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ПРОСТРАНСТВЕННАЯ ИЗМЕНЧИВОСТЬ СОДЕРЖАНИЯ ТЯЖЕЛЫХ МЕТАЛЛОВ В МАКРОФИТАХ ОЗЕР БЕЛАРУСИ

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Проанализирована пространственная дифференциация концентрации тяжелых металлов (Ti, V, Cr, Mn, Ni, Cu, Pb) в высшей водной растительности озер Беларуси. Данные о содержании элементов в макрофитах Беларуси сопоставимы с показателями, полученными в Польше и других соседних странах. Озерным растениям свойственна избирательность в накоплении металлов, различающаяся для экологических групп погруженных, надводных растений и макрофитов с плавающими листьями. Установлены статистически значимые отличия между бассейнами рек по содержанию Mn, Cu, Pb в погруженных макрофитах озер. Наибольшими концентрациями Mn в тканях макрофитов всех экологических групп характеризуются бассейны рек Днепр, Припять, Западный Буг, наименьшими – р. Березины. Наименьшее количество Pb обнаружено в водных растениях озер бассейнов рек Западный Буг и Днепр. Водные растения озер различной степени трофности отличаются на статистически значимом уровне по содержанию Mn и Cu, наименьшие концентрации Mn в тканях макрофитов характерны для мезотрофных озер с признаками олиготрофии. С помощью пространственного кластерного анализа выделены восемь групп озер по содержанию Mn, Cu и Pb в высшей водной растительности. Группа озер Браславского района характеризуется повышенным содержанием Mn и Cu в тканях макрофитов, озера бассейна р. Вилии отличаются наименьшей среди других групп средней концентрацией Cu и Pb в водных растениях, озера северной части Беларуси выделяются повышенным содержанием Cu и Pb в тканях растений.

Ключевые слова: тяжелые металлы; высшая водная растительность; экологические группы; пространственная изменчивость; мониторинг; трофический статус озер.

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SPATIAL VARIATIONS OF TRACE ELEMENTS CONTENTS IN MACROPHYTES WITHIN BELARUSIAN LAKES

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The spatial variation of trace elements contents of heavy metals (Ti, V, Cr, Mn, Ni, Cu, Pb) in higher aquatic plants of Belarusian lakes has been analyzed according to monitoring data. Natural variability limits of metals contents in aquatic plants of lakes within principal rivers basins of Belarus have been determined. The data on trace elements contents in macrophytes of Belarus are comparable with the data obtained in Poland and other neighbouring countries. Aquatic plants in lakes are characterized by selective metals accumulation, which is different for ecological groups of submersed, emergent and macrophytes with floating leaves. Statistically significant differences between river basins in the contents of Mn, Cu and Pb have been established in the submersed macrophytes. For all ecological groups, the highest concentrations of Mn in lakes macrophytes tissues are observed in the basins of the Dniapro, Prypiać, Zachodni Buh, and the lowest – the Biarezina. The lakes of the Zachodni Buh and Dniapro basins are distinguished by lower Pb concentrations in aquatic plants. Significant differences in the content of Mn and Cu in the plant tissues within different trophicity lakes have been established. The lowest concentrations of Mn are observed in mesotrophic lakes with signs of oligotrophy. Group analysis of lakes based on the content of Mn, Cu, Pb in macrophyte tissues and spatial constraints has been performed. Among the allocated groups are the lakes of the Braslav district characterized by elevated content of Mn and Cu; lakes of the Vilija basin, distinguished by the lowest average levels of Cu and Pb; lakes of the northern part of Belarus, notable for increased contents of Cu and Pb.

Keywords: trace elements; higher aquatic plants; ecological groups; spatial variability; monitoring; lakes trophic level.

Introduction

Aquatic macrophytes may accumulate chemical elements in concentrations exceeding their content in the environment. The concentrations of chemical elements in aquatic plants can be more than 100 000 times higher than in the associated water [1]. This accumulation activity determines their use in the system of monitoring higher aquatic plants and monitoring the state of water bodies in the National Environment Monitoring System of the Republic of Belarus. A major limit to use macrophytes as bioindicators is the variability of elements in the organisms. The most important causes of the variability are a seasonal cycle, the biological state of organisms (species, size, age, and probably growth rate) and physical environment [2]. Chemical composition of water and bottom sediments is the result of climatic, hydrological, mechanical, physical, chemical, biological and others processes occurring both on the catchment area and in the reservoir itself. The aim of this paper is to identify the spatial characteristics of trace elements (Ti, V, Cr, Mn, Ni, Cu, Pb) accumulated by aquatic plants in Belarusian lakes.

Materials and methods

In the present study we have used data from the National Environment Monitoring System. The accumulation of heavy metals by higher aquatic plants within Belarus reservoirs and lakes from 2000 to 2015 has been analyzed. A monitoring network on lakes includes 46 key sites (fig. 1). The representativeness of the network is ensured by the monitoring objects distribution in accordance with the lake percentage and physiographic zoning of Belarus. The lakes differ in the hollows origin, morphometry, and degree of overgrowing.

Bottom sediments in macrophytes growing locations are mainly represented by sand and silted sand in littoral zones and deeper sandy silts. The samples were formed from macrophytes tissues of various ecological groups and have been considered in this study: emergent (*Acorus calamus* L., *Phragmites australis* (Cav.) Trin. ex Steud., *Carex rostrata* Stokes, *Carex lasiocarpa* Ehrh. and *Carex acuta* L., *Sparganium erectum* L., *Sparganium natans* L., *Glyceria maxima* (O. Hartm) Holmb, *Glyceria fluitans* (L.) R. Br., *Cladium mariscus* (L.) Pohl, *Schoenoplectus lacustris* (L.), *Scirpus sylvaticus* L., *Typha angustifolia* L., *Typha latifolia* L., *Sagittaria sagittifolia* L., *Butomus umbellatus* L., *Equisetum fluviatile* L., *Zizania palustris* L., *Zizania latifolia* (Griseb.) Stapf, *Alisma plantago-aquatica* L.); submersed (*Hydrilla verticillata* (L. fil.) Royle, *Potamogeton lucens* L., *Potamogeton perfoliatus* L., *Potamogeton trichoides* Cham. et Schlecht., *Potamogeton praelongus*

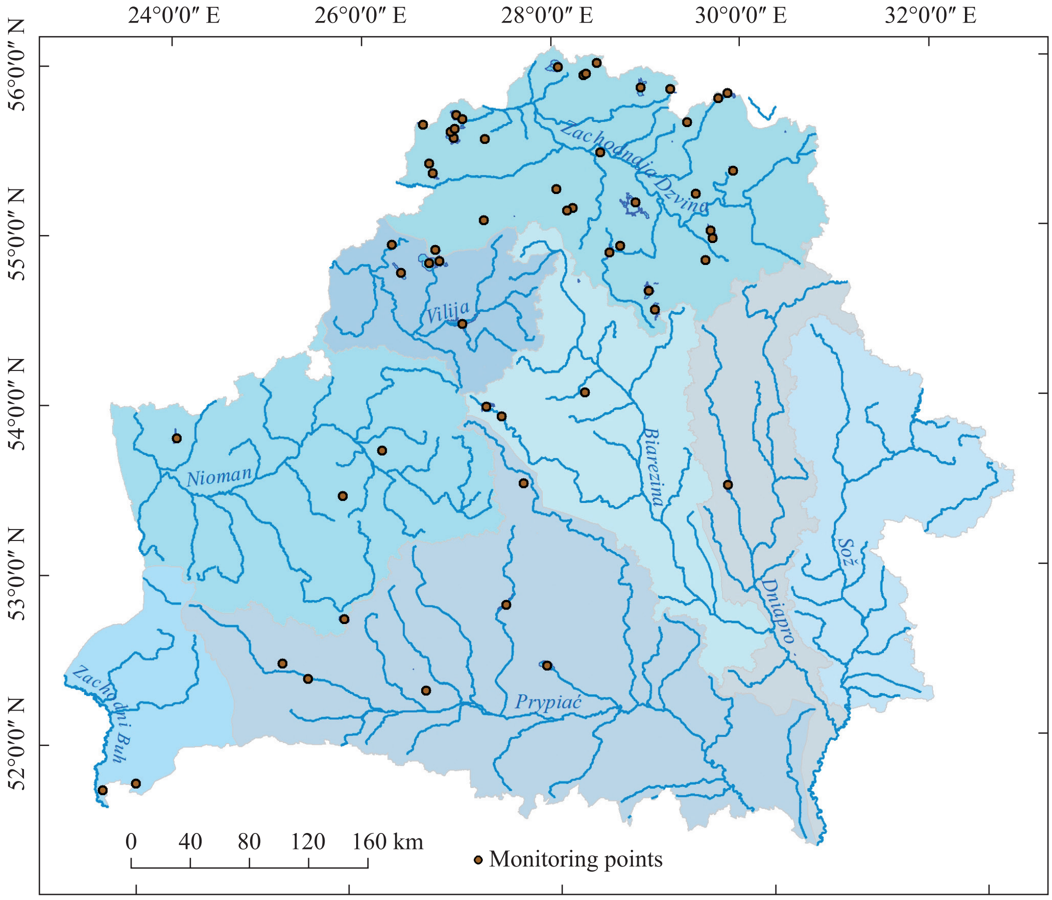

Fig. 1. Macrophyte sampling locations

Wulf., *Potamogeton crispus* L., *Potamogeton acutifolius* Link, *Potamogeton compressus* L., *Potamogeton obtusifolius* Mert. et Koch, *Potamogeton nodosus* Poir., *Potamogeton* friesii Rupr., *Myriophyllum spicatum* L., *Myriophyllum verticiliatum* L., *Elodea canadensis* Michx., *Ceratophyllum submersum* L., *Ceratophyllum demersum* L., *Stratiotes abides* L., *Isoetes lacustris* L., *Litorella uniflora* (L.) Aschers); floating-leaved (*Persicaria amphibian* (L.), *Nuphar lutea* (L.) Smith., *Nymphaea candida* J. et C. Presl., *Potamogeton natans* L.). Charophyta, which are often referred to as higher aquatic vegetation.

The time of sampling corresponds to maximum biomass development and chemicals accumulation by plants during the flowering period (July – August).

Analytical determination of trace elements (Ti, V, Cr, Mn, Ni, Cu, Pb) is performed by emission spectral analysis methods described by Zyrin, Obukhov [3].

For the analysis and visualization of spatial variability of trace elements contents in lake macrophytes, ArcGIS 10.3 geographic database has been designed and developed. Vectors datasets have been created based on OpenStreetMap data[1]. Point feature class «lakes_monitoring» contains characteristics of monitoring points. The relationship class has been created to associate a table with data on trace elements contents in macrophytes and the «lakes monitoring» feature class. Watersheds of principal rivers within Belarus have been identified based on SRTM digital relief model[2] using ArcGIS Hydrology tools.

Statistical data analysis includes the variable distribution assessment with the help of histograms, normal quantile – quantile (Q – Q) plots and fitting criterions (the Kolmogorov – Smirnov test, the Shapiro – Wilk test), as well as data transformation, calculating descriptive statistics, the Kruskal – Wallis test which is the most effective for samples with a markedly different number of observations. For the lognormal (ln) distribution, the geometric mean (g) is taken as the average. In the case of truncated samples, with frequency of trace elements occurrence more than 50 % the median is used as the average. The level of significance is set at $p \leq 0.01$ (two-tailed).

[1]Download OpenStreetMap data for this region: Europe [Electronic resource]. URL: http://download.geofabrik.de/europe.html (date of access: 11.01.2019).

[2]SRTM data // CGIAR – Consortium for Spatial Information (CGIAR-CSI) [Electronic resource]. URL: http://srtm.csi.cgiar.org/srtmdata/ (date of access: 11.01.2019).

Cluster analysis of the examined lakes on the base of trace elements contents in macrophyte tissues and spatial limitation has been performed using the ArcGIS Grouping Analysis tool (uses a K-means algorithm).

Distribution parameters of trace elements in lakes macrophytes are compared in terms of principal Belarusian river basins by ecological groups of aquatic plants: submersed, floating-leaved, emergent.

Results and discussion

Geochemical features of aquatic plants are largely determined by their membership in ecological groups, among which systematic differences can appear [4]. Data analysis has shown that the average elemental contents are different in aquatic plants groups. The highest concentrations of all analyzed elements are characteristic of submersed macrophytes (table 1).

Such a high accumulation capability of submersed macrophytes in relation to trace elements was noted by many authors [5; 6]. Submersed plant leaves have a very thin cuticle. The leaves of submersed plants are therefore very good at taking up metals directly from the water [7].

Table 1

Metals contents in macrophytes of various ecological groups within reservoirs

Element (frequency, %)	Submersed, mg/kg ($n = 305$)	Floating-leaved, mg/kg ($n = 132$)	Emergent, mg/kg ($n = 320$)
Ti (51–67)	4.3 (n. d. – 973)	1.28 (n. d. – 305)	1.18 (n. d. – 184)
V (30–39)	5.37 (n. d. – 141)	2.01 (n. d. – 19.0)	2.34 (n. d. – 19.3)
Cr (23–42)	4.32 (n. d. – 94.2)	0.58 (n. d. – 7.32)	0.85 (n. d. – 14.8)
Mn (100)	296 (0,60–9158)	101.4 (0.23–3957)	23.1 (0.03–3259)
Ni (23–40)	1.18 (n. d. – 23.6)	0.094 (n. d. – 0.87)	0.39 (n. d. – 23.3)
Cu (100)	2.25 (0.07–235.6)	0.32 (0.07–12.2)	1.37 (0.05–76.1)
Pb (100)	2.93 (0.08–471.2)	0.39 (0.04–18.3)	0.42 (0.03–93.1)

Note. N. d. means not detected.

Ti, V, Mn and Pb concentrations in all examined aquatic plants are within the range described by Markert [8]. Cu and Ni abundance is lower than the average content in a plant. The data on trace elements contents in macrophytes of Belarus are mainly comparable with the data obtained in Poland and other neighboring countries (table 2).

Table 2

Elemental composition of aquatic macrophytes obtained in this study compared with data from [5; 8–14], mg/kg dry wt

Indicator	Ti	V	Cr	Mn	Ni	Cu	Pb
Average contents in plant [8]	0.02–56.0	0.001–10.0	0.02–1.0	1–700	0.4–4.0	5–20	0.1–5.0
Normal level in plant leaves [9]	–	0.2–1.5	0.1–1.5	30–300	0.1–1.5	5–30	5–10
Poland							
Słup Dam Reservoir [10]							
Potamogeton crispus L.	–	–	–	–	5.9	17.5	5.4
Ceratophyllum demersum L.	–	–	–	–	6.9	9.7	5.6
Phragmites communis Trin.	–	–	–	–	5.7–8.0	5.4–12.3	2.6–9.9
Dominickie Lake [11]							
Ceratophyllum demersum L.	–	–	1.4	304	1.28	2.5	16.9
West Poland lakes [12]							
Nymphaea alba	–	–	1.2–4.7	88–247	1.1–1.2	1.7–4.8	8.7–4.8
Nuphar luteum	–	–	1.4–3.1	253–345	1.4–1.6	1.8–2.2	10.5–11.9
Lake Symsar [12]							
Myriophyllum spicatum L.	–	–	3.9	1190	24	4.2	6.0
Nymhaea alba L.	–	–	1.0	510	3.0	0.9	Less 1
Typha angustifolia L.	–	–	3.6	540	23	3.3	15

Ending table 2

Indicator	Ti	V	Cr	Mn	Ni	Cu	Pb
The Russian Federation							
Bugach Lake [13]							
Macrophytes	297	1.71	8.66	407	7.30	50.5	0.57
Ivan'kovskoe Reservoir [5]							
Potamogeton perfoliatus L.	–	2.6	5.0	1240	7.1	8.8	1.4
Ceratophyllum demersum L.	–	0.44	11.8	5260	14	55.3	4.5
Myriophyllum spicatum L.	–	Less 0.45	3.0	2898	1.8	14.5	1.0
Ukraine							
Zaporozhian Reservoir [14]							
Potamogeton perfoliatus L.	–	–	–	960–1830	6.2–19.0	6–18	3.0–6.1
Phragmites austrális	–	–	–	29–112	1.7–4.6	3.1–6.2	0.7–1.3
Belarus							
Lakes and reservoirs							
Potamogeton perfoliatus L.	2.7	3.4	1.8	186	0.41	1.4	1.8
Potamogeton crispus L.	4.0	0.66	1.7	225	0.99	1.8	2.77
Myriophyllum spicatum L.	4.0	5.6	4.7	269	1.15	2.8	4.4
Ceratophyllum demersum L.	1.3	5.4	6.2	702	1.2	3.3	4.3
Nymhaea alba L.	3.0	2.1	0.25	69	0.11	0.28	0.18
Nuphar luteum	0.14	1.6	0.34	79	0.07	0.25	0.18
Phragmites australis	0.05	2.1	0.35	11.8	0.09	2.0	0.49
Typha angustifolia L.	1.47	0.35	0.20	110.0	0.02	1.2	0.17

Non-parametric dispersion analysis of Kruskal – Wallis has been used to compare Mn, Cu and Pb contents (elements with 100 % occurrence) in lake macrophytes. The results of the test demonstrate statistically significant differences between river basins in Mn ($H = 26.7$, df = 6, $p < 0.001$), Cu ($H = 23.3$, df = 6, $p < 0.001$) and Pb content ($H = 31.8$, df = 6, $p < 0.001$) in submersed macrophytes; Mn ($H = 32.7$, df = 6, $p < 0.001$) and Pb ($H = 17.0$, df = 6, $p < 0.009$) content in emergent macrophytes; Mn ($H = 31.2$, df = 6, $p < 0.001$) content in submersed macrophytes with floating leaves.

The highest spatial variations is noted in taking up of Mn by macrophytes (fig. 2). The average Mn content in submerged macrophytes within different catchments ranges from 1736 (the Dniapro River Basin) to 208 mg/kg (the Biarezina River Basin).

A similar pattern of spatial variability for examined trace element contents in lakes macrophytes for all ecological groups has been revealed (fig. 2 and 3). The highest concentrations of Mn in lakes macrophytes tissues are observed in the basins of the Dniapro, Prypiać, Zachodni Buh, and the lowest – in the Biarezina. The lakes of the Zachodni Buh and Dniapro basins are distinguished by the lowest Pb contents in aquatic plants. The average rank variation of Mn, Cu and Pb contents in submersed and emergent macrophytes in river basins is presented in fig. 4 and 5. The analyzed elements are distinguished by the spatial variability nature. Spatial variation of Pb and Cu contents in submersed as well as emergent macrophytes at principal river basins level is similar in nature.

Metals concentration levels in macrophytes depends on a large number of various factors. The chemical composition of aquatic plants reflects the geochemical features of lakes bottom sediments, rocks and soils within catchment areas and it depends on lake morphometrical characteristics and production processes, on tehnogenesis products flow into reservoirs from local sources.

In general, trace elements contents in rocks and soils of Belarus are lower than the average world values. So, Belarusian soils are depleted of Ti, Mn, V, Ni, Cu about 3 times, Cr – 2 times, the Pb content is comparable to Clarke values [15]. In lake sediments elements accumulate in lower concentrations than in soils, with the exception of Mn and Pb. Glacial complexes of the poozersky and pripyat ages [16], as well as poozersko-holocene alluvial, lake-alluvial and aeolian accumulations, holocene alluvial and bog formations prevail among the covering deposits. In some areas, due to a variegated lithological composition, the covering deposits can be characterized by elevated trace elements concentrations [17].

The territory within the Zachodniaja Dzvina River Basin is characterized by the highest lake density. In conditions of a significant vertical dissection of relief the lake hollows have a deep (up to 30–50 m) erosional incision, and the catchments have been developed and plowed up. A lot of allochtonic terrigenous material enters the reservoirs. Silicate type of sedimentation is typical for lakes [18]. The soils within the Zachodniaja Dzvina River Basin are distinguished by the highest concentrations of Cu, Ni, Cr, to a lesser extent Ti, the lowest – Zr [19].

Within the basins of the Vilija and the Nioman as well as the Biarezina (the right tributary of the Dniapro) both low-flowing lakes with organo-silicate, mixed and carbonate sediments, and biogenic lithogenesis lakes with an increased amount of organic matter prevail. The soils of the Nioman River Basin are characterized by a high content of Mn, low – Ni, Co and Cr.

The territories of the Dniapro and Sož river basins are distinguished by low lakes density, well-defined surface runoff and the development of suffusion processes. A reduced content of trace elements except Ni has been noted, the accumulation of which is associated with the minerals aleuritic fraction that predominates in the composition of covering deposits [20]. The low forest cover within the Dniapro Basin (22 %) indicates an increase in the intensity of the input of biogenic and terrigenous material into water bodies.

In the Zachodni Buh Basin, there is a high level of forest cover (60 %), water-glacial plains dominate with sandy soils which are poor of trace elements. Within the Prypiać River Basin, extensive plains of river terraces and sandurs with swampy lowerings and flat lake hollows are widespread. Lake density is low, silicate-organic, organo-silicate, mixed and carbonate sediments form in weak-flow lakes. The geochemical specificity of soils in this basin reveals Fe accumulation, low contents of Mg and trace elements (Ti, Mn, Ni, Co, Cr) compared with the average values in Belarus [19].

The modern formation of lake sediments on the territory of Belarus is influenced by technogenesis. There is increasing the flow of terrigenous material (mainly clayey) from watersheds (with which Ti, Mn, Zn, Cr, V, Pb are associated) as a result of the agricultural and reclamation use of the land. The geochemical mobility of Mn, Cu, Zn is increasing as a result of organo-mineral interaction [18]. Some abnormal concentrations of Pb, Ni, Cu, Cr in lake sediments are associated with the impact of local technogenic sources [21].

Direct inheritance of the chemical composition of bottom sediments from elements content in soils and rocks within catchment areas has not been revealed. Farhat and Aly [22] suggested that the organic matter was more important in controlling heavy metals distribution. Statistically significant relationships between analyzed trace elements contents in macrophytes tissues and bottom sediments has been determined only for Mn.

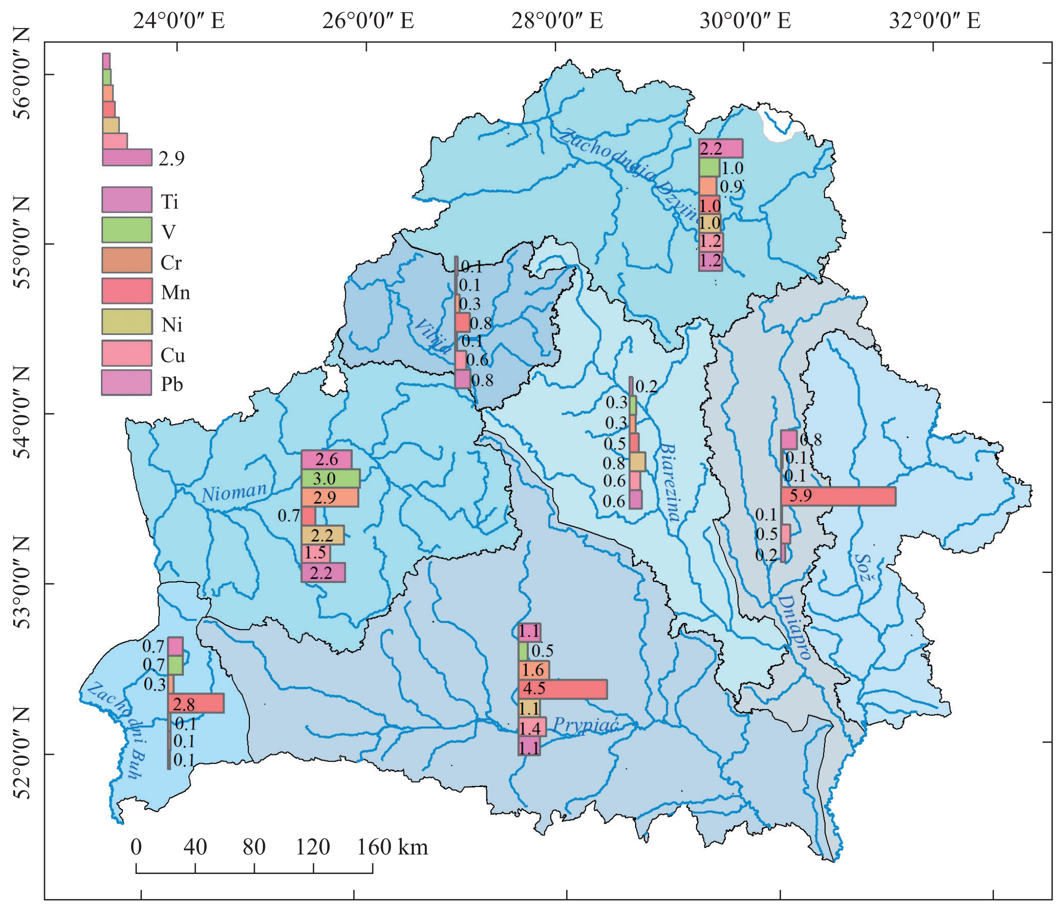

Fig. 2. Relative trace element abundances in submersed macrophytes of Belarusian lakes within principal river basins

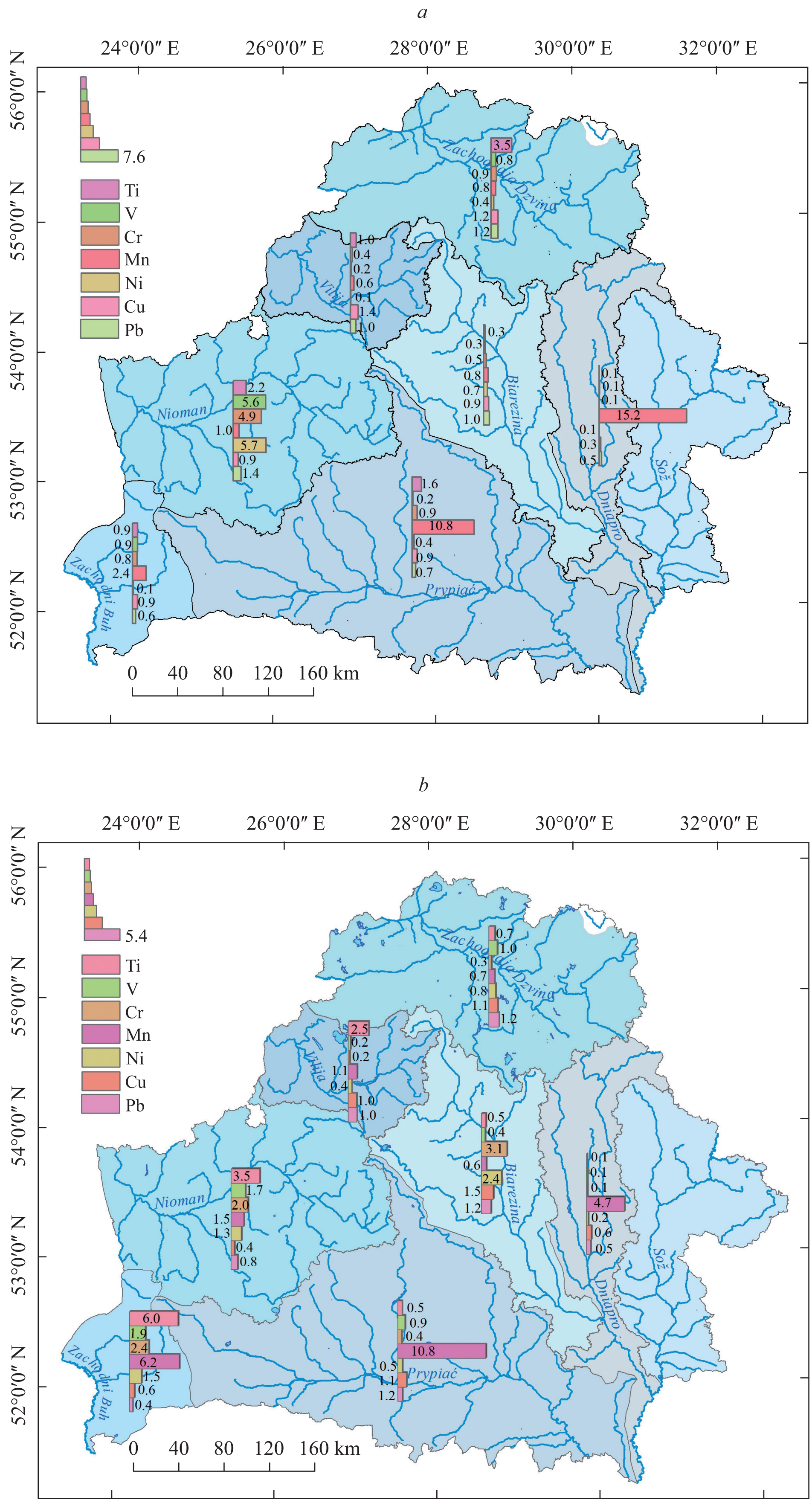

Fig. 3. Relative trace element abundances in emerged (*a*) and submersed with floating leaves (*b*) macrophytes of Belarusian lakes within principal river basins

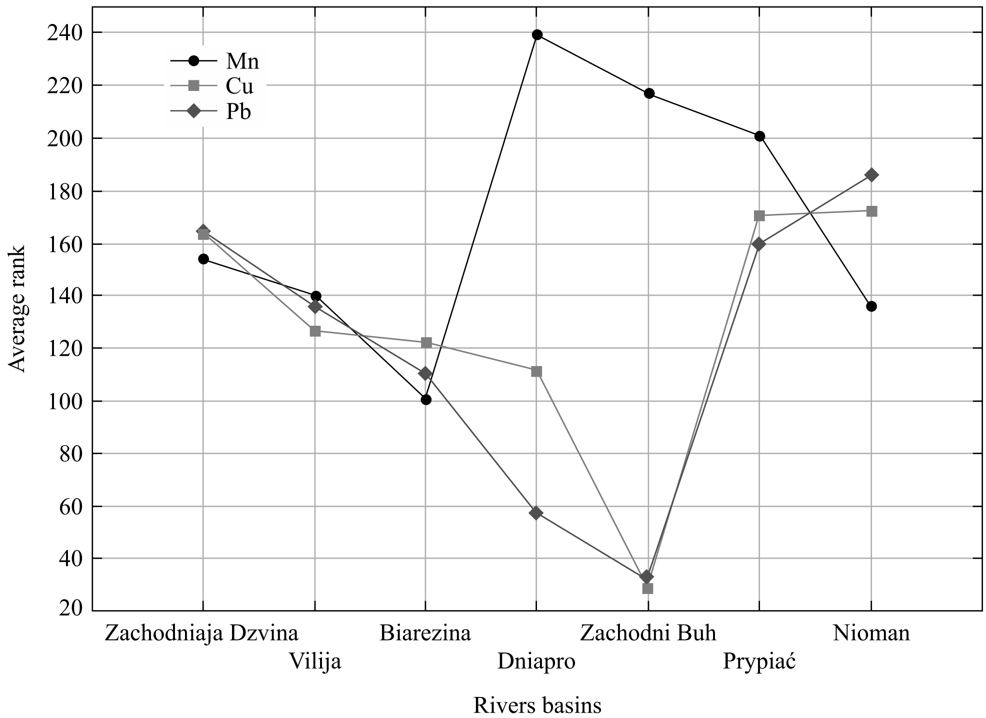

Fig. 4. Average rank variation of Mn, Cu, Pb contents in submersed lake macrophytes by principal river basins

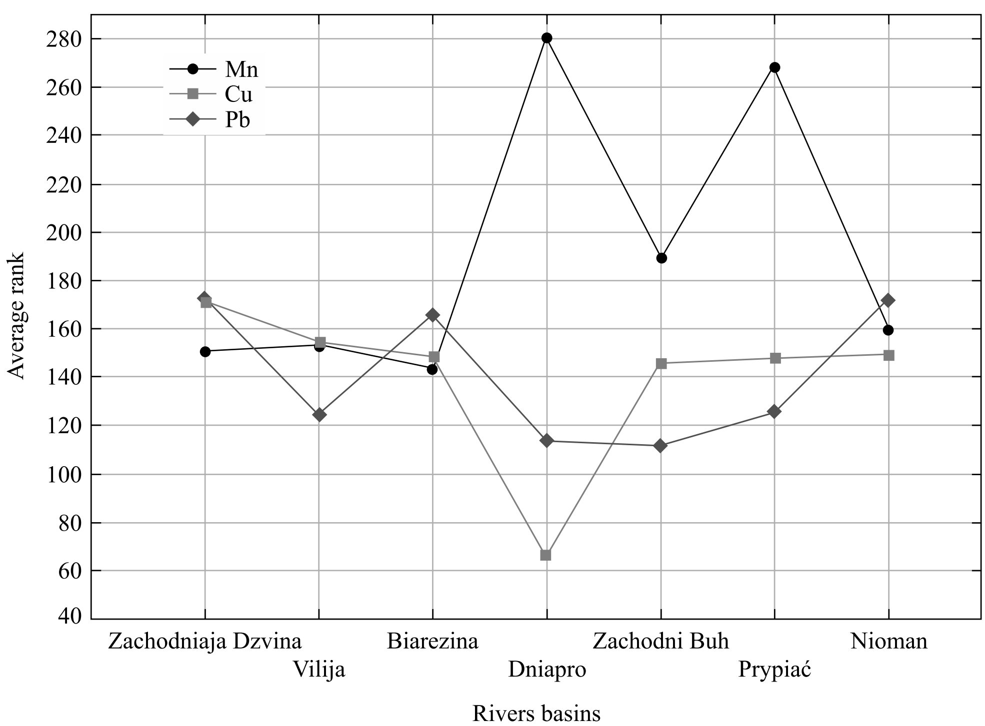

Fig. 5. Average rank variation of Mn, Cu, Pb contents in emerged lake macrophytes by principal river basins

A fairly complete picture of the ecological conditions for the growth of macrophytes gives the degree of trophic water bodies. The effect of trophic status on trace elements contents in aquatic plants was estimated using the example of submersed macrophytes (table 3). Statistically significant differences in Mn and Cu contents in the tissues of plants growing in lakes of varying trophicity have been established (*H* variates from 16.2 to 16.9, $p < 0.01$). The lowest concentration of Mn has been observed in plant tissues of mesotrophic lakes with signs of oligotrophy. This dependence is also typical of plants in other ecological groups (fig. 6).

It should be noted that within the Zachodni Buh and Dniapro basins standing out for high Mn content in aquatic plants, eutrophic lakes make up 100 % of the sample (fig. 7).

Cluster analysis of monitoring points based on Mn, Cu and Pb contents in macrophyte tissues and spatial constraints has been performed. Eight clusters have been allocated (fig. 8).

Table 3

Trace elements contents in submersed plants within lakes of different trophic status, mg/kg

Trophic status	Ti	V	Cr	Mn	Ni	Cu	Pb
Mesotrophic lakes with signs of oligotrophy ($n = 64$)	3.87	9.24	7.37	125	2.04	2.84	3.1
Mesotrophic ($n = 87$)	13.6	6.38	4.45	363	1.23	3.18	4.2
Eutrophic ($n = 146$)	1.65	3.16	3.12	464	0.76	1.82	2.39
Dystrophic ($n = 8$)	0.14	2.30	–	237	–	0.35	2.04

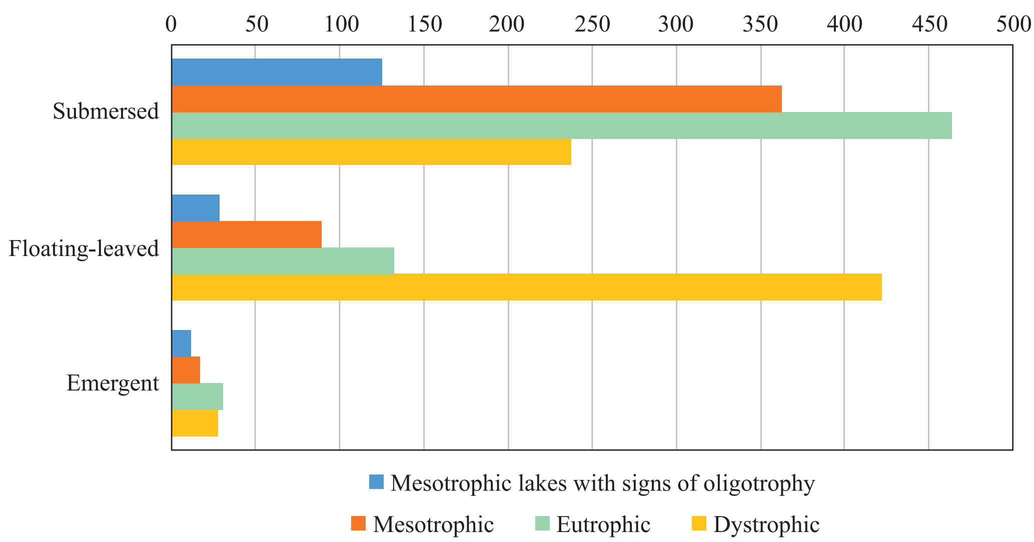

Fig. 6. Mn average content in macrophytes within lakes of different trophic status, mg/kg

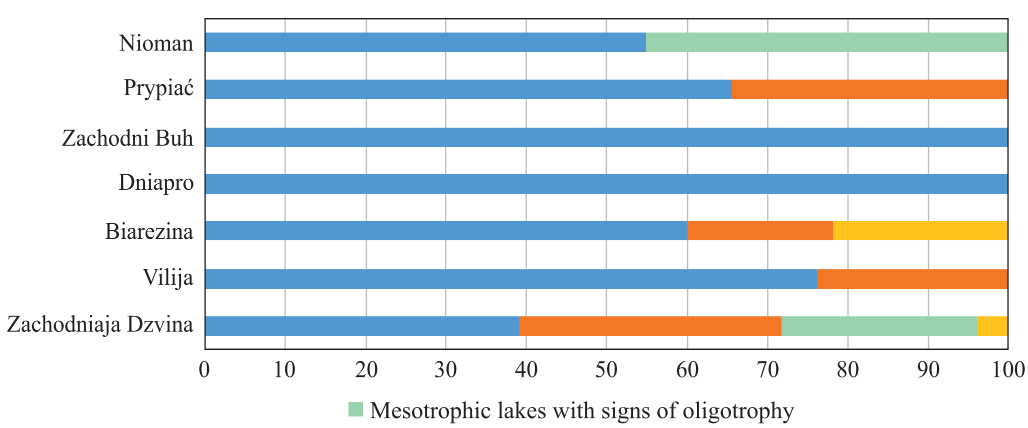

Fig. 7. Percentage of different trophic status lakes, %

The first group consists of the Vilija Basin lakes, which are distinguished by lower average levels of the elements (Mn, Cu, Pb). The second group includes examined lakes of the Braslav district characterized by elevated content of Mn and Cu (fig. 9). Bredna Lake (maximum Pb content), Lieskavičy Lake (maximum Mn content) and Sviciaź Lake (elevated Pb and Cu contents) form separate groups. Lakes of the northern part of Belarus, which are notable for elevated contents of Cu and Pb are combined into the sixth group. The lakes of the Zachodni Buh and Prypiać basins form a separate group described by elevated Mn concentration in macrophytes. The latter cluster includes lakes within the Biarezina, Dniapro and Sož basins and the southern part of the Zachodniaja Dzvina Basin.

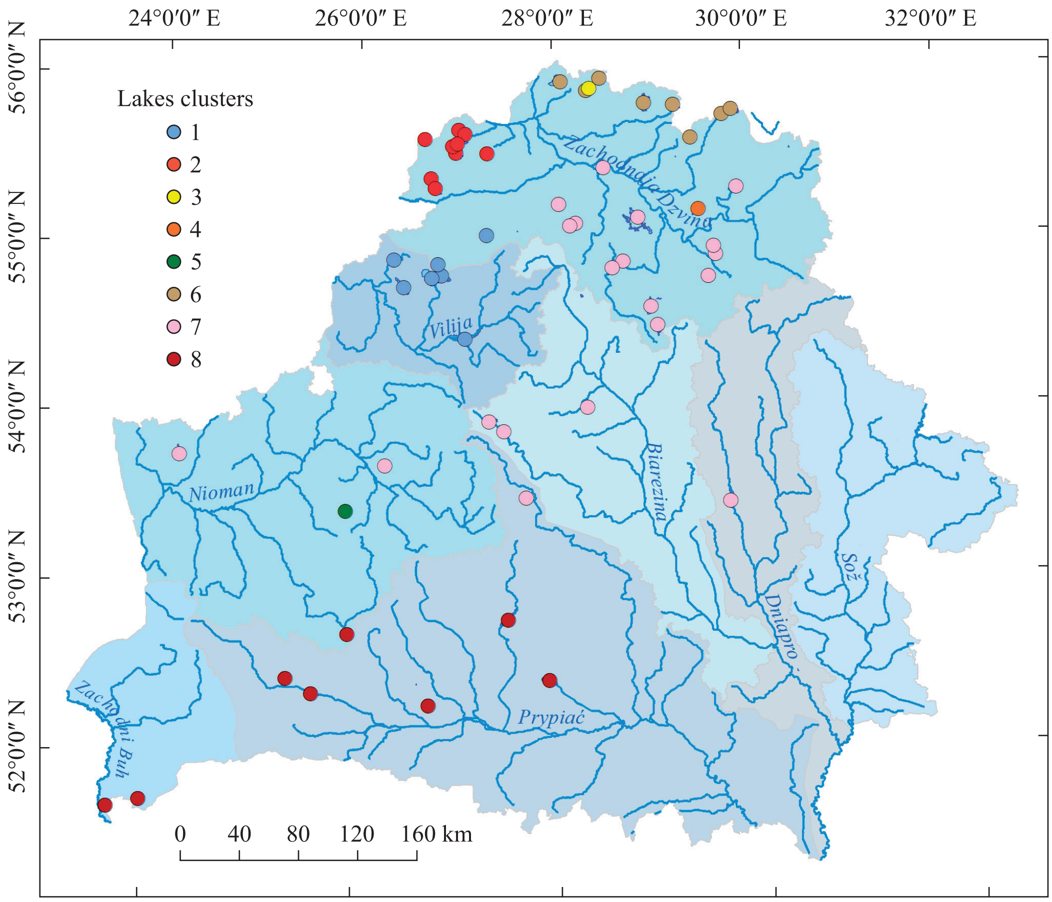

Fig. 8. Cluster analysis of lakes based on the content of Mn, Cu, Pb in macrophyte tissues

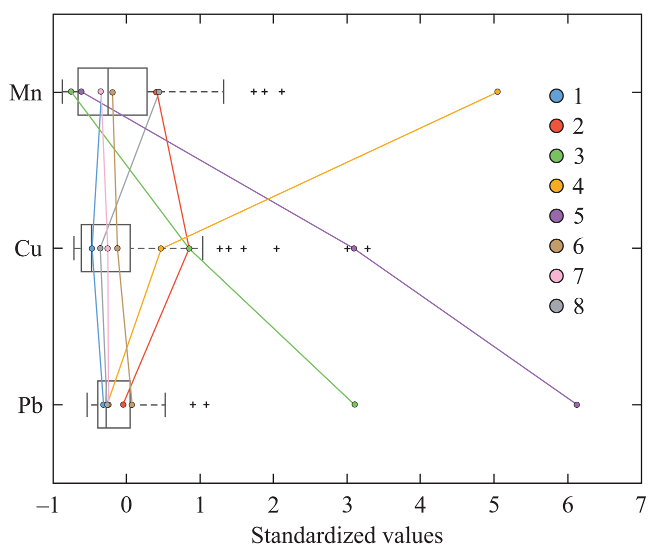

Fig. 9. Mn, Cu and Pb average contents (standardized values) in submersed macrophytes of identified lakes groups

Conclusion

The variation of trace elements contents in lake macrophytes on principal river basins has been investigated. Statistically significant differences between river basins in the contents of Mn, Cu and Pb in submersed macrophytes, Mn and Cu in emergent macrophytes and Mn in macrophytes with floating leaves have been established. For all ecological groups the highest concentrations of Mn in lake macrophytes tissues are observed in the basins of the Dniapro, the Prypiać and the Zachodni Buh, and the lowest – in the Biarezina. The lakes of the Zachodni Buh and Dniapro basins are distinguished by the lowest Pb contents in aquatic plants.

The lakes trophic status is an important factor determining the spatial variability of trace elements accumulation in marophyte tissues. Within the Zachodni Buh and Dniapro basins standing out for the highest Mn content in aquatic plants, eutrophic lakes make up 100 % of the sample.

Based on Mn, Cu and Pb contents in macrophyte tissues and spatial constraints eight lakes clusters has been allocated. Among the groups are the lakes of the Braslav district characterized by elevated content of Mn and Cu; lakes of the Vilija Basin, which are distinguished by lower average levels of the elements; lakes of the northern part of Belarus, which are notable for elevated contents of Cu and Pb. Separate groups form Bredna Lake (maximum Pb content) and Sviciaź Lake (elevated Pb and Cu contents).

Cognition of spatial distribution features of trace elements contents in macrophytes tissues contributes to the improvement in the system of monitoring higher aquatic plants and monitoring the state of water bodies in general.

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