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Main trends in accumulation of trace elements from surface sediments of the Baltic Sea (Lithuanian waters)

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This article presents some results of two projects on a geological mapping programme at a scale 1:50 000 in the Lithuanian part of the Baltic Sea water area. The main task of this article was to determine main regularities in the accumulation of trace elements in the surface sediments. For this purpose several statistic rations were applied. According to concentration coefficients and anomaly values it was established with greater precision how mechanical composition had influenced the accumulation of trace elements in the sediments. Also zones with different trace element contents have been distinguished on the basis of variable indicators, describing the intensity of accumulation, i.e. the summary index of concentration coefficients, and multi-element index.

▱ Baltic Sea, surface sediments, accumulation, trace elements, concentration coefficient (Kk), anomaly values, summary index of concentration coefficients (Zc), multi-element index.

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INTRODUCTION

One of the research fields in geochemistry of marine sediments is related to the characterisation and identification of sediment sources (Degens 1967, Chester 1990). The distribution of trace elements in marine sediments can be used as an indicator of the various geochemical processes and conditions of the ancient and modern depositional environment. These studies, however, require better knowledge about the behaviour of the elements in the modern environments.

At present quite a few investigations have been done to document regional and sub-regional spatial variation of trace elements in the sediments from Gdansk Basin (Emelyanov 1976, Blazhchishin, Emelyanov 1977, Emelyanov 1986, Emelyanov 1995, Galkus, Jokšas 1999, Jokšas 1994, Pustelnikovas 1999, Szczepańska, Uścinowicz 1994, Szczepańska 1995, Emelyanov, Ed. 2002). These investigations enabled to determine various factors such as technogenic load, chemical and sedimentation conditions as well as influence on trace element variations in the sediments. Despite sedimentation conditions, sediment grain size and mineral composition has more important influence on trace element variation and accumulation. For example, lithium hardly concentrates in sediments that contain low amounts of clayey particles. So, in this paper we related the geochemistry of surface sediments to their mechanical composition.

The investigation area is located in the Baltic Sea Lithuanian water area (Fig. 1). Here the sea depth does not exceed 70 m (Fig. 2). Along the coast, the near-shore zone extends at the depths of 0-10-25 m, while the offshore zone is limited by the Palanga ridge (at 10-35 m depths) in the north and the Kuršiu plateau (at 20-50 m depths) in the south of the studied water area. The Pra-Nemunas channel separates these bottom relief forms.

Fine sand and coarse aleurite sediments are widespread here (Fig. 2). Coarse grained sediments (boulders, pebbles, gravel, coarse and medium sand) are closely related to plateaus. According to mineral composition of sand-aleurite fractions, these surface sediments belong to the Sambia-Vistula mineral province (Blazhchishin, Usonis 1970, Blazhchishin 1976, Trimonis, Gulbinskas 2002). The Sambia-Vistula province is characterised by higher amount of ilmenite, glauconite, and minerals of amphiboles group. Particularly these sediments are frequently enriched with heavy allotigenous minerals in the shallow zone. Here the amount of these minerals exceeds 1%. Fine grained (muddy) sediments are spread locally in the deepest part (sea depths more then 65 m) of the studied water area.

The main task of presented study was to find main reasons for trace element accumulation in the surface sediments and to locate zones of their concentration in the investigated water area. For this purpose some statistical parameters were applied to determine how studied chemical element accumulation depends on mechanical composition in the investigated water area. The medians of concentration coefficients and "anomaly indexes" were used to determine main trends in the distribution of trace elements in four sediment groups. The summary index of concentration coefficients (Zc) and "multi-element index" were applied to determine the concentration zones of major and trace elements. A correlation analysis was used to find out how major and trace element concentrations depend on grain-size composition and on the amount of allotigenous accessory minerals.

METHODS AND DATA

This study is based mainly on the data from two projects of geological mapping programme carried out at a scale of 1:50 000 in the Lithuanian part of the Baltic Sea water area. The sampling was performed since 1993 to 1998 (Grigelis, Satkūnas 1997). The database of this survey includes chemical analyses and sedimentological parameters of superficial sediment samples from 3126 sites in the investigated area. The main results of this study are based on 651 sediment samples, which were subjected to chemical analysis (Fig. 2) (Radzevičius 2000, Radzevičius 2001).

Field sampling. All sampling locations were recorded with a global positioning system (GPS). The positioning precision is 50 metres. Two types of sampling techniques are used for collecting sediment samples from sea bottom. The Van Veen grab sampler was used to take samples (0-5 and 5-15 cm intervals) of gravely, sandy, aleurite (silty) sediments. The Niemisto gravity corer was applied to collect cores of muddy sediments (sampling thickness 2 cm). Only the top of a grab and gravity corer sample was used for this study. All superficial sediment samples were subsampled and subjected to grain size, mineralogical, major and trace element analyses.

Laboratory test. The grain-size composition of the sediments was determined following the sieving method for the gravely-sandy-aleuritic (silty) fractions and pipette methods for the aleuritic (silt)-clay fractions (Petelin 1967). In general, the first method was applied for the gravely, sandy, aleuritic (silty) sediments and second one for muddy sediments (Repečka

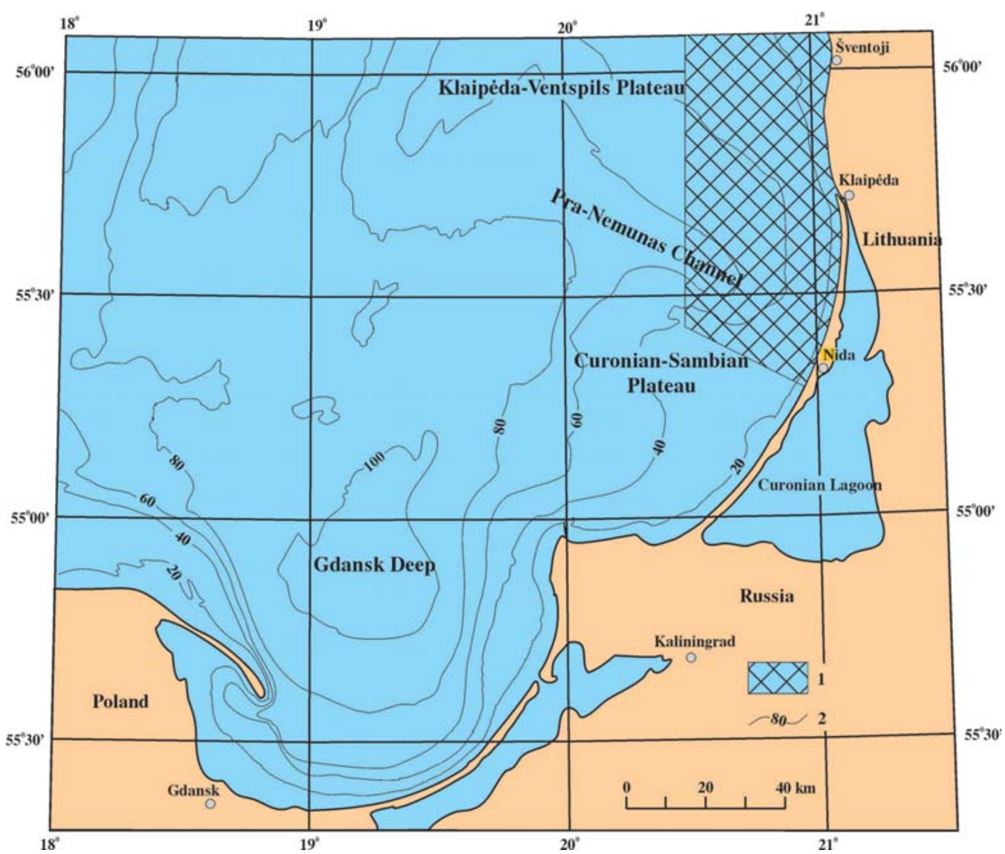

Fig. 1. Location of investigation area in the southeastern Baltic Sea. Note: 1 – area of investigation, 2 – isobathes, m.

1997). The sieving method provides 25 fractions ranging over a <0.01 mm - >10 mm particle sizes (Analizette 3 vibrator sieve shaker with 23 sieves). The pipette method provides 4 fractions (range <0.001-0.05 mm). These results with varying details were presented and published previously (e.g., Gadeikis, Repečka 1999, Gulbinskas, Trimonis 1999, Kairytė 2000, Repečka 1997, Repečka 1999a, Repečka 1999b, Žaromskis 1999).

The amount of heavy minerals was determined in 92 samples (Fig. 2). The samples have been treated first by removing (washing out) particles smaller than 0.01 mm. Residual fraction (>10-0.01 mm) was screened by a sieve of 0.5 mm diameter. The remained sediment fraction 0.5-0.01 mm was separated using isodynamic electromagnetic separator SIM-1 at 1.5 A current. This has enabled to determine all electromagnetic light and heavy minerals (Ruchin 1969, Berlinskij, Shepeliova 1972, Tarakanova 1972). Further electromagnetic minerals were separated into the heavy and light fractions using bromoformium liquid (density of 2.89).

Subsamples (651 in total) for trace element analyses (Fig. 2) were dried in an oven (at 45°C temperature), and all passed through a 1.0 mm nylon sieve to separate >0.1 mm fractions from bulk sediments. The remaining material (<1.0 mm) was powdered in an agate mortar. "Total" content of trace element (Ag, B, Ba, Co, Cr, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, P, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zn) was determined using an optical analysis of element atomic emission spectrum in direct current arc (DC Arc Emission Spectrometry). The X-Ray fluorescence (XRF) analysis was applied to determine Zr total content. Detection limits of analyses are 30 ppm for Ba, 10 ppm for Mn, Ti, and 5 – 0.03 ppm (most of which is 1 ppm) for Ag, B, Co, Cr, Cu, Ga, La, Li, Mo, Nb, Ni, Pb, Sc, Sn, Sr, V, Y, Yb, Zn. The results were consistent with the reference values, and the differences were generally within 25% (Kadūnas

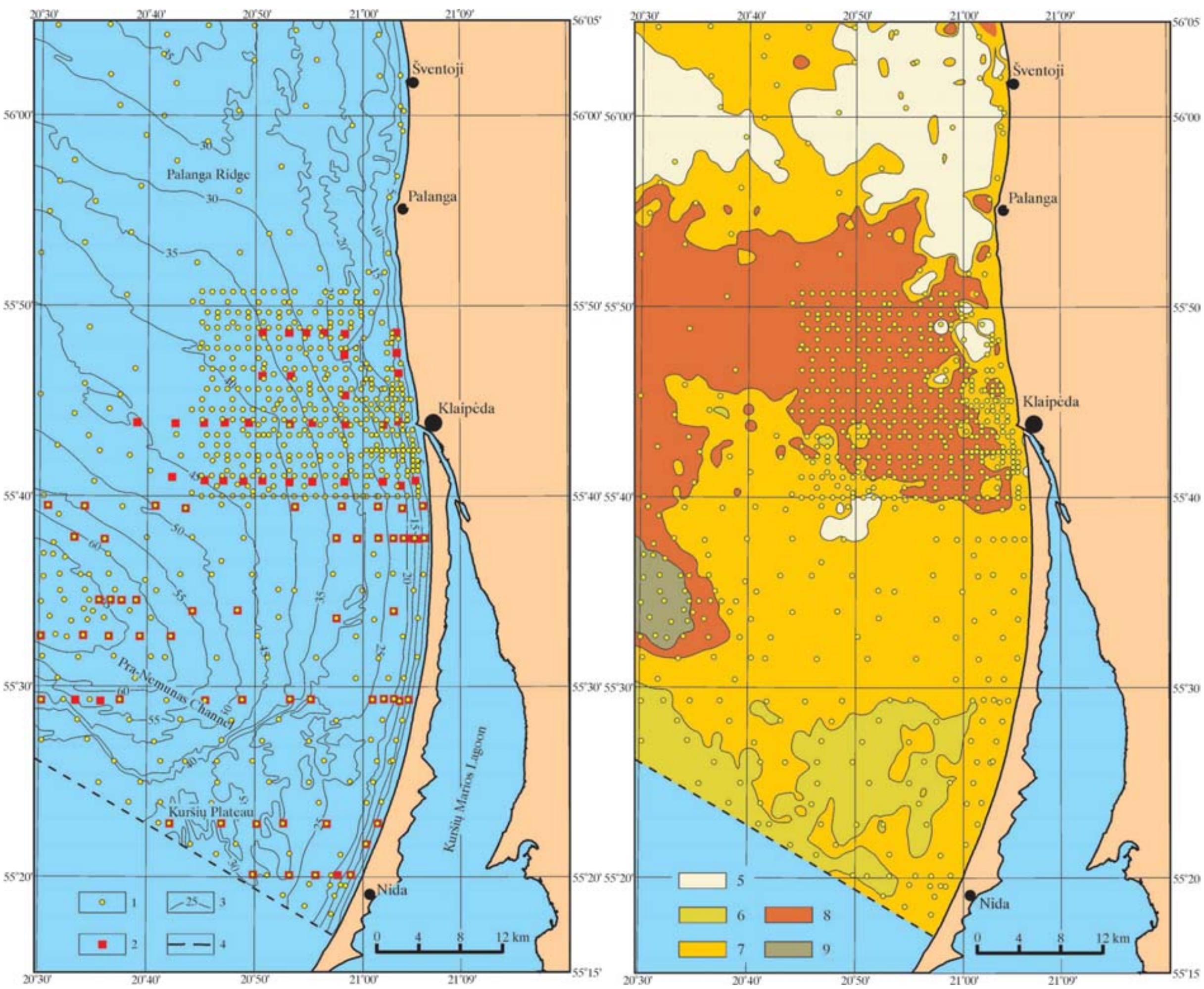

Fig. 2. Geography of investigation area (on the left) and distribution of sediment groups (on the right). Sample sites: 1 – accomplished chemical analyses, 2 – determined heavy minerals content, 3 – isobathes, m (isobathes are taken from Gelumbauskaitė (Ed.) 1998), 4 – Lithuanian-Russian boundary. Sediment groups: 5 – coarse grained sediments did not explored chemical composition, 6 - coarse grained, 7 – fine sand, 8 – coarse aleurite, 9 – fine grained (muddy).

1998, Taraškevičius, Zinkutė 1999). The subsamples analysed by DC Arc Emission Spectrometry after burning at a temperature of 450^{0}C and the loss on ignition was calculated. The following international reference standards were used for quality control: OOKO 301, 302, 303 and OOPE 101, 201, 401. The concentrations of elements obtained by DC Arc Emission Spectrometry were recalculated to dry matter.

For investigation four groups were made up. Sediment subdivision into four groups was made by reference median diameter of their particles (Table 1). There is first group with >0.25 mm Md, composed of coarse sediments. A second group comprises fine sand with Md ranging from 0.25-0.1 mm. There is a third group of coarse aleurite having Md from 0.1-0.05 mm. The fourth group is formed of fine (muddy) sediments with <0.05 mm Md (Fig. 2). Also it is necessary to note that boulders, pebbles, gravel, i.e. sediments coarser than coarse sand (Md>1.0 mm) and deposits such as clays, tills, had not been studied here.

In data processing, standard statistical methods (descriptive statistics and correlation analysis) and software (EXCEL) were used. Geochemical rations and indexes were applied for this study (Saet etc. 1990, Kadūnas 1998, Zinkutė 1998, Kadūnas et al. 1999). The concentration coefficients were determined by dividing trace element concentration in each sediment sample by their median value in all sediments not differentiated according to median diameter of their particles. The trace element median values and methodology of calculation were presented elsewhere (Radzevičius 2000, Radzevičius 2001). The anomaly values for each trace element was calculated according to percentage contribution of samples with Kk>1.5 in each sediment groups. The lower limit of the anomaly was taken as 1.5 of the concentration coefficient (Saet etc. 1990). The summary index of concentration coefficient (Zc) was obtained by summing up concentration coefficients of elements. The multi-element index indicates abundance of elements with Kk>2 (Zinkutė 1998, Radzevičius 2002).

Table 1. Concentration coefficients and anomaly values of trace elements in the sediments.

El.	(r)	Sediment groups							
		Coarse grained (Md>0.25 mm)		Fine sand (Md=0.25-0.1 mm)		Coarse aleurite (Md=0.1-0.05 mm)		Fine grained (Md<0.05 mm)	
		KkMd	An., %	KkMd	An., %	KkMd	An., %	KkMd	An., %
Mn	**-0.79**	0.98	11.1	1.07	34.5	1.01	47.6	0.82	5.3
Ti	0.56	0.34	5.6	0.95	38.3	1.24	66.7	1.02	5.3
Zr	0.04	0.11	5.6	1.15	46.7	1.63	77.3	0.54	0.0
Nb	**-0.68**	0.83	0.0	1.02	17.2	0.99	12.1	0.59	0.0
Y	0.31	0.66	2.8	1.10	34.9	1.09	51.2	0.92	0.0
La	0.01	0.89	5.6	1.01	31.0	1.30	37.3	0.97	10.5
Yb	0.33	0.41	0.0	1.05	31.0	1.20	35.8	0.86	5.3
Li	**0.89**	1.22	8.3	0.95	11.5	1.11	8.2	3.26	94.7
Ga	**0.90**	1.18	19.4	0.94	6.5	1.37	16.1	2.81	94.7
Mo	**0.90**	1.24	11.1	0.99	11.1	1.00	17.3	4.37	89.5
Pb	**0.95**	0.97	2.8	1.03	15.3	1.61	17.3	4.70	94.7
Ag	**0.95**	0.96	5.6	1.01	15.7	1.45	7.3	3.39	84.2
Sn	**0.95**	0.98	2.8	1.01	7.3	1.10	4.2	1.77	63.2
B	**0.97**	0.50	0.0	0.94	23.0	1.28	39.1	1.95	73.7
V	**0.98**	0.58	2.8	0.94	14.6	1.35	21.5	2.54	78.9
Cr	**0.95**	0.49	0.0	0.94	26.4	1.46	36.1	2.23	84.2
Co	**0.95**	0.84	8.3	0.99	11.5	1.39	28.8	2.09	89.5
Ni	**0.94**	0.97	11.1	0.96	10.3	1.42	23.3	4.48	94.7
Cu	**0.98**	0.24	5.6	0.90	16.1	1.42	21.5	5.49	94.7
Zn	**0.96**	0.74	16.7	0.89	36.4	1.32	74.8	4.02	94.7
Sc	**0.99**	0.32	8.3	0.97	29.9	1.49	54.2	3.73	84.2
P	0.50	1.02	2.8	1.00	6.5	0.97	1.5	1.05	10.5
Ba	**0.79**	0.98	11.1	0.84	2.3	1.10	1.2	1.33	15.8

Note: Bolding indicates significant correlation coefficients (r) when n=4 q=0.01 at r=|0.66|. KkMd – median value of concentration coefficients, An. % - anomaly value.

RESULTS AND DISCUSSION

One way to determine trace element accumulation in the sediments is to sort out trace elements according to their concentration coefficients and to describe the obtained rank (Saet 1990, Kadūnas 1998, Zinkutė 1998). The concentration coefficient medians and anomaly values of trace elements are presented for each sediment group (Table 1).

Only concentration coefficient median (KkMd) values of Mo, Li, Ga and P are higher then 1.0 but did not exceed the lower limit of anomaly (1.5) in the coarse grained sediments (Table 1). The rest of trace elements KkMd values are lower 1.0. Anomaly values of trace elements are 10-20% for Ga, Zn, Mn, Ni, Mo, Ba and less 10% for rest of trace elements in the coarse sediments (Table 1). The KkMd values of all trace elements did not exceed lower limit of anomaly level in the fine sand as in the coarse sediments (Table 1). The KkMd values higher then 1.0 are determined for Zr, Y, Mn, Yb, Pb, Nb, Ag, La, Sn, and P. Other elements (Mo, Co, Sc, Ni, Li, Ti, Ga, V, Cr, B, Cu, Zn and Ba) KkMd values are lower then 1.0. The anomaly values of Sn, Ga, P and Ba are lowest (<10%) in the fine sand. Zirconium is the most anomalous (46.7%) element in the fine sand, then passing Ti, Zn Y, Mn, La, Yb and Sc with anomaly values ranging in 29.9-38.3%. Such anomaly values show uneven accumulation of Zr, Ti, Zn Y, Mn, La, Yb and Sc in the fine sand sediments.

Only KkMd values of Nb and P are lower then 1.0 in the coarse aleurite (Table 1). The rest of trace elements KkMd values are exceeding 1.0. The concentration coefficients median values overpass the lower limit of anomaly level (1.5) shown intense accumulation of Zr and Pb in the coarse aleurite. Also more intense accumulation of Sc, Cr, Ag, Ni, Cu, Co, Ga, V, Zn La, B, Ti and Yb were determined (KkMd range 1.2-1.5) in the coarse aleurite comparing to those accumulation in the coarse sediments (KkMd<1.2) and fine sand (KkMd<1.05). Most of trace elements anomaly values (>30%) indicate uneven accumulation in the coarse aleurite sediments. The anomaly value of Zr and and Zn are higher then 70% then follow Ti, Sc, Y – higher then 50% and Mn, B, La, Cr, Yb – higher then 30% (Table 1). The anomaly values (<10%) of Li, Ag, Sn, P and Ba indicate gradually accumulation in the coarse aleurite sediments.

Most intense accumulation of trace elements was determined in the fine (muddy) sediments (Table 1). The medians of concentration coefficients of Cu, Pb, Ni, Mo, Zn, Sc, Ag, Li, Ga, V, Cr, Co, Cu, B and Sn exceeding (most of them two and more times) the lower limit of anomaly level (1.5). Titanium, barium and phosphorus accumulation is slightly weakness (KkMd range 1.0-1.5), and La, Y, Yb, Mn, Nb and Zr are dispersed or did not accumulate (KkMd<1.0) in the fine (muddy) sediments. Highest anomaly values (most of them >70%) were determined for Zn, Ni, Cu, Pb, Ga, Li, Co, Mo, Sc, Cr, Ag, V, B, Sn, and smallest – for Zr, Yb, Nb, Ti, Mn, Yb (<10%).

Small median values of concentration coefficients (KkMd<1.5) and low anomaly values (<30%) show the trace elements are dispersed in coarse grained sediments. According to these values, Zr, Ti, Zn, Y, Mn La, Yb and Sc were unevenly accumulating in the fine sand. In coarse aleurite, intense accumulation of Zr and Pb (KkMd>1.5) as well as Zr, Zn, Ti, Sc, Y, Mn, B, La, CR and Yb (anomaly values >30%) were observed. The most intense accumulation was determined for Cu, Pb, Ni, Mo, Zn, Sc, Ag, Li, Ga, V, Cr, Co, B and Sn (KkMd>1.5 and anomaly values >50%) in fine grained (muddy) sediments.

Three principal groups of trace elements were formed basing on the variability of median concentration coefficients and the anomaly values in the sediment rank: coarse-grained sediments, fine sand, coarse aleurite, fine-grained (muddy) sediments.

The first group comprises Zr, Yb, Y, Ti, Mn, Nb and La. The medians of concentration coefficients of these trace element distributions in the sediment rank resemble an arc (Fig. 3). The median concentration coefficients of first group trace elements exceed 1.0 in fine sand and coarse aleurite (Table 1, Fig. 3). Coarse grained and fine-grained (muddy) sediments show them smaller then 1.0 (except for Ti). Similarly variations are also seen in anomaly values of Zr, Yb, Y, Ti, Mn, Nb and La (Fig. 4). Except for Nb the anomaly of rest ones exceeds 30% in fine sand and coarse aleurite (Table 1). In the coarse grained and fine grained (muddy) sediments (except for Mn), their anomaly value is lower than 10%. Insignificant correlation coefficients (r<|0.66|) between the median concentration coefficients and the sediments groups demonstrate that accumulation of Zr, Yb, Y, Ti and La in the sediments is less depending on grain-size composition (Table 1). The significant negative relationships indicate the weakening of accumulation with sediments becoming finer.

The accumulation of trace elements belonging to the first group is greatly influenced by the amount of heavy allotigenous accessory minerals (Table 2). It virtually confirms significant and positive correlation coefficients (r=|0.66|) between concentration coefficients of Zr, Yb, Y, Ti, Mn, Nb, La and the content of heavy electromagnetic minerals. Besides, the median concentration coefficients of Zr being 3.0, Ti – 2.1, Yb – 2.1, Y – 2.0, La – 2.0, Mn – 1.5 and Nb 1.3 in the sediments with the amount of heavy minerals are higher than 1% (Table 2). The median concentration coefficients of all of them, except for Nb, exceed the limit of anomaly level (1.5). To the contrary, the median concentration coefficients of following trace elements are lower 1.0 in the sediments containing up to 1% of heavy minerals. It demonstrates evidently an influence of heavy allotigenous accessory minerals on the accumulation of Zr, Yb, Y, Ti, Mn, Nb and La in sandy and coarse aleurite sediments.

The second group, most abundant in trace elements, comprises Cr, B, Co, V, Sc, Cu, Ag, Zn, Pb, Sn, Ni, Ga, Li and Mo. Some common peculiarities are characteristic of this group. The median concentration coefficients increase with sediments going finer (Fig. 3). Concentration coefficients of all trace elements exceed the anomaly level in the fine grained (muddy) sediments, and for most of them are higher in 2, 3 or 4 times (Table 1). The trace elements linked to the largest anomaly are concentrated in the fine (muddy) sediments (more than 60% of samples). The rest sediment groups show smaller anomaly values of trace elements (Table 2). Significant correlation coefficients between the median concentration coefficients and the groups of sediments (higher 0.70) confirm their direct dependence on the grain-size composition. With the sediments

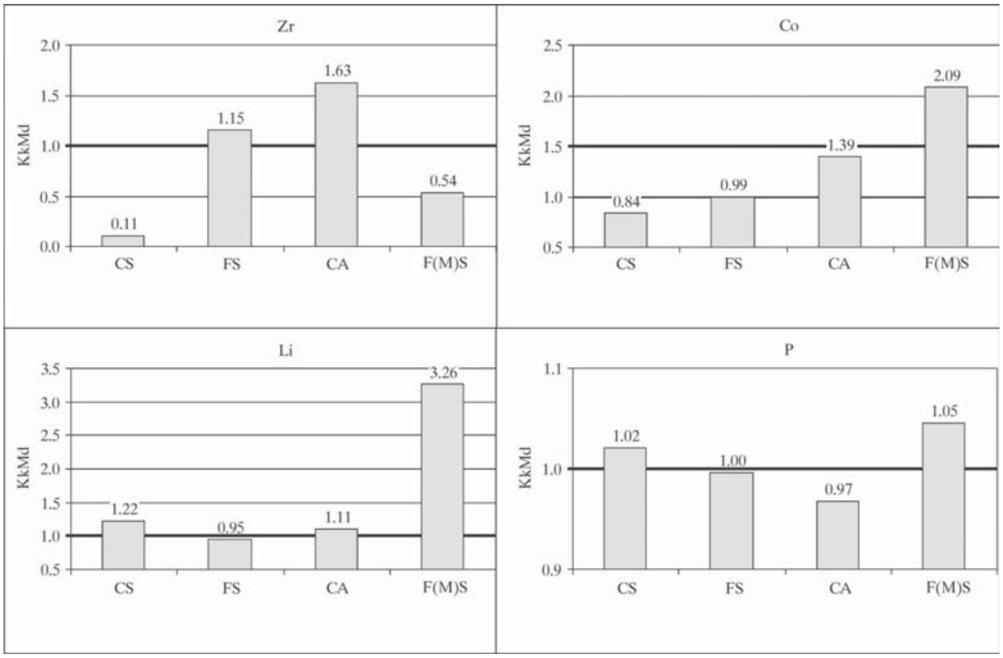

Fig. 3. Examples of main types of trace element accumulation in the sediment rank: CS – coarse grained, FS – fine sand, CA – coarse aleurite, F(M)S – fine grained (muddy) sediments. Note: KkMd – medians of concentration coefficients.

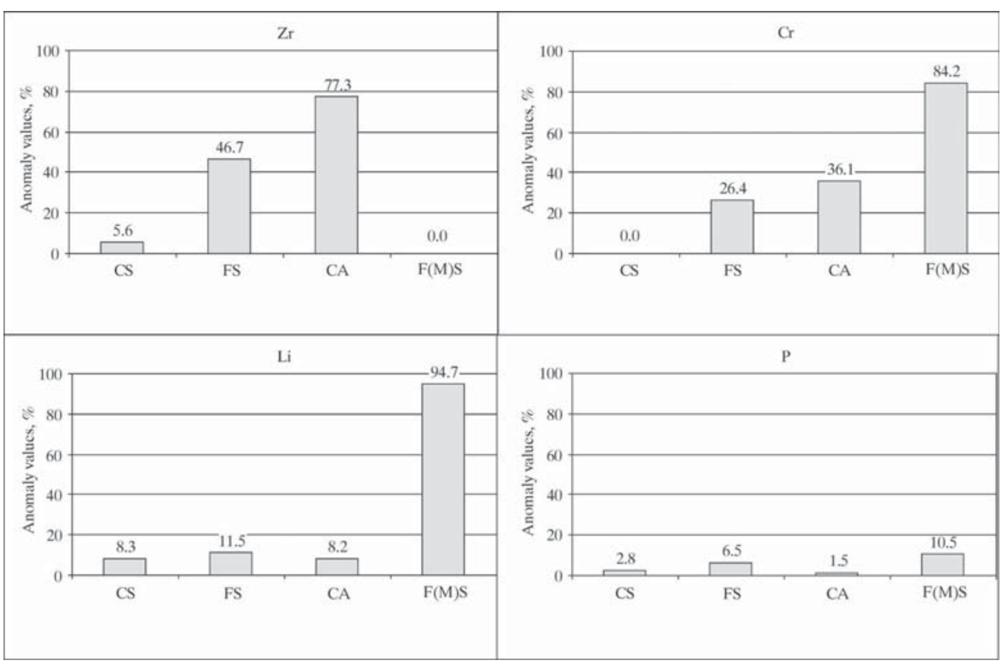

Fig. 4. Examples of anomaly value variability for trace elements in the sediment rank: CS – coarse grained, FS – fine sand, CA – coarse aleurite, F(M)S – fine grained (muddy).

going finer, their accumulation increases and proceeds in most intensive way in the fine-grained (muddy) varieties. Despite of mentioned common peculiarities, the accumulation of the second group trace elements was found to differ slightly in the coarse-grained sediments, fine sand and coarse aleurite.

Median concentration coefficients and anomaly values of Li, Mo and Ga vary similarly in the sediment row (Fig. 3, Fig. 4). Their medians are the lowest in the fine sand, and exceed 1 in the coarse aleurite. This seems to be related to the clay minerals (Li, Ga), as they can form insignificant admixtures in weakly differentiated coarse deposits. A thin layer of sediments of this kind covers tills and clays of the southern part of Kuršių plateau. The increased amounts of Mo may occur because of the Fe and Mn hydroxides sorbing Mo.

The exclusive feature of Ni, Cu, Zn, Sc, B, Cr, V and Co is the median concentration coefficient lower than 1.0 in the coarse sediments and fine sand, whereas in the coarse aleurite and fine (mud) sediments they exceed 1.0. The accumulation of these trace elements is mostly caused by a fine-dispersed fraction. Despite that, concentrations of Sc, Cr, B, V, Co and Cu in fine sand and coarse aleurite were mostly influenced by the heavy allotigenous minerals. This is confirmed by median concentration coefficients of the sediments containing more than 1% of heavy minerals (Sc – 1.5, Cr – 1.4, B – 1.4, V – 1.4, Co – 1.0, Cu – 1.0) and less than 1% (Sc – 1.3, Cr – 0.7, B – 0.7, V – 0.8, Co – 0.8 and Cu – 0.5) (Table 2). Significant correlation between concentration coefficients of Cr, B and V and the amount of heavy minerals shows, that the accumulation of these trace elements was significantly influenced by heavy allotigenous minerals. The role of the latter factor in accumulation of Sc, Co, Cu and is not determined yet.

The third subgroup comprises Ba and P. Median concentration coefficients of Ba are similar to those of Li, Ga and Mo. The same indices of P go lower with a fineness of sediments. Despite the differences, median concentration coefficients of Ba and P do not exceed the anomaly level and anomaly values do not reach 20% (Table 1, Table 2). The mentioned features based the opinion that Ba and P are dispersed in the studied water area and they were weakly accumulated there.

Such trends of trace element accumulation in the studied sediments slightly differ from regional trace element variations in the Baltic Sea sediments (Blazhchishin, Emelyanov 1976, Emelyanov 1986, Emelyanov ed. 2002). These differences, in author's opinion, originate from sediment sub-regional grain-size composition, i.e. content of fine dispersed material and heavy mineral. Making reference to the content of particles <0.01 mm fine dispersed material input to sediment composition was illustrated (Fig. 5). The amount of particles <0.01 mm vary from 0 to 64.5%. According to our data at the 60 m sea depth the amount of particles <0.01 mm increase from 1-2 % to 5-10% in the sediments. Sediments with small amount of these particles (average 2.1%) are widespread in the studied water area. Low amounts of particles <0.01 mm predetermine weak accumulation of trace elements associated with fine

Table 2. Impact of heavy minerals on trace element accumulation in the sediments.

El.	(r)	**Concentration coefficients**					
		when HM>1%			**when HM<1%**		
		Min	Max	**Md**	Min	Max	**Md**
HM, %	-	1.08	4.46	1.74	0.32	0.98	0.62
Mn	**0.89**	0.72	4.03	1.53	0.31	1.35	0.77
Nb	**0.75**	0.54	2.87	1.32	0.60	1.19	0.94
Ti	**0.74**	0.22	6.10	2.13	0.23	1.35	0.72
Zr	**0.69**	0.08	7.81	3.01	0.03	1.30	0.43
Yb	**0.65**	0.52	5.71	2.09	0.15	1.46	0.77
Cr	**0.65**	0.46	2.81	1.43	0.32	1.93	0.71
La	**0.65**	0.71	5.25	2.02	0.32	1.57	0.77
Y	**0.64**	0.62	4.08	1.98	0.49	1.52	0.86
B	**0.53**	0.39	2.20	1.40	0.39	1.60	0.74
Zn	0.52	0.73	5.23	0.75	0.73	4.38	0.74
V	0.52	0.52	2.05	1.35	0.37	2.37	0.78
Co	0.37	0.59	1.78	1.03	0.68	2.10	0.83
P	0.29	0.58	1.46	1.11	0.70	1.44	1.01
Ba	0.10	0.29	4.74	0.62	0.30	1.54	0.95
Cu	0.08	0.12	1.92	0.97	0.12	3.28	0.48
Sc	0.07	0.32	2.24	1.49	0.32	3.90	1.35
Sn	0.03	0.84	1.58	1.08	0.84	2.04	1.09
Ag	0.01	0.40	9.76	1.11	0.70	3.28	0.98
Mo	-0.03	0.98	1.64	1.04	0.98	3.88	0.99
Ni	-0.07	0.63	1.79	0.89	0.62	2.67	0.94
Ga	-0.08	0.63	1.45	0.96	0.67	2.13	1.03
Pb	-0.16	0.69	2.09	0.92	0.69	3.55	0.98
Li	**-0.47**	0.39	1.49	0.81	0.68	2.39	1.23

Note: HM, % - amount of heavy minerals in the 0.5-0.01 mm size sediment fraction, bolding indicates significant correlation coefficients (r), when n=53 q=0.01 at r=|0.66|.

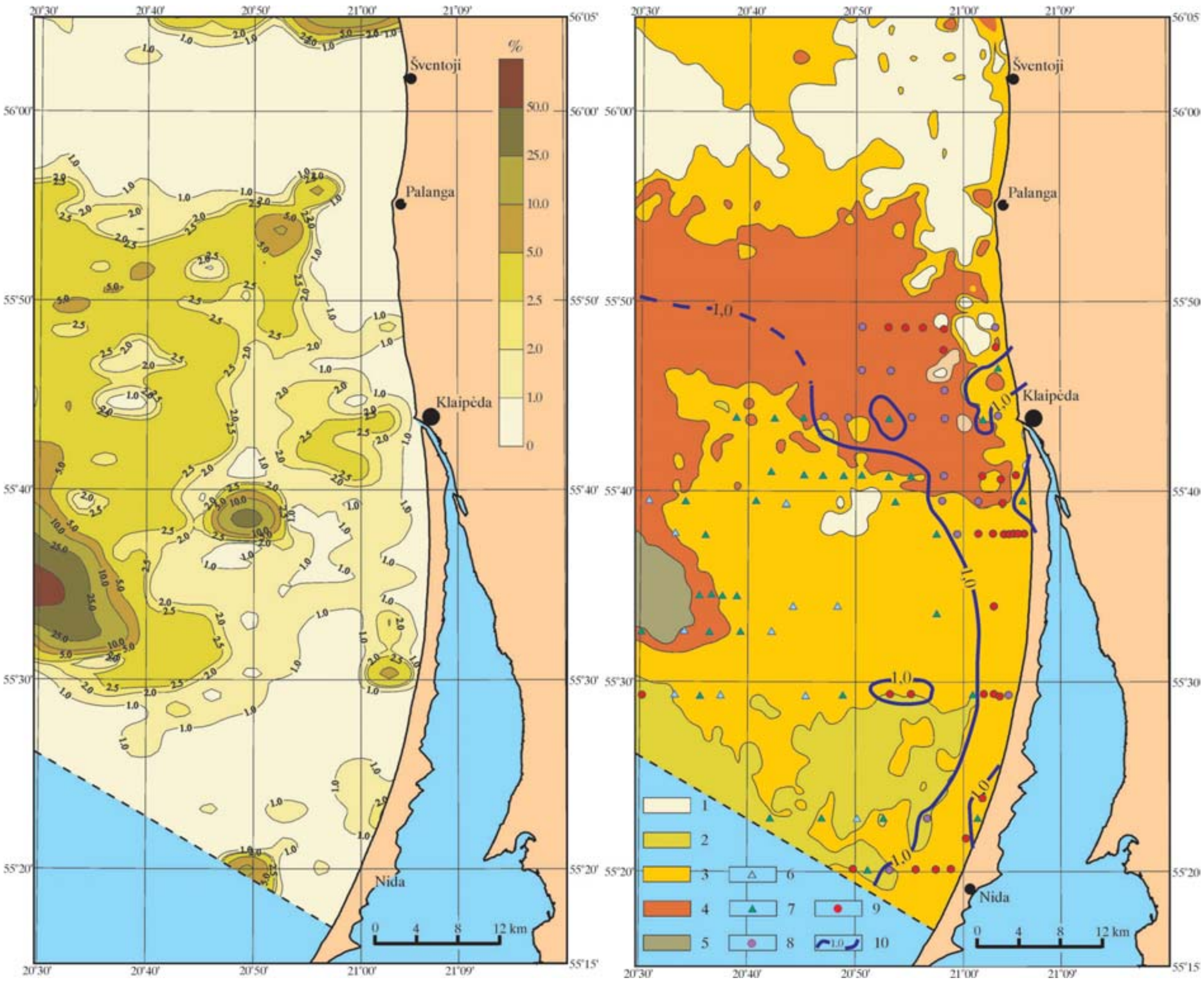

Fig. 5. Distribution of fine grained (<0.01 mm) particles (on the left) and amount of heavy minerals (on the right) in the sediments. Sediment groups: 1 – coarse grained sediments did not explored chemical composition, 2 - coarse grained, 3 – fine sand, 4 – coarse aleurite, 5 – fine grained (muddy). Samples with amount of heavy minerals: 6 – 0 – 0.5%, 7 – 0.5 - 1.0%, 8 – 1.0 – 1.5%, 9 - >1.5%.

dispersal matter. On the other hand in the shallow zone of studied water heavy minerals (Fig. 5) frequently enrich area sediments. Here the amounts of heavy mineral range from 1.0 to 4.46% (2.12% mean). This factor has influenced mostly Zr, Yb, Y, Ti, Mn, Nb, La and partly Ni, Zn, B, Cr, V, (Sc, Cu, Co) accumulation in the studied sediments and irregularity of their regional distribution (rules) in the sediments.

The uneven accumulation of trace elements in the studied sea area is well illustrated by the total index of concentration coefficients (Zc_{23}), where 23 – is a number of applied trace elements. According to the distribution of this index in the area, three large zones are distinguished (Fig. 6). In the east and west parts the highest Zc23 indices (>16) are established. The most intensive accumulation of trace elements of the shallow sea area occurs in the east, whereas in the west of the area this happens at the deepest sea zone. Eastern zone of intense trace elements accumulation is related to sediments with heavy mineral content higher then 1%, the western zone is related to fine grained or muddy sediments (Fig. 5, Fig. 6). These two zones are separated by the third one, where the accumulation is not defined (Zc23<8). These three zones are also distinguished by the "multi-elemental index" (Fig. 6). In the eastern and western parts it increases from 2 to 10, whereas the intermediate zone has it lower than 2. The higher Zc23 indices and "multi-element index" are related to the shallow sedimentation zone, where trace elements are concentrating in the sediments under the concentration of heavy allotigenous minerals in the eastern part of the studied area and the deep zone in the western part.

CONCLUSIONS

Based on the medians of concentration coefficients and anomaly values, the trace elements have been subdivided into three main groups. These groups reflect how trace element accumulation depends on sediment grain size composition from the studied water area. The first group is made up of Zr, Yb, Y, Ti, Mn,

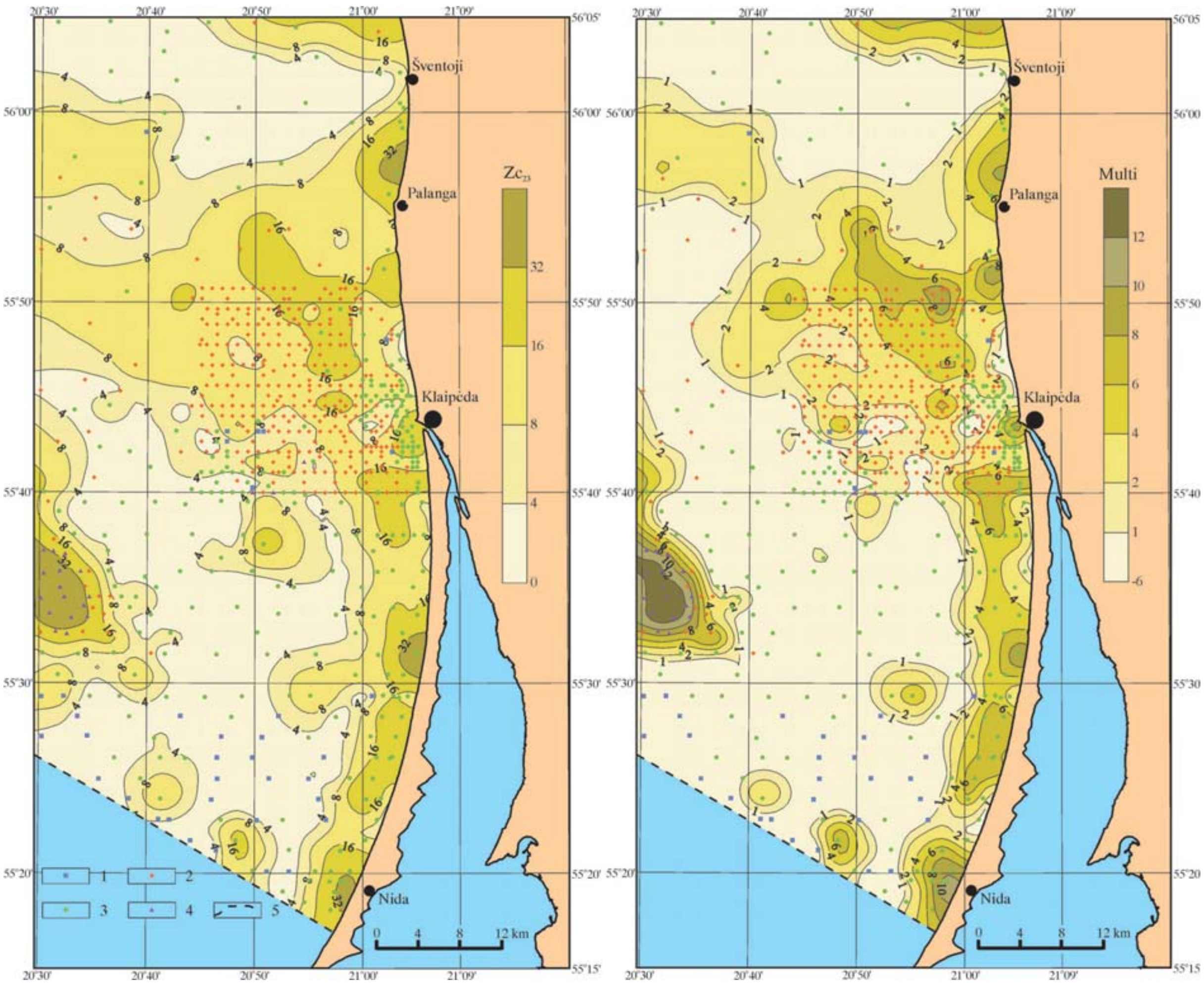

Fig. 6. The summary index of concentration coefficients (Zc23) (on the left) and multi-element index (Multi) (on the right) in the sediments.

Nb and La, and their accumulation weakly depends on grain size composition. They are intensively concentrating in the fine sand and coarse aleurite, though they are randomly dispersed or are sparse in the coarse grained and fine-grained (muddy) sediments. The second group consists of Li, Mo, Ga, Sn, Ag, Pb, Ni, B, Cu, Cr, Zn, V, Sc and Co. Their concentration change is growing with the shift towards the fine-grained sediments. The third group comprises Ba and P. These trace elements are sparse in the sediments from the studied water area.

The trace elements of the first group accumulation weakly depend on sediment grain size composition but their accumulation is consistent with the amount of heavy allotigenous minerals. The heavy allotigenous minerals, however, had influenced the accumulation of Ni, Cu, Zn, Sc, B, Cr, V and Co from second group in the fine sand and coarse aleurite.

The summary index of concentration coefficients obtained from 23 studied elements, and the multi-element index (i.e. the abundance of trace elements with Kk>2) characterise uneven distribution and accumulation of trace elements in the sediments. In respect to their values, three main zones have been distinguished. The intense accumulation of trace elements was located in the eastern and western part of studied area and transitional with week accumulation. These zones coincided with the zones of the modern terrigenic sedimentation in the Baltic Sea. Trace elements intensively accumulate in the shallow (eastern) and the deep (western) sedimentation zones, whereas the accumulation is week in the transitional zone.

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