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GEOCHEMICAL ANALYSIS OF BELARUSIAN LAKES BOTTOM SEDIMENTS

Łukaszow O. W., Własow B. P., Żukowskaja N. W. **Analiza geochemiczna jeziornych osadów dennych Białorusi**. Przeprowadzono analizę danych dotyczących zawartości pierwiastków śladowych w sapropelach różnych typów (krzemionkowe, organiczne, węglanowe) oraz we współczesnych osadach dennych jezior na Białorusi. Stwierdzono statystycznie istotne różnice pod względem zawartości Ti, Zr i Ba w sapropelach organicznych oraz V, Mn i Ba – w węglanowych w różnych prowincjach geochemicznych Białorusi. Za pomocą metody komponentów głównych wydzielono asocjacje pierwiastków śladowych we wszystkich analizowanych typach osadów. Sapropele krzemionkowe i współczesne osady denne cechują się podobną strukturą oraz składem asocjacji pierwiastków śladowych. Pierwiastki asocjacji pierwszej (V, Cr, Co, Ni, Cu, Pb) koncentrują się głównie w drobnych frakcjach. Asocjacja druga składa się z pierwiastków małoruchliwych (Ti, Zr, Nb). Mn z kolei tworzy asocjację trzecią, oddzielną, co może mieć związek z dominującą ruchomą formą jego występowania w jeziornych osadach dennych.

Лукашёв О. В., Власов Б. П., Жуковская Н. В. **Геохимический анализ донных отложений озер Беларуси.** Выполнен анализ данных содержания химических элементов в сапропелях различных типов (кремнеземистые, органические, карбонатные) и современных донных отложениях озер Беларуси. Установлены статистически значимые различия между геохимическими провинциями Беларуси по содержанию Ti, Zr, Ba в органических сапропелях и V, Mn, Ba в карбонатных. С помощью метода главных компонент выделены ассоциации химических элементов во всех анализируемых типах осадков. Кремнеземистые сапропели и современные донные отложения характеризуются схожей структурой и составом ассоциаций химических элементов. Элементы первой ассоциации (V, Cr, Co, Ni, Cu, Pb) концентрируются преимущественно в тонких фракциях. Вторая ассоциация состоит из малоподвижных элементов (Ti, Zr, Nb). Mn образует отдельную ассоциацию, что может быть связано с преобладающей подвижной формой его нахождения в донных отложениях озер.

Key words: sapropels, bottom sediments, trace elements, principal component analysis, elements assosiations
Słowa kluczowe: sapropele, osady denne, pierwiastki śladowe, podstawowa analiza komponentów, zespoły pierwiastków
Ключевые слова: сапропели, донные отложения, рассеянные элементы, метод главных компонент, ассоциации элементов

Abstract

The trace elements contents and distribution features in sapropels (siliceous, organic, carbonate) and lakes bottom sediments of Belarus are presented. Statistically significant differences have been established between the geochemical provinces on the contents of Ti, Zr, Ba in organic and V, Mn, Ba – in carbonate sapropels. Using principal component analysis the elements associations in all the analyzed sediments types have been identified. Siliceous sapropels and modern bottom sediments are characterized by the similar structure and composition of the geochemical associations. The elements of the first association (V, Cr, Co, Ni, Cu, Pb) are concentrated mainly in the fine fractions. The second association is composed of the slightly mobile elements (Ti, Zr, Nb). Mn has made up the separate association that can be explained by predominant mobile its form in the lakes sediments.

INTRODUCTION

Trace element composition of the bottom sediments of lakes is determined by a complex interaction of various factors: the lithologic-petrographic and geochemical features of the catchments rocks, its landscape structure and economic maturity; the level of production-destruction processes in the lake; its morphometric features, that is all the factors controlling sedimentation of organic and mineral substances. In this regard, percularities of the trace elements accumulation and relations between them appear to be most informative indices in the analysis of geochemical environment as the water body and its catchment.

MATERIALS AND METHODS

In the present study we have used data from the two large-scale geochemical surveys carried out in Belarus. The first is the result of different sapropels types study sampled from the 256 Belarusian lakes in the last two decades of the XXth century (fig. 1). The total sample consists of 590 examples of which 215 are siliceous sapropels, 161 are organic sapropels, 134 are carbonate sapropels and 80 are mixed sapropels.

The second is the result of the modern bottom sediments study collected during the 2000–2014 years within the monitoring of Belarusian lakes. The total sample consists of 111 examples (fig. 2).

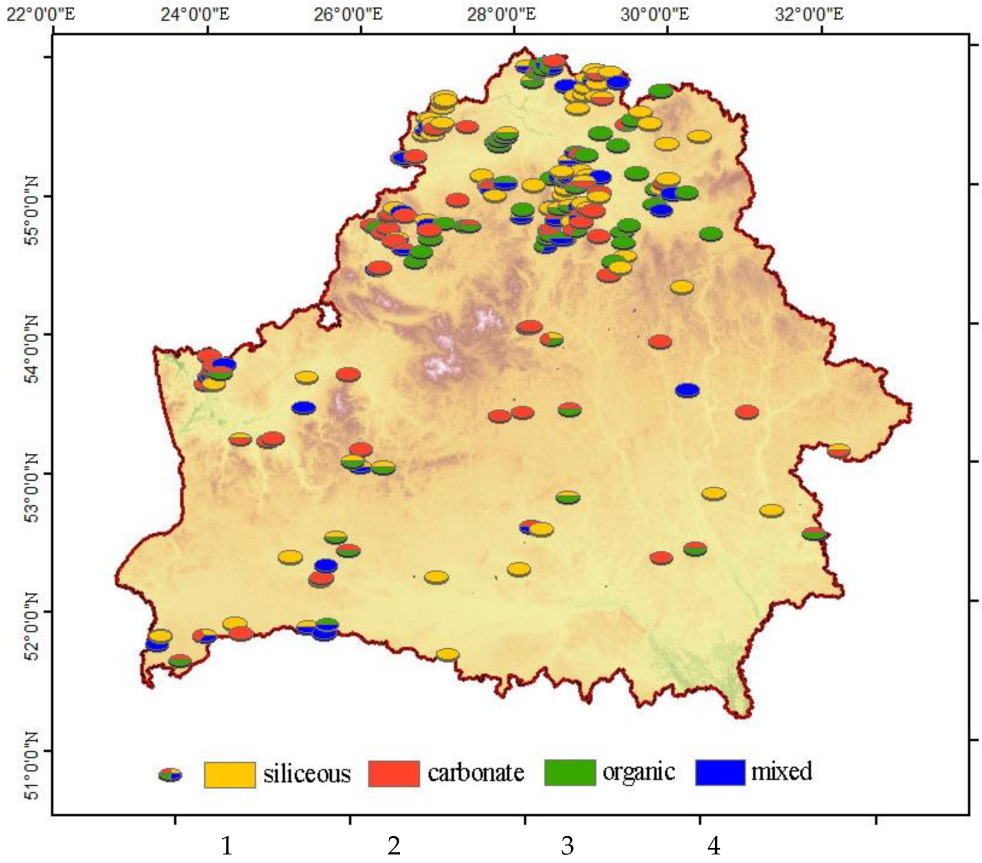

Fig. 1. Sapropel sampling locations
Rys. 1. Lokalizacja miejsc poboru próbek sapropeli:
1 – krzemionkowe, 2 – węglanowe, 3 – organiczne, 4 – mieszane
Рис. 1. Опробование сапропелей Беларуси:
1 – кремнеземистые, 2 – карбонатные, 3 – органические, 4 – смешанные

Analytical determination of trace elements (Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Ba, Pb) were performed by emission spectral analysis methods described by ZYRIN, OBUKHOV (1977).

Statistical data analysis included 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, correlation analysis and factor analysis. The main statistical software in use was SPSS (v. 17).

To obtain a normal distribution and the use of parametric methods there was applied the logarithmic transformation in the case of log-normal distribution and square root transformation at the gamma distribution. The suitability of the data for factor analysis was assessed with Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy and Bartlett's test of sphericity.

Factor analysis was performed on the base of the correlation matrix, the method of principal components (PCA). Varimax orthogonal rotation was applied to the PCA in order to minimize the number of variables with a high loading on each component and to facilitate the results interpretation. All principal component extracted from the variables were retained with eigenvalues as suggested by the Kaiser criterion.

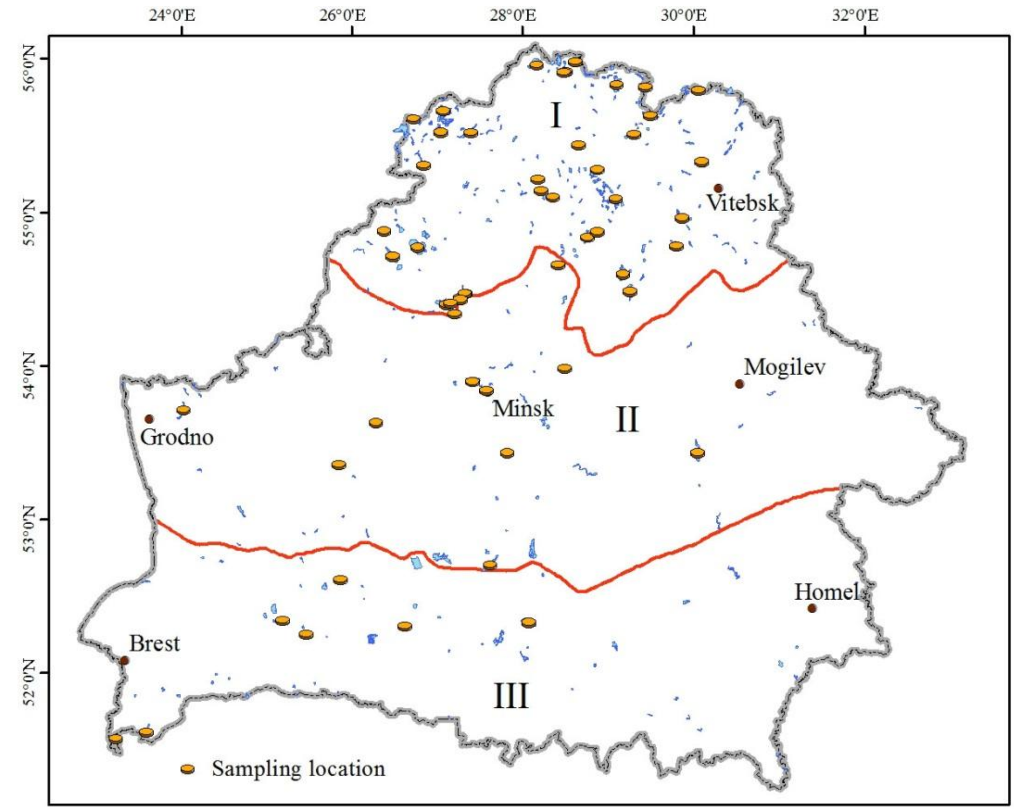

Fig. 2. Sediment sampling locations:
Geochemical provinces: I – north, II – central, III – south
Rys. 2. Lokalizacja punktów poboru współczesnych osadów dennych:
Prowincje geochemiczne: I – północna, II – centralna, III – południowa
Рис. 2. Опробование современных донных отложений озер::
Геохимические провинции: I – северная, II – центральная, III – южная

RESULTS AND DISCUSSION

Sapropels

The total contents of trace elements (Ti, V, Cr, Mn, Co, Ni, Cu, Zr, Ba, Pb) in different types of sapropels in Belarus have been studied. The contents of trace elements in the ash of sapropels fluctuate within (mg/kg):Ti – <10–6 000, V – <1–300, Cr – 1–360, Mn – 10–10 000, Co – 1–70, Ni – 1–170, Cu – 1–400, Zr – 3–2 000, Ba – 30–20 000, Pb – 1–1 000.

There is detected a tendency for a number of examined elements (Co, Ni, Cu, Ba, Pb) to reduce the total concentration among organic → siliceous → carbonate (fig. 3). The maximum Mn content is observed in the ash of carbonate sapropels, Ti, V, Zr – in siliceous, indicating the terrigenous nature of their accumulation predominantly.

To study the spatial differentiation of sapropels geochemical compositions relevant data were grouped according to three lithogeochemical provinces of Belarus. These provinces reflect the geological structure of the territory, the main features of the material differentiation during the transport, weathering features in different periods and modern geological processes (*Geochemical provinces...*, 1969). The corresponding average content in different sapropels types from three geochemical provinces of Belarus is presented in the table 1.

Kruskal-Wallis test was used to compare the geochemical provinces on the contents of trace elements in different sapropels types. This test is considered as the most effective for samples with a substantially different amount of observations. Statistically significant differences have been established between geochemical provinces on the contents of Ti, Zr, Ba in organic and V, Mn, Ba – in carbonate sapropels.

One of the tasks of the geochemical study is to isolate and analyze of the chemical element associations. Geochemical associations attainments are an effective tool for assessing the behavior of chemical elements in the natural environment and in technogenesis.

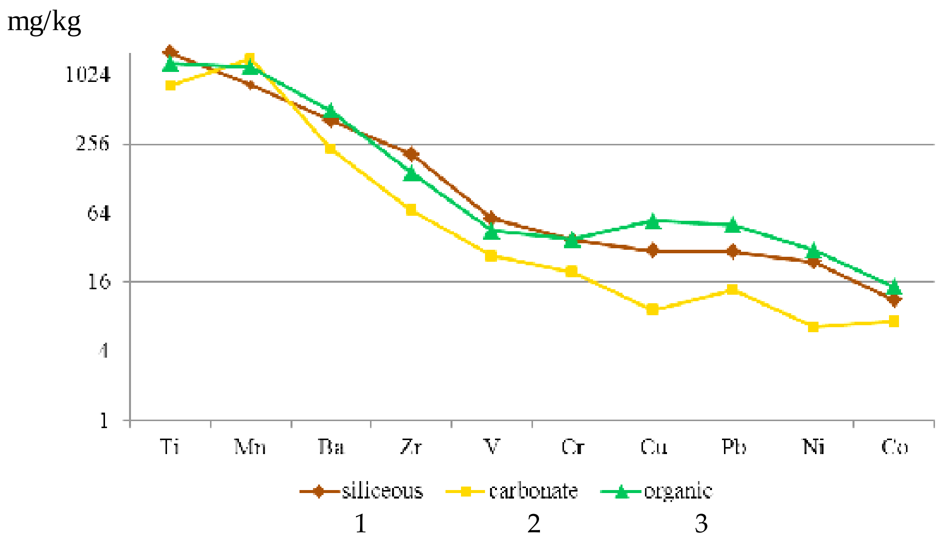

Fig. 3. Average concentrations of trace elements in the ash of different sapropels types
Rys. 3. Średnia zawartość pierwiastków śladowych w różnych typach sapropelów Białorusi:
1 – krzemionkowe, 2 – węglanowe, 3 – organiczne
Рис. 3. Средние концентрации микроэлементов в золе различных типов сапропелей Беларуси:
1 – кремнеземистые, 2 – карбонатные, 3 – органические

Table 1. Average contents of trace elements in the sapropels of Belarusian geochemical provinces, mg/kg of ash
Tabela 1. Średnia zawartość mikroelementów w sapropelach prowincji geochemicznych Białorusi, mg/kg popiołu
Таблица 1. Содержание микроэлементов в сапропелях геохимических провинций Беларуси, мг/кг золы

Geochemical province, n	Ti	V	Cr	Mn	Co	Ni	Cu	Zr	Ba	Pb
Siliceous sapropels										
North, 166	1 700	62,1	40,5	754	11,1	25,4	28,6	217	434	29,2
Central, 13	1 360	42,7	35,6	732	10,6	24,0	28,4	203	296	28,6
South, 36	1 090	42,7	26,1	1 260	15,6	18,9	38,3	177	347	31,2
In total, 215	1 580	57,0	37,3	836	11,3	24,0	30,0	209	409	29,5
Carbonate sapropels										
North, 64	1 120	33,2	20,1	1 580	6,6	7,3	10,9	85,9	299	13,7
Central, 55	671	25,5	18,6	883	7,1	5,6	7,0	58,7	192	15,1
South, 15	189	8,6	21,7	2 490	11,8	6,6	12,9	43,4	144	10,5
In total, 134	825	27,3	19,7	1 400	7,3	6,5	9,2	68,0	230	13,8
Organic sapropels										
North, 109	1 470	51,5	42,3	1 200	14,6	31,7	61,4	170	548	50,3
Central, 26	1 040	28,7	30,3	976	12,1	29,6	46,9	68,9	317	83,2
South, 25	707	39,9	31,7	1 390	17,6	25,8	41,3	153	490	45,5
In total, 160	1 280	45,0	38,0	1 190	14,6	30,4	55,2	144	493	50,5

The most effective method to evaluate the geochemical associations is the factor analysis. The factor analysis assumption about existence of the hypothetical (latent) factors determining the correlation between a large number of observed variables answers the purpose to identify the elements associations which may be formed by natural processes and technogenic pollution.

Siliceous sapropels

The distributions of Mn, V, Cu, Pb, Ba in the siliceous sapropels are approximated by lognormal distribution, Zr, Ni, Co, Cr are fit to gamma-distribution.

Statistical analysis of relationship between the contents of trace elements in the siliceous sapropels have revealed the positive correlation between the most of the elements (table. 2). The strongest correlations ($r > +0,5$) are observed for Ni-Cr, Ti-Zr, Cu-Ni.

The suitability of the data for factor analysis has been confirmed by the sufficient result of Kaiser-Melkina-Olkin test (0,751) and the significant level of Bartlett's test of sphericity ($\chi 2 = 647$; $df = 45$, $p < 0,001$). Three principal components (factors) explaining 63% of the total variance has been extracted while using PCA.

Table 2. Pearson correlation matrix for trace elements in the ash of siliceous sapropels (n = 215)
Tabela 2. Macierz korelacyjna Pearsona zawartości pierwiastków śladowych w popiołach sapropelów krzemionkowych (n = 215)
Таблица 2. Корреляционная матрица содержания химических элементов в золе кремнеземистых сапропелей (n = 215)

Elements	V	Cr	Mn	Co	Ni	Cu	Zr	Ba	Pb
Ti	0,063	***0,333***	*0,157*	0,009	0,090	***0,188***	***0,551***	*0,142*	***-0,180***
V		***0,392***	-0,100	***0,326***	***0,414***	***0,338***	0,084	***0,396***	***0,448***
Cr			0,103	***0,366***	***0,565***	***0,404***	***0,235***	***0,326***	*0,174*
Mn				*0,154*	***0,195***	***0,321***	*0,145*	***0,182***	0,063
Co					***0,633***	***0,417***	0,107	***0,470***	***0,201***
Ni						***0,526***	*0,151*	***0,411***	***0,277***
Cu							***0,250***	***0,387***	***0,270***
Zr								***0,338***	-0,029
Ba									***0,232***

Explanations: values in bold letters show significant correlations at the 0,01 level (2-tailed), in italic at the 0,05 level (2-tailed).

The first principal component is associated with Ni, V, Co, Cu, Ba, Cr, Pb explaining 35% of the total variance (table 3, fig. 4). These elements are concentrated mainly in the fine fractions, the contents of which are apparently reflected by factor 1.

Table 3. Trace elements associations in lake sediments of different types
Tabela 3. Asocjacje pierwiastków śladowych w osadach jeziornych różnych typów
Таблица 3. Ассоциации химических элементов в озерных осадках различных типов

Type of sapropels	$n(r_{0,01})$	Factor	FVP	CFVP	Associations
Siliceous sapropels	215 (0,117)	F1	35	63	$Ni_{0,80}$– $V_{0,72}$–$Co_{0,72}$–$Cu_{0,66}$–$Ba_{0,64}$–$Cr_{0,62}$–$Pb_{0,59}$
		F2	17		$Ti_{0,88}$–$Zr_{0,81}$
		F3	11		$Mn_{0,87}$
Carbonate sapropels	134 (0,145)	F1	51	65	$Ni_{0,88}$–$V_{0,87}$–$Zr_{0,81}$–$Ti_{0,82}$–$Cr_{0,77}$–$Cu_{0,76}$–$Pb_{0,69}$–$Co_{0,56}$–$Ba_{0,55}$
		F2	14		$Mn_{0,88}$–$Ba_{0,53}$
Organic sapropels	161 (0,135)	F1	40	66	$Cr_{0,87}$–$Ti_{0,86}$–$Cu_{0,66}$–$Zr_{0,61}$–($Ni_{0,58}$)–$Pb_{0,42}$
		F2	15		$Mn_{0,73}$–$Ni_{0,71}$–$Co_{0,60}$–$Cu_{0,58}$
		F3	11		$Ba_{0,86}$–($Zr_{0,56}$)
Modern bottom sediments	67 (0,203)	F1	37	74	$Ni_{0,88}$–$Cr_{0,88}$–$Cu_{0,86}$–$Co_{0,73}$–$V_{0,66}$–($Zn_{0,49}$)–$Pb_{0,42}$
		F2	19		$Zr_{0,89}$–$Ti_{0,71}$–$Nb_{0,66}$
		F3	18		$Mn_{0,83}$–$Zn_{0,62}$–($V_{0,61}$)

Explanations: $n(r_{0,01})$ – number of samples and the absolute limit value of significant factor loading at 0,01 significance level given in parentheses; FVP – factor variance percentage; CFVP – cumulative factor variance percentage. Elements of association are written in descending order of significant at 0,01 level loading; elements in parentheses are associated with more than one factor. Lower index after the element symbol – load on the factor.

The second principal component accounts for 17% of the total variance and it has high positive loading on Ti and Zr. The above elements are considered to be slightly mobile in the most geochemical environments. Major minerals of Ti (rutile, ilmenite) and Zr (zircon) are highly resistant to weathering and are concentrated mainly in the sand and aleurite fractions. A weak negative correlation has been revealed between sampling depth and Ti–Zr association (r = -0,27, p < 0,001).

The third principal component (11% of the total variance) is mainly related to Mn. According to ZHUKHOVITSKAYA, GENERALOVA (1991), the share of potentially mobile forms of Mn in the sapropels was ranged from 47% to 62%. Mn is the most mobile element in sapropels, what is probably caused its extraction into separate association.

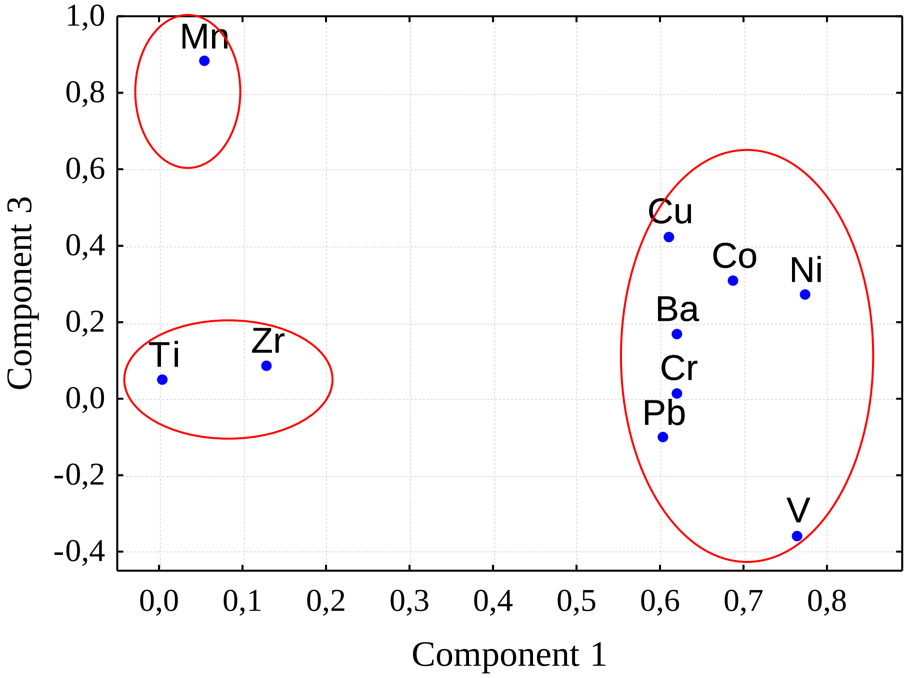

Fig. 4. Principal Component Analysis loading plot (PC1 vs. PC3) for trace elements in siliceous sapropels
Rys. 4. Wykres ładunków na płaszczyźnie pierwszej i trzeciej asocjacji pierwiastków w sapropelach krzemionkowych
Рис. 4. График нагрузок в координатной плоскости первой и третьей главных компонент

It should be noted that the first two elements associations in the siliceous sapropels which have been extracted by factor analysis generally correspond to the natural elements associations in soddy-podzolic soils in Narochansky National Park (LUKASHEV et al., 2009). The exception is Mn.

The composition and structure of the chemical elements associations in the carbonate and organic sapropels are changed in comparison with siliceous (table 3), indicating the specifics of the trace elements accumulation processes.

In the carbonate sapropels according to the result of the principal component analysis (table 3) 65% of the total variance has been explained by the first two components. The majority of examined trace elements (Ni, V, Zr, Ti, Cr, Cu, Pb, Co, Ba) constitute the first principal component accounting for 51% of the total variance. A statistically significant negative correlation has been found between values of the first component and sampling depth ($r = -0{,}278$, $p = 0{,}019$). The principal component 2 is associated with Mn and Ba.

The principal component analysis has revealed 3 components in organic sapropels which can explain 40%, 15%, 11% of the variance respectively (table 3). The first component is positively related to Cr, Ti, Cu, Zr, Ni, Pb. Statistically significant negative correlation between the dedicated association and sampling depth has been found ($r = -0{,}449$, $p < 0{,}001$). The second component has strong positive loadings on Mn, Ni, Co and Cu. The third component is associated mainly with Ba and Zr.

Kruskal-Wallis test was used to confirm the hypothesis of a correlation between the types of the lake basins (impounded, thermokarst, pothole, karst etc.) (*Lakes of Belarus*, 2004) and the received elements associations. It has revealed the dependence of Ti-Zr association in siliceous sapropels and Ni-V-Zr-Ti-Cu-Pb-Co-Ba in carbonate from the type of lake basins ($H = 16{,}7$, $df = 6$, $p = 0{,}01$ and $H = 16{,}2$, $df = 6$, $p = 0{,}01$, respectively). The relationship between the trace elements accumulation in organic sapropels and type of lake basins has not been found.

Modern bottom sediments

The descriptive statistics of the trace elements concentrations in bottom sediments are listed in table 4.

Statistically significant differences between trace elements contents in lake sediments of Belarusian geochemical provinces has been revealed only to the Zn ($H = 7{,}42$, $df = 2$, $p = 0{,}02$; table 5).

Studying the relationship between trace elements on the basis of the factor analysis allowed revealing three of its main associations in bottom sediments of Belarusian lakes. The resulting model is able to explain 74% of the total variance.

The first principal component explained the 37% of total variance and it has statistically significant loading on Ni, Cr, Cu, Co, V, Zn, Pb (table 3, fig. 5). The

Table 4. Descriptive statistics of trace elements concentrations in modern bottom sediments, mg/kg DW
Tabela 4. Statystyczne charakterystyki zawartości pierwiastków śladowych w osadach dennych jezior
Таблица 4. Статистические характеристики содержания химических элементов в донных отложениях озер

Element	x (range)	σ	s_x
Ti	1378_g (24,2–9 939)/$7,13_{ln}$	$1,09_{ln}$	$0,133_{ln}$
V	$14,1_g$ (2,17–99,1)/$2,45_{ln}$	$0,962_{ln}$	$0,118_{ln}$
Cr	$11,6_g$ (0,96–99,9) /$4,54_{ln10x}$	$1,09_{ln10x}$	$0,118_{ln10x}$
Mn	426_g (65,4–6934)/$5,98_{ln}$	$0,974_{ln}$	$0,119_{ln}$
Co	3,37 (н.о.–29,7)		
Ni	$4,24_g$ (0,30–52,2)/$3,59_{ln}$	$1,06_{ln10x}$	$0,129_{ln10x}$
Cu	$7,45_g$ (0,99–96,4)/$4,23_{ln}$	$0,808_{ln10x}$	$0,099_{ln10x}$
Zn	36,2 (н.о.–524)		
Zr	$85,2_g$ (0,90–991)/$4,45_{ln}$	$1,50_{ln}$	$0,183_{ln}$
Nb	3,48 (н.о.–49,5)		
Mo	0,98 (н.о.–5,24)		
Pb	$17,9_g$ (4,88–74,9)/$2,80_{ln}$	$0,655_{ln}$	$0,080_{ln}$

Explanations: x –mean; x_g– geometric mean; σ – standard deviation; s_x – standard error of the mean; the denominator as the arithmetic mean of the data logarithm

Table 5. The trace elements contents in lake bottom sediments of Belarusian geochemical provinces, mg/kg DW
Tabela 5. Zawartość pierwiastków śladowych w osadach dennych jezior w prowincjach geochemicznych Białorusi, mg/kg popiołu
Таблица 5. Содержание микроэлементов в донных осадках озер геохимических провинций Беларуси, мг/кг золы

Geochemical province, n	Ti	V	Cr	Mn	Co	Ni	Cu	Zn	Zr	Pb
North, 47	1 650	13,6	11,0	458	4,16	4,52	7,40	30,2	110	18,2
Central, 9	1 345	11,4	12,7	270	2,26	2,13	4,81	37,1	91,3	13,7
South, 11	1 197	26,3	13,5	453	1,90	7,70	10,7	77,4	27,6	20,4
In total, 67	1 378	14,1	11,6	426	3,37	4,24	7,45	29,6	85,2	17,9

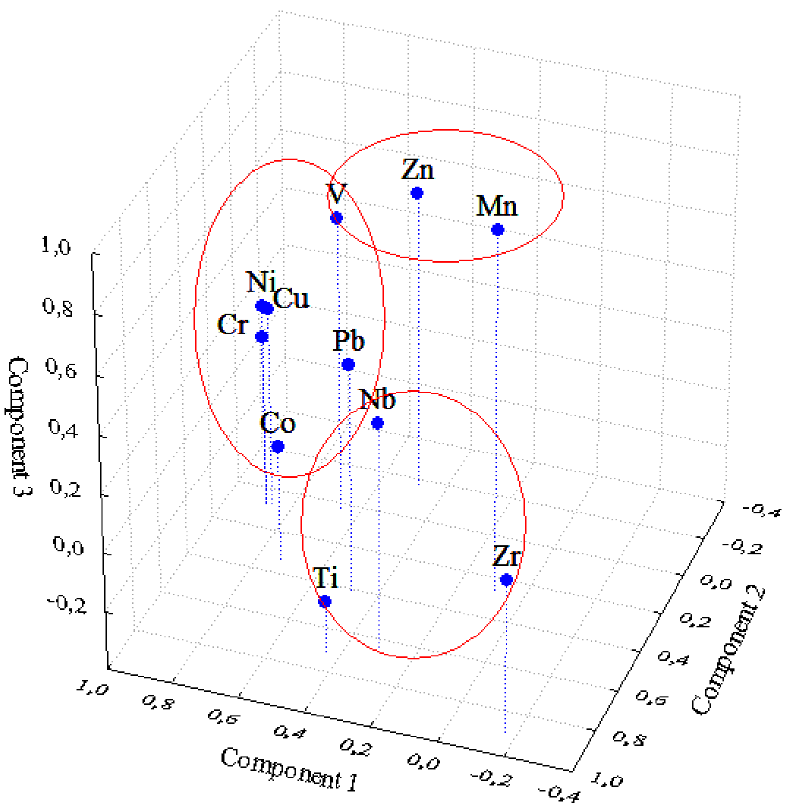

Fig. 5. Principal component analysis loading plot for trace elements in modern bottom sediments
Rys. 5. Wykres ładunków w przestrzeni trzech głównych asocjacji pierwiatków chemicznych we współczesnych osadach dennych
Рис. 5. График нагрузок в пространстве трех главных компонент

accumulation of the elements association is determined by the content of the sediments fine fraction.

The second component (19% of the total variance) forms an association of slightly mobile elements (Zr-Ti-Nb) concentrating mainly in the sand and aleurite fractions of the bottom sediments.

The third component corresponds to the elements association of Mn-Zn (explaining 18% of the total variance). We emphasize that the extracted trace elements associations in modern sediments are similar to the geochemical associations in the siliceous sapropels (table 3).

CONCLUSIONS

Thus using PCA the trace elements associations in different types of sapropels and modern bottom sediments have been identified. Most of the examined elements (Ti, V, Cr, Ni, Cu, Zr, Pb) form similar associations in all types of sediments and are primarily related to the terrigenous sediments component. The association of Ti-Zr in siliceous sapropels is apparently caused by the granulometric differentiation of substance. Mn has made up the separate association that can be explained by its predominant, relatively mobile form in the bottom sediments of lakes.

The article has been prepared within the project "The geoecological estimation of natural-resource potential of anthropogenically disturbed lake basins and the data base creation of the geochemical pollution by heavy metals of modern sediments in Belarusian rivers and lakes".

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