poiskovoj i ekologicheskoy geohimii [Fundamentals of exploratory and environmental geochemistry]. Mineralogical Journal. 36(3), 7–11 (in Russian).
- Zhovinsky, E.Ya., Kryuchenko, N.O., Paparyga, P.S., 2013. Geochemistry of the Environmental Objects of the Carpathian Biosphere Reserve. Kyiv: Interservice, 100. ISBN 978-966-02-6957-6
- Zhovinsky, E.Ya., Kuraeva, I.V., 2002. Geohimiya tyazhelykh metallov v pochvah Ukrainy [Geochemistry of Heavy Metals in Soils of Ukraine]. Kiev: Scientific Thought, 213. ISBN 966-00-0761-2 (in Russian).