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Chemical element distribution in vertical profiles of bottom sediments of Lithuanian lakes

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The variability of the content of chemical elements related to terrigenous material (Al, Fe, Ti, Ni, V, Zr, Y, Yb) in the vertical section of lake sediments was found to be not high. Most variable are Ca, Mg, Sr, Ba, Mn related to autigenic minerals. The upper part of the sediment section is rich in biogenic–technogenic elements, especially Ag, Cu, P, Pb, Sn and Zn.

Keywords: lake sediments, trace elements, Lithuania

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INTRODUCTION

Lithuanian lakes belonging to the Pleistocene continental glaciation zone are a very important part of the ecosystem. Their sediments reflect the development of each lake and the whole basin very well. Research carried out in the vertical profile of the bottom sediments helps to restore the chronology of natural and anthropogenic changes of the environment, the history of lake development, to make conclusions about the future tendencies.

Geochemical peculiarities of the distribution of macroelements were investigated by Garunkštis (Garunkštis ir kt. 1969; Гарункштис 1975), I. Klimkaitė and F. Martinkėnienė (Климкайте, Мартинкенене 1978). Trace element distribution in the top of the bottom sediments was investigated by J. Galčienė-Jarošiūtė, V. Baltakis, A. Radzevičius, V. Kadūnas, K. Jokšas, K. Galkus and the author (Гальчене, Прокопайте 1970; Budavičius, Kadūnas 1999; Kadūnas, Budavičius 2000, 2001; Jokšas 1999; Galkus, Jokšas ir kt. 1995; Galkus 1997). However, trace element distribution in the vertical profiles of the bottom sediments in Lithuanian lakes and its changes that occurred in the course of time were not explored.

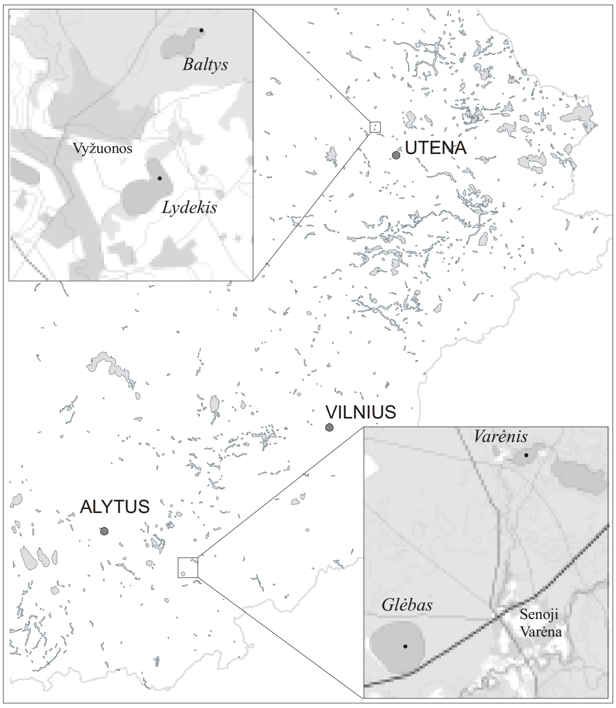

Fig. 1. The study lakes with specified boreholes for sampling
1 pav. Pažymėti tirtų ežerų gręžiniai, kuriuose buvo imami dugno nuosėdų mėginiai

Recently a group of scientists from the Institute of Geology and the Institute of Botany, supported by the Lithuanian State Science and Studies Foundation, carried out a joint research of lake sediments. In 2000 and 2001, samples from four lakes in Eastern Lithuania, namely Varėnis and Glėbas (Varėna district), Baltys and Lydekis (Utena district), were taken (Fig. 1). Their chemical, pigment, flint alga, spore and pollen, radioisotope as well as trace element analysis was carried out. The latter method enabled to determine time-related changes of the distribution in the vertical profiles and to evaluate the influence of anthropogenic pollution on the composition of the bottom sediments in the lakes.

1. METHODS

Samples of bottom sediments from vertical profiles of the lakes were taken using two methods: Niemist type gravity-tube for water-bearing sediments (depth – up to 50 cm) and peat type corer for deeper sediments (depth – up to 12 m). In winter the reconnaissance boreholes through the whole profile of the sediments were done in Lydekis and Baltys lakes and their sediment distribution charts were compiled. According to these results, places for taking samples were optimally selected. Samples for geochemical research were taken at a 5–10 cm interval in the water-bearing layer and 50–80 cm interval in the deeper layer. In total, 72 samples were taken (20 samples in Lake Baltys, 20 in Lake Glėbas, 9 in Lake Lydekis, and 23 in Lake Varėnis). Due to a not very reliable method of sampling in Glėbas, Varėnis and Lydekis lakes, investigation of trace element distribution in the present work is based on the samples of bottom sediments taken in Lake Baltys (in the whole sediment profile). Samples from all four lakes (27) were used when analysing a correlation and element associations in the water-bearing layer, whereas only samples from Lake Baltys (19) were used when analysing a correlation and associations of the elements in the deeper layers.

The samples were dried at a room temperature and sifted though a nylon sieve taking <1 mm fractions. Organic matter was mineralised by heating in furnace at 450 °C. Later the samples were crushed into powder.

The samples were analysed by DC Arc Emission Spectrometry using a DFS-13 spectrograph and a DM-100 microdensitometer. This analytical method was used to determine total Ag, Al, B, Ba, Ca, Co, Cr, Cu, Fe, Ga, La, Li, Mg, Mn, Mo, Nb, Ni, P, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn, Zr quantities in the samples. International standard samples OOKO 153 (SP2) and OOKO 151 (SP3) were used to ensure the reliability of the analysis. The established quantities of the elements were recalculated to air dry material.

The mathematical statistical package STATISTICA was used to estimate the parameters of trace element distribution. Associations of elements were determined according to their content correlation matrix and sorted factor loading matrix, which were obtained by principal component analysis and rotated by a varimax method.

The associations were named after the dominating elements, which were differentiated according to their form in the sediments and grouped into allotigenous-accessory (Ti, Zr, Nb, Y, Yb, La), allotigenous (Li, Ga, Sc, B, V, Cr, Ni, Co), biogenic-technogenic (Pb, Zn, Ag, Mo, Cu, Sn), and autigenous, namely, related to carbonates (Sr and Ba) and hydroxides (Mn) (Kadūnas, Budavičius, 2000).

2. THE STUDY LAKES IN BRIEF SURVEY

Varėnis and Glėbas lakes belong to the basin of Merkys. Varėnis is a running-water lake, with the Varėnė river flowing across it, and with a nameless streamlet falling into it (which is running from Lake Glūkas). Its maximum depth is 8.6 m. Water-bearing sediments (to 4.7 m deep) are blackish, with remnants of mollusc shells and macroremnants of higher plants. The deeper layers (to 7.2 m deep) contain black, clayey and very compact lake sediments. Glėbas is a thermokarst lake, it has a rather straight coastline. The bottom relief of the lake is uniform and plain. Its deepest place reaches 11 m. Bottom sediments in Lake Glėbas have several layers: grey carbonaceous aleurite (to 1 m deep), dark brown sediments (from 1 to 2.6 m), light brown sediments (from 2.6 to 3.5 m), whitish sediments with brown interlayers (from 3.5 to 4.5 m), several light- and dark-brown lake sediment interlayers (from 4.5 to 7.2 m). Hydrodinamically Glėbas is a lake without any outlet (Garunkštis, Stanaitis, 1969).

Baltys and Lydekis, two lakes of the Šventoji basin, were also analysed in more detail. Hydrodynamically, Lake Baltys is a lake with no outlet, with a characteristic sedimentation of organic (sapropel and peat) and carbonaceous sediments. The lake is relatively not deep, with the deepest place in the central part of the lake reaching 7 m. The bottom sediment profile is more than 12 m. According to a ^{14}C study of by J. Mažeika, peat taken from the depth of 12.0–12.25 m is dated to 9085 ± 60 years BP. It formed in the end of the preborealis or beginning of borealis climate period. Most part of the profile has been formed by Atlantis sediments and lies at a depth of 6–12 m (Kabailienė, 2001).

Lake Lydekis is a running-water lake, with the Vyžuona stream running through it. This lake has a characteristic sedimentation of terrigenous material. Lake Lydekis is deeper, reaching 20 m in its south-western part.

3. CHEMICAL ELEMENT DISTRIBUTION IN VERTICAL PROFILES OF BOTTOM SEDIMENTS

3.1. Macroelement distribution

The macroelements that were analysed (Al, Fe, Ca, Mg) according to their distribution can be grouped into two couples: Fe–Al and Ca–Mg.

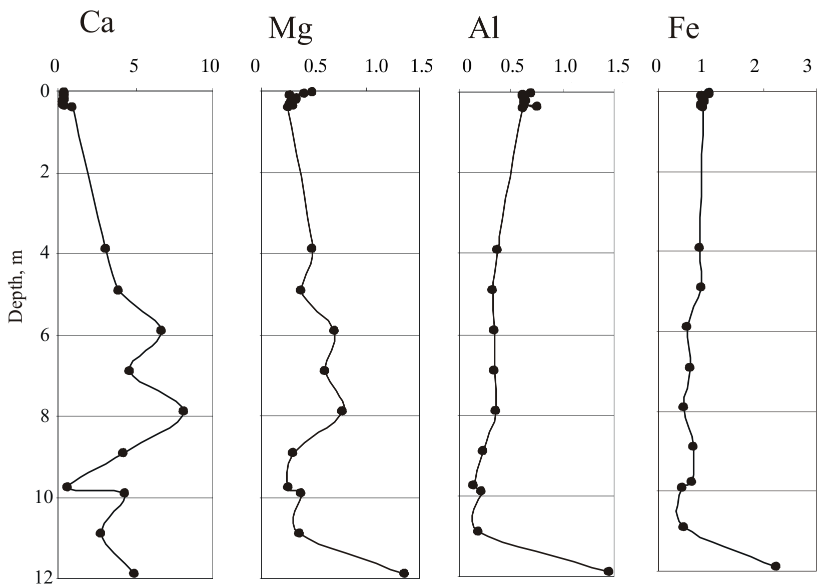

Fig. 2. Microelement distribution
2 pav. Mikroelementų pasiskirstymas Balčio ežero dugno nuosėdų pjūvyje

In the greatest part of the sediment profile Fe and Al are distributed rather evenly (Fig. 2). The maximum quantities of both elements (Fe 2.24% and Al 1.45%) are determined in the lower part of the profile, in Preborealis sediments. During the Atlantic–Subatlantic period, a significantly smaller content of these elements accumulated in the sediments (the median quantity of Fe is 0.6 and of Al 0.32%) with a rather even distribution (variation coefficients are 21.6 and 31.2%, respectively). Their quantities, especially of Al, greatly increased in the modern sediments (Fe up to 0.86 and Al up to 0.63%).

Calcium and magnesium distribution is not very even, especially in sediments of the Atlantic period. In these sediments we have clearly determined two periods of maximum Ca accumulation (up to 6.7% at a depth of 5.8–6 m and 8.2% at a 7.8–8 m interval) (Fig. 2). This would correspond to the IV and V carbonate formation maximum levels in the middle and end of the Atlantis. There is no Ca accumulation in modern sediments (median quantity is 0.37%). The highest content of Mg was established in the Preborealis sediments (1.37%). There is less Mg in the Atlantic sediments (0.37%). Mg distribution in the profile is similar to that of Ca, though it is more even (coefficient of Ca variation is 44.9 and of Mg 23.1%).

3.2. Trace element distribution in vertical profiles of bottom sediments

When analysing their distribution in the vertical profile of bottom sediments, trace elements were subdivided into groups. Ag, Cu, P, Pb, Sn and Zn belong to the first group. The contents of these elements are increased (from 5.5 times for copper to 34 times for lead) in the upper part of the sediment profile if compared with its middle part (Fig. 3a). These elements indicate technogenous pollution, which is proved also by their increased coefficients of variation (Table 1).

Table 1. **Trace element distribution is bottom sediments (Lake Baltys)**
1 lentelė. **Mikroelementų pasiskirstymas Balčio ežero dugno nuosėdų sluoksniuose**

Elements	S			V*			X			Md			Max			Lower **
	Total	Upper	Middle	Total	Upper	Middle	Total	Upper	Middle	Total	Upper	Middle	Total	Upper	Middle	
1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*	*15*	*16*	*17*
KN*	10.0	1.4	13.5	13.4	1.8	18.3	74.74	77.35	73.94	76.70	76.99	76.57	92.30	79.49	92.30	58.5
Ag	0.1	0.05	0.003	108.9	39.3	49.6	0.061	0.121	0.007	0.012	0.137	0.007	0.186	0.186	0.011	0.012
Al*	0.3	0.05	0.1	58.2	7.2	31.2	0.52	0.65	0.28	0.62	0.63	0.32	1.45	0.76	0.37	1.45
B	16.7	4.4	3.2	53.9	9.6	22.3	31.0	45.7	14.3	38.6	46.0	14.2	51.3	51.3	21.6	49.8
Ba	41	33	36	62.2	77.9	43.5	65	42	82	49	29	102	125	119	122	125

Table 1 continued
1 lentelės tęsinys

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17
Ca*	2.5	0.2	2.2	100.3	45.0	50.8	2.48	0.42	4.28	0.90	0.37	4.22	8.17	0.90	8.17	4.98
Co	0.5	0.2	0.1	37.1	13.2	17.4	1.22	1.57	0.79	1.21	1.54	0.84	1.87	1.86	0.94	1.87
Cr	4.5	1.2	0.9	71.0	13.0	40.3	6.41	9.23	2.31	7.10	9.43	2.11	17.85	11.0	4.45	17.8
Cu	9.2	3.9	1.1	72.9	18.3	29.4	12.7	21.5	3.9	11.6	20.5	3.9	30.3	30.3	6.1	11.6
Fe*	0.4	0.1	0.1	46.7	7.4	21.6	0.82	0.87	0.61	0.81	0.86	0.60	2.24	0.98	0.82	2.24
Ga	0.7	0.1	0.1	71.2	6.4	33.4	0.96	1.53	0.27	1.40	1.48	0.27	1.99	1.68	0.39	1.99
La	1.7	0.3	1.6	40.6	5.2	49.4	4.28	4.89	3.17	4.71	4.83	3.58	8.72	5.22	5.4	8.7
Mg*	0.3	0.1	0.2	59.4	23.1	38.3	0.45	0.33	0.47	0.36	0.30	0.37	1.37	0.49	0.77	1.37
Mn	98	22	118	51.7	13.4	63.3	189	166	186	163	161	204	422	200	422	415
Mo	0.7	0.1	0.2	54.6	6.4	30.4	1.32	1.78	0.66	1.59	1.79	0.63	3.07	1.98	1.16	3.07
Nb	0.8	0.5	0.9	41.2	30.3	51.9	1.87	1.81	1.82	1.83	2.07	1.64	3.58	2.42	3.58	2.91
Ni	4.2	2.1	0.3	64.7	24.1	8.9	6.56	8.85	3.02	5.63	8.79	2.95	17.85	12.6	3.46	17.8
P	1517	454	92	95.3	14.6	48.2	1591	3113	191	498	3077	173	3866	3866	358	498
Pb	44.6	22.1	2.5	107.3	26.1	99.7	41.5	84.7	2.5	8.7	94.3	2.5	102	102	8.7	4.6
Sc	1.0	0.1	0,5	110.3	15.8	69.0	0.87	0.61	0.72	0.59	0.58	0.84	4.57	0.84	1.53	4.5
Sn	1.2	0.7	0.1	94.6	29.6	41.7	1.24	2.34	0.20	0.71	2.36	0.17	3.14	3.14	0.36	0.71
Sr	32.1	4.9	30.5	85.3	32.3	57.8	37.7	15.3	52.8	22.7	13.3	44.5	103	22.7	102	104
Ti	231	44	48	66.3	8.8	35.3	348	497	136	438	488	149	913	575	216	913
V	10.0	2.5	1.1	80.0	12.7	35.2	12.55	19.58	3.04	15.44	19.57	3.06	34.86	24.47	4.92	34.8
Y	8.0	0,6	2.9	145.2	19.9	64.6	5.50	3.02	4.45	3.03	2.80	3.39	37.35	3.96	10.9	37.3
Yb	0.7	0.1	0.2	122.4	12.9	68.1	0.55	0.46	0.34	0.39	0.46	0.26	3.24	0.54	0.94	3.24
Zn	62.4	34.6	9.5	81.7	25.6	44.3	76.4	135.3	21.5	39.4	141.8	17.3	177	177	35.8	39.4
Zr	24.4	5.2	8.3	89.3	23.6	38.2	27.3	22.2	21.7	25.0	23.0	25.0	124	29.1	35.1	124

* %, other – ppm. ** One reliable sample.

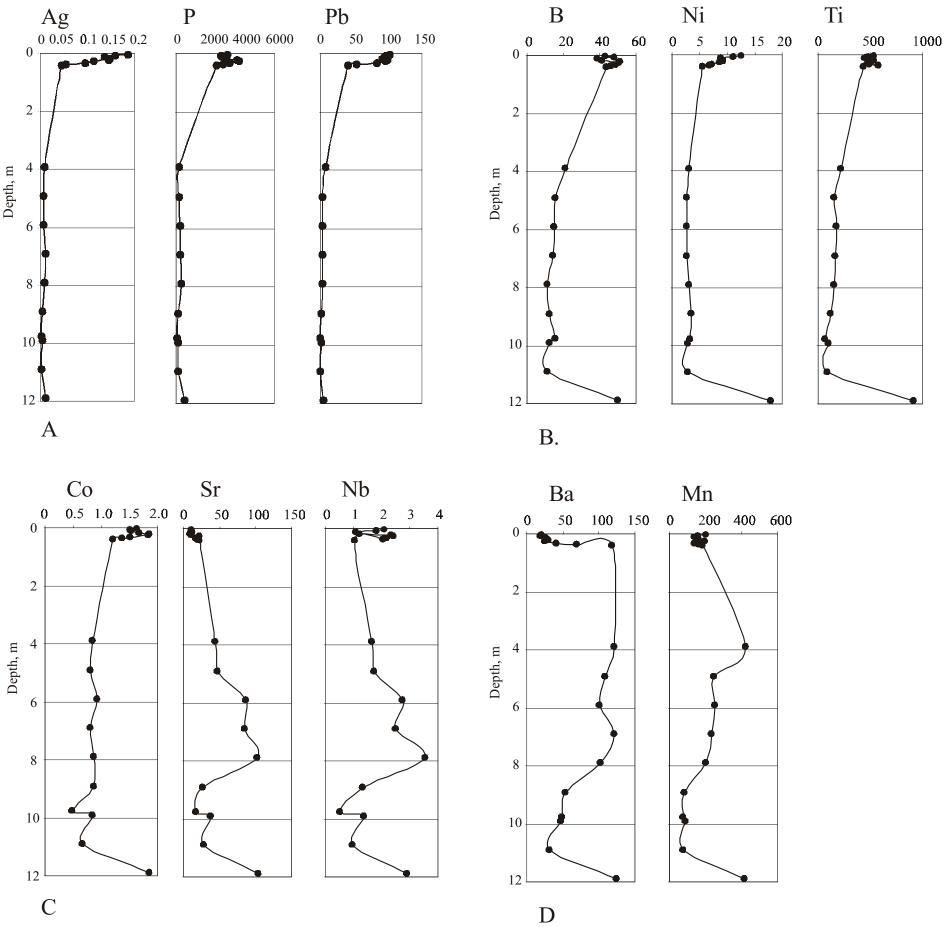

Fig. 3. Trace element distribution in the bottom sediments (Lake Baltys)
3 pav. Mikroelementų pasiskirstymas Balčio ežero dugno nuosėdų pjūvyje

The second group of elements (B, Cr, Ni, Ti, V, Y, Yb, Mo, Zr, Ga) shows increased levels in the upper and lower parts of the profile. This can be related to anthropogenous pollution (in the upper part) and a higher content of clay in the sediments (in the lower part). It should be noted that the heavily increased concentration of certain elements (V – 11.5 times, Yb – 9.5 times, Y, Cr – 8 times, Ga – 7 times) and a decreased loss on ignition (LOI) in the deepest sample (11.8 at 12.0 m depth) show the sample to be more mineralised, enriched by pellitic fraction material (Fig. 3b), which is a characteristic of Preborealis sedimentation. Trace elements of the third group (Sr, Co, La ir Nb) are characterized by greatest changes of their content in the profile. This can be influenced by the changes in hydrochemical and hydrodynamical water regimes (Fig. 3c). Ba and Mn belong to the fourth group. They show the concentrations increasing in sediments within a 4–8 m interval of depth and decreasing within 9–11 m (Fig. 3d).

To sum it up, it is possible to distinguish three different horizons according to trace element distribution in the vertical profile, namely, the upper (to the depth of 0.5 m), the middle (2–11 m) and the lower (about 12–13 m). The upper layer consists of modern sediments, the middle one of Borealis–Subatlantic, and the lower of Preborealis sediments. Each of these layers reflects the regularities of trace element distribution as well as of their interrelated changes.

3.3. Associations of trace elements

The upper layer. The most important trace element association is biogenic-technogenic one, which includes Sn, Pb, Zn, Co, Ag, P, Ni, and Cu (Table 2). This association is characteristic of the bottom sediments of other technogenically polluted Lithuanian lakes (Kadūnas, Budavičius, 2001). Pb with Ag, Sn and Zn, Ni have a particularly strong correlation ($r > 0.9$) with Ag and Cu, Zn with Co, Sn and Pb, showing their common source, which in this case is surface washout or wastewater (in Lake Lydekis).

Table 2. **Trace element association of the bottom sediments**
2 lentelė. **Mikroelementų asociacijos ežerų dugno nuosėdose**

Association (factors)	Upper layer	Middle layer
F1	Sn–Pb–Zn–Co–Ba–Ag–P–Ni–Cu	Nb–Sr–P–Cu–Sc–Ga–Ag–Sn–Co–Ti
F2	Y–Ti–Yb–V–Sc–La	Cr–B–V–Y–Zr–Mn–Pb–Ba–La
F3	Ga–Cr–Sr	Zn–Mo

The second association (Y, Ti, Yb, V, Sc, La) is a mixed allothigenous and allothigenous-accessory association, where trace elements are mostly related to clay minerals of pellitic fraction and weathering-resistant accessory minerals. Trace elements of the latter (Ti, Y) have high correlation coefficients (>0.9). Trace elements related to clay minerals (V, Sc, La) have lower correlation coefficients (0.7–0.8). The third association (Ga, Cr, Sr) is also mixed. It is an authigenous-allothigenous association, where part of trace elements related to clay minerals (Ga, Cr) are in one group with Sr related to carbonates.

The middle layer. This layer reflects distinct changes in the correlation of trace elements. The most important associations (F1 and F2) are very heterogeneous and consist of trace elements from different groups (Table 2). Typical biogenic Zn and Mo make up the third, less significant association. Such a mixed association is characteristic of the organic sediments of other Lithuanian lakes and shows the influence of organic material, acting as a diluent of trace element concentration (Budavičius, Kadūnas, 1999). Most trace elements have high correlation coefficients (>0.9); this shows that they have entered the organic sediments of the lakes from the same source, most probably from the pellitic fraction.

Associations were not analysed in the bottom layer, because only one reliable sample was taken from this layer.

CONCLUSIONS

The distribution of chemical elements in the greater part of the bottom sediments of the lakes studied depends on sedimentation processes and is influenced by changes in the interrelation of terrigenous, biogenic and carbonaceous material.

A rather even distribution of typical chemical elements of clay minerals shows that during sedimentation the nature of terrigenous material and its accumulation (except Preborealis period) were mostly rather stable. The distribution of more changeable quantities of Nb and partly Zr can be an indicator of a periodically intensifying surface washout. Biogenic sedimentation had an insignificant influence on the changes of trace element contents. Carbonaceous sedimentation changes, and especially its unevenness during the Atlantis period, had a great influence on the uneven distribution of Ca, Mg and Sr.

The upper layer of the bottom sediments (to the depth of 0.5 m) clearly shows an influence of anthropogenous processes, which is reflected in the increased contents of many elements-pollutants (Ag, Pb, Zn, Cu) and in the fact that these trace elements comprise the most important association.

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Ričardas Budavičius

CHEMINIŲ ELEMENTŲ PASISKIRSTYMO YPATUMAI LIETUVOS EŽERŲ DUGNO NUOSĖDŲ VERTIKALIUOSE PROFILIUOSE

S a n t r a u k a

Ištyrus keturių Lietuvos ežerų (Varėnio, Glėbo, Balčio ir Lydekio) dugno nuosėdų makro- ir mikroelementinę sudėtį, nustatyti kai kurie cheminių elementų pasiskirstymo dėsningumai vertikaliame nuosėdų pjūvyje. Makroelementai pagal pasiskirstymą pjūvyje išskirti į dvi poras: į kaičius pjūvyje Ca ir Mg ir tolygiai pasiskirsčiusius Fe ir Al. Mikroelementai suskirstyti į keturias grupes: 1 – Ag, Cu, P, Pb, Sn ir Zn, 2 – B, Cr, Ni, Ti, V, Y, Yb, Mo, Zr ir Ga, 3 – Sr, Co, La, Nb ir 4 – Ba ir Mn. Pirmos grupės mikroelementų kiekis ryškiai išauga viršutiniame nuosėdų sluoksnyje (dešimtis kartų). Antrosios grupės mikroelementai pasiskirsto vertikaliame pjūvyje labai tolygiai, o trečiosios grupės – labai netolygiai, ir tai gali būti susiję su karbonatų kaupimosi intensyvumo kaita. Pagal mikroelementų kiekį ir jų pasiskirstymo pobūdį pjūvyje išsiskiria trys horizontai. Viršutinis (iki 0,5 m gylio), vidurinis (0,5–12 m) ir apatinis (12–13 metrų gylyje). Viršutiniame sluoksnyje svarbiausia mikroelementų asociacija yra biogeninė-technogeninė (Sn–Pb–Zn–Co–Ag–P–Ni–Cu), viduriniame sluoksnyje – mišrios sudėties, tačiau daugiausia sudaryta iš alotigeninių mineralų mikroelementų (Nb–Sr–P–Cu–Sc–Ga–Ag–Sn–Co–Ti).

Mikroelementų kiekio kaita ir asociacijos rodo gamtinių sedimentacijos procesų įvairovę holoceno metu ir aiškų technogeninį poveikį šiuolaikinių nuosėdų mikroelementinei sudėčiai.

Ричардас Будавичюс

ОСОБЕННОСТИ РАСПРЕДЕЛЕНИЯ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ В ВЕРТИКАЛЬНЫХ ПРОФИЛЯХ ДОННЫХ ОТЛОЖЕНИЙ ОЗЕР ЛИТВЫ

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На основе исследования макро- и микроэлементов в донных осадках четырех озер Литвы (Варенис, Глебас, Бальтис и Лидякис) установлены некоторые особенности распределения химических элементов по вертикальному разрезу донных отложений (мощностью до 12,5 м). По характеру распределения в вертикальном разрезе отложений исследуемые макроэлементы разделяются на две группы: равномерно распределяющиеся по разрезу (Fe и Al) и неравномерно (Ca и Mg). Микроэлементы подразделены на четыре группы: 1 – Ag, Cu, P, Pb, Sn и Zn, 2 – B, Cr, Ni, Ti, V, Y, Yb, Mo, Zr и Ga, 3 – Sr, Co, La и Nb, 4 – Ba и Mn. Содержание микроэлементов первой группы резко увеличивается в верхнем слое осадков (в десятки раз). Элементы второй группы распределяются по вертикальному разрезу осадков наиболее равномерно, а третьей – наиболее неравномерно, что в основном связано с неоднократной сменой интенсивности садки карбонатов. По валовым содержаниям микроэлементов и их характеру распределения в разрезе отложений выделяются три слоя. Верхний (глубина – до 0,5 м), средний (0,5–12 м) и нижний (12–13 м). В верхнем слое главную ассоциацию микроэлементов составляет биогенно-техногенная ассоциация (Sn–Pb–Zn–Co–Ag–P–Ni–Cu), в среднем – ассоциация смешанного состава, но в основном состоящая из микроэлементов аллотигенных минералов (Nb–Sr–P–Cu–Sc–Ga–Ag–Sn–Co–Ti).

Неравномерное распределение валовых количеств микроэлементов и их ассоциации показывают изменчивые условия седиментации в Голоцене и явное влияние техногенных процессов в настоящее время.