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# Sedimentation in the eastern Baltic Sea: lead-210 dating and trace element data implication

*Jonas Mažeika, Rimantė Dušauskienė-Duž, Rolandas Radzevičius*

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**Abstract** Sediment cores, collected from fourteen stations along the eastern coast of the Baltic Sea during cruises of different research vessels between the years 1979–1999, were dated using natural $^{210}$Pb (radiochemistry and beta spectrometry). Two additional cores collected close to Lithuanian coast were dated using natural $^{210}$Pb and artificial fallout radionuclide $^{137}$Cs (direct gamma ray spectrometry). For five sites the sedimentation rates were found to be relatively high – between 2.5 and 6.5 mm/year. At most of the sites the sedimentation rates were relatively uniform – between 1.0 and 2.0 mm/year. One site showed low sedimentation rate (0.3 mm/year). For most of the sites the $^{210}$Pb activity versus depth profile was regular, and in consequence the $^{210}$Pb dates were relatively unambiguous. Some sites were notable for irregularities in the $^{210}$Pb activity versus depth profiles, indicating significant variations in the sedimentation rate during the past 120 years and especially after 1960. Together with high resolution dating the cores were also analysed for trace elements and then multivariate statistical analysis was carried out. The influence of clay minerals on element occurrence in studied sediments was obvious. The factor analysis showed that anthropogenic load in cores could be different despite that they were located very close to each other. The trace element concentrations in the sediment core taken from aleuritic-pelitic mud were more evenly distributed and can be explained by better sorting of sediments. The data obtained by radioisotope dating and trace elements methods showed to be in sufficiently good accordance for the eastern part of the Baltic Sea.

**Keywords** *Baltic Sea, radioisotope dating, lead-210, trace elements, sedimentation rate, multivariate statistical analysis.*

*Jonas Mažeika [mazeika@geo.lt], Rolandas Radzevičius [rolandas.radzevicius@geo.lt], Institute of Geology and Geography, Ševčenkos 13, LT-03223, Vilnius, Lithuania; Rimantė Dušauskienė-Duž, Institute of Botany, Žaliųjų ežerų 49, LT-08406, Vilnius, Lithuania.* *Manuscript submitted 15 September 2004; accepted 10 November 2004.*

## INTRODUCTION

During the recent years there has been renewed focus on the Baltic Sea. Not only because the Baltic is one of the world's largest estuarine systems but also because it is the area of focal importance for 15 countries as a transportation channel, recreational area and fishing ground.

The Lithuanian scientists have been investigating the Baltic Sea as far as their potential allowed. Participation in various projects of recent years resulted in efforts of more detailed examination of cores with high resolution sampling and assessing by radioisotope methods and determining the distribution patterns of trace elements. Some of material presented in this study had been collected in the years of Soviet power. Yet the research possibilities then were limited – methods and part of equipment were insufficient to carry out investigations on a modern level. The recently introduced gamma and beta spectrometric systems allowed examining cores with higher resolution by new methods, to unify the methodical interpretation of all available core material and to determine the rates of sedimentation on the basis of cores obtained in 1978–1999.

The main goal of this study was to find out the rates of recent sedimentation in the eastern part of the Baltic Sea on the basis of radioisotope methods and to characterise the sediment cores – especially the ones collected close to the Lithuanian coast – according to the distribution patterns of trace elements and basing on factor analysis. Moreover, the present study is the first one dealing with the factor analysis of the geochemical data of sediment cores taken close to the Lithuanian coast. Together with radioisotope dating it gives a closer view onto relationships between the natural and anthropogenic factors influencing sedimentation peculiarities.

## ENVIRONMENTAL AND GEOLOGICAL SETTINGS

The Baltic Sea is a brackish-water body with a surface salinity gradient from *c*. 1‰ in the north to *c*. 10‰ in the south. It consists of a number of basins, including the gulfs of Bothnia, Finland and Riga as well as the Baltic proper. The study area is attributed to the Eastern Baltic and is comprised of the gulfs of Finland and Riga as well as the eastern part of the Baltic proper (Fig. 1).

The Baltic Sea covers an area of *c*. 400 thousand km$^2$ and is characterised by large fluxes of river water inputs and periodic inputs of more saline water from deeper layers of the North Sea. It is a semi-enclosed sea. The water exchange occurs through the narrow Öresund and Store Bælt, mainly driven by the sea-level difference between the southern Kattegat and the Southwestern Baltic (Wulff *et al.* 1990). The intervals between major inflows of highly saline oxygen-rich deep water are irregular, but such events occur predominantly in autumn and winter. The circulation in the Baltic Sea is not very pronounced, but there is a cyclonic salinity distribution with high-salinity deep water flowing inwards along the eastern coasts and low-salinity surface water flowing out along the Swedish coast. The main oceanographic feature of the Baltic Sea today is the permanent salinity stratification (Kullenberg 1981). The largest rivers discharging into the Baltic proper are Vistula and Nemunas. A well-stratified water column and sufficient supply of nutrients leads to algal blooming in the central Baltic. Blooming periods generate finely laminated sediments by settling of larger flocks of nutrient remains. In the periods of increased wind forcing (normal conditions), a relatively thick and well-ventilated surface water layer is formed with normal primary production. Particle transport to the seafloor is then restricted and more homogeneous sediments are deposited (Andrén *et al.* 2000).

The last deglaciation of the Baltic basin occurred between *c*. 13 500 and 13 000 (Ringberg 1988) and 9000 $^{14}$C yr BP (Andrén 1990) and its history thereafter has been controlled by the interaction between isostatic rebound and eustatic sea-level fluctuations caused by climate change. The several freshwater and marine stages in the history of the Baltic Basin, following the end of the Late Weichselian glaciation, have been distinguished. These stages, e.g., Baltic Ice Lake, Yoldia Sea (consisted of two freshwater phases with a short brackish-water phase in between), Ancylus Lake, Initial Litorina Sea, Litorina Sea, Post-Litorina Sea, Recent Baltic Sea, Present Baltic Sea, recorded in the sediments lithostratigraphy and adjusted to $^{14}$C dates are discussed in detail in many studies (Jensen 1995, Andrén *et al.* 2000).

For assessment of sediments in this study the short gravity corers were available. Short cores could be illustrative of only the last few hundred years of sedimentation, reflecting mainly the changes over the Present and Recent Baltic Sea stages. The trends of those changes are overviewed in a number of papers. Investigations of diatom assemblage in the Southern Baltic coastal areas have shown evidence of the sea eutrophication that have been dated to *c*. AD 1850-1900 (Witkowski & Pempkowiak 1995). A significant change during the last Baltic Sea stages is traced by a shift from dominance by brackish-marine periphytic taxa to principally planktonic taxa, interpreted as being the effect of increased water turbidity in response to increased nutrient availability (Andrén *et al.* 2000). Since the turn of the century the P load entering the Baltic Sea has increased by a factor 8, and the N load by a factor 4 (Elmgren 1989). Significant indications of eutrophication have been reported in the Baltic coastal areas in recent decades, e.g., the increased primary production, increased turbidity, altered benthic/pelagic ratio, lower growth limit for phytobenthos and hypoxia/anoxia in sediments, expanding areas of laminated sediments, and elevated organic carbon content of the uppermost sequence, whereas there are only few reports of increased primary production, alteration in phytoplankton species composition or other changes in the open Baltic Sea (Elmgren 1989, Bonsdorff *et al.* 1997). Alteration in the diatom assemblage parallel to the changes in organic carbon content, however, has been shown to be a natural response to climatic influence and has previously been recorded in the history of the Baltic Sea. Warm climate seems to increase nutrient availability in the Baltic basin, depending on increased upwelling or increased river discharge. According to Elmgren (1989), the recorded changes in freshwater input and wind stress are not large enough to explain the anoxic conditions in the deep water of the Baltic proper. The increase in input of nutrients is likely to have taken place since AD 1950, which supports suggestion on increased nutrient availability in the Baltic coastal and even open waters (Rosenberg *et al.* 1990).

Discussing trace elements in marine sediments it is important to consider sources of sedimentation. It is evident that terrestrial erosional transport and nutrient productivity in surface waters are among main sources of sedimentation. Airborne particle transport to the sea is however an important source as well (Nriagu 1989).

## METHODS

Short Niemistö-type or similar gravity corer (with inner diameter of 54 mm) were used to take the sediment cores from all the stations located mainly in the Eastern Baltic during cruises of Estonian (R/V *Arnold Veimer* in 1986, 1987, 1988), Latvian (R/V *Livonia* in 1992), Lithuanian (R/V *Vėjas* in 1999) and Russian (R/V *Aju-Dag* in 1978) research vessels. Most samples were taken in 1989–1999. The total amount of cores taken for lead-210 dating was 16; two cores (stations 21/01-99 and 21/05-99) were also examined for trace elements (Fig. 1).

Sediment cores were usually sliced onboard ship into disks of different thickness (from 2 cm in recent cores to even 10-15 cm in earlier cores) and stored in

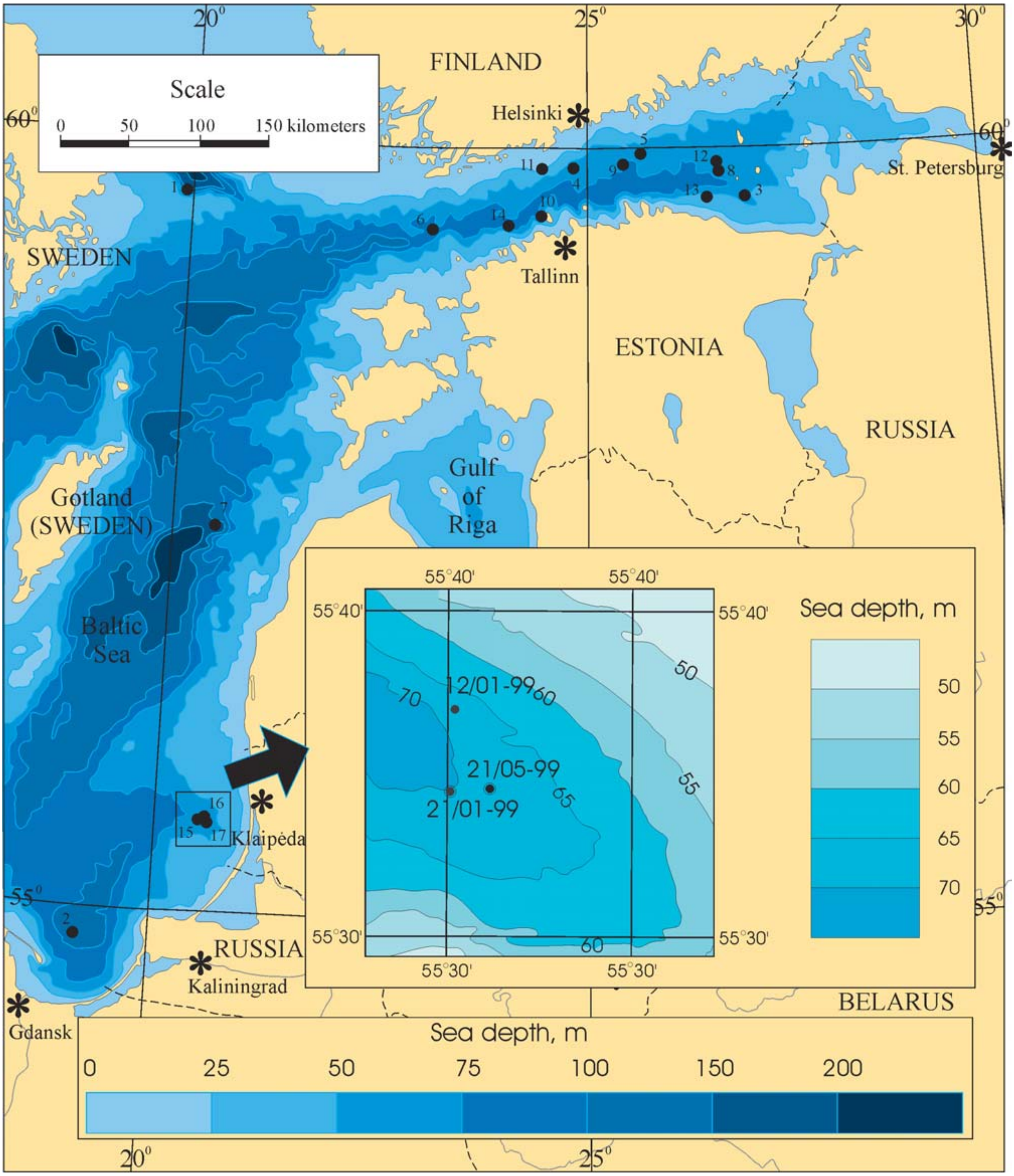

Fig. 1. Study area with sampling sites and bathymetric data (Gelumbauskaitė L.-Ž. (Ed.) 1998). Situation around sampling sites close to Lithuanian coast is shown in detail.

plastic bags in the freezer room. After the cruise termination the sliced sediment material was weighed for wet weight, dried in an oven (at 45°C), weighed again for dry weight, homogenised and powdered in an agate mortar (for trace element determinations) in the home laboratory. The samples were then analysed for radionuclides and trace elements.

Measurements of lead-210 activity in sediments were performed by two methods. The activities of $^{210}$Pb in earlier cores (1978-1992) were measured by low-level beta counting of its daughter radionuclide $^{210}$Bi after classical radiochemical separation of $^{210}$Pb carrier from the sample material (Dušauskienė-Duž 1997, Dušauskienė-Duž 1999). Radiochemical separation was based on ion-exchange method using the anionit EDE-IOP ($Cl^-$ form). The prepared measuring forms were usually stored for about 3 weeks to allow the establishment of radioactive equilibrium between $^{210}$Pb and $^{210}$Bi.

The cores of 1999 were examined by direct gamma-ray spectrometry of $^{210}$Pb (Kunzendorf *et al.* 1998). The gamma-ray spectrometry was performed using well-type detector (GWL-series) with a sensitive volume of 170 cm$^3$ and the well inside the germanium crystal of 16 mm in diameter and 40 mm in depth. It can accommodate small samples with the effective volume up to 4 cm$^3$. The tightly closed sample containers were usually stored for about 3 weeks to allow the re-establishment of radioactive equilibrium after possible radon escape from the sample material. The calibration procedure of the gamma ray spectrometric system used in this study is described elsewhere (Gudelis *et al.* 2000). A number of naturally occurring radioisotopes from the U and Th decay series, as well as man-made radioisotopes, e.g., $^{137}$Cs, were determined. The gamma-ray spectrometric system was periodically calibrated against samples with known $^{210}$Pb and $^{137}$Cs activities.

Using the thickness of wet sediment slices from earlier cores and unsupported $^{210}$Pb activities, a constant rate of supply (CRS) model (Goldberg 1963, Robbins 1982) was applied to calculate mean sedimentation rate and to construct the sediment chronology for the past 200 or even more years of sedimentation. The unsupported $^{210}$Pb activity was calculated by subtracting the supported activity, which was estimated by statistical calculations of total $^{210}$Pb activity distribution in the lower slices of cores, from the total activity.

Using bulk sediment density, calculated as dry weight of the slice material from cores of 1999 divided by its wet volume, and unsupported $^{210}$Pb activities, a constant rate of supply (CRS) model with variations (Bollhöfer *et al.* 1997) was applied to evaluate recent sedimentation. The unsupported $^{210}$Pb activity was calculated by subtracting the supported activity, which was estimated from $^{226}$Ra or any other gamma-emitting decay product ($^{214}$Pb mainly), from the total activity. The $^{210}$Pb dating results were compared and adjusted according to the occurrence of known $^{137}$Cs main markers (Chernobyl, nuclear bomb testing, etc.).

Two analytical methods for trace elements determination were applied. Bulk content of 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 by atomic emission spectrometry (AES) method (DC-Arc Emission Spectrometry) using DFS-13 spectrograph and MD-1000 microdensitometer. Sub-samples for this type of analysis were burned at a temperature of 450°C to mineralise organic matter. Loss on ignition (LOI) was calculated using sample weight before and after mineralisation. X-Ray fluorescence (XRF) analysis was applied to determine Zr and Rb amount in the sediments. Detection limits of analyses were 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 and Zn. The results were consistent with the reference values of international standards OOKO 151, 152, 153, 301, 302 and 303 for quality control. Analytical error comparing with reference material was within 25% (Kadūnas 1998, Taraškevičius 1998, Taraškevičius & Zinkutė 1999).

Concentrations of trace elements detected by both methods were also treated statistically. Each core was studied separately. Means, maximum values, minimum values and standard deviation of the trace elements were calculated using Microsoft Office Package Excel. To study the relationships between trace elements and to classify the samples, the principal component analysis (PCA) was carried out. Factor analysis, a well-known statistical technique, offers a powerful tool to study the interrelationship among the various components. It compresses the total information content of the multivariate data in terms of a few factors. Principal component factor analysis was performed using SPSS WIN software. PCA is a widely applied statistical technique. It was used to clarify the correlations between bioavailable metals and organic matter in the Antarctic marine sediments (Ravanelli *et al.* 1997), the spatial distribution of heavy metals in the river sediments (Chang *et al.* 1998), the identification of trace elements anomalies and sources in various aquatic and non-aquatic systems (Jimenez-Espinoza *et al.* 1993, Baltakis 1993, Lass *et al*. 1997, Sanchez *et al*. 1997, Danielsson *et al.* 1999, Liua *et al.* 2003), the pollution distribution in the river basins (Soares *et al*. 1999, Loska & Wiechuła 2003), the pollution identification in the urban soil (Zinkutė 1998), the availability of various binding fractions of Ni to plants (Wang et al. 1997), the distributions of benthic macroinvertebrate community (Cosser 1989), and for the regional geochemical exploration (Reiman *et al.* 2002, Kadūnas *et al.* 1999).

## RESULTS

The present paper combines relatively old unpublished data on previously taken but not re-analyzed sediment cores and new unpublished data on sediment cores from the Eastern Baltic. Most sediment cores were only examined by $^{210}$Pb. In some of them only trace elements were assessed. The core from station 21/01 was subjected to most complex examination including determinations of $^{210}$Pb, $^{137}$Cs and trace element analysis. Most of the cores were taken from deeper sites (45–130 m sea depth), where various types of mud are widespread (Fig. 2). The vertical distribution of the total and unsupported $^{210}$Pb in the sediment cores from different parts of the East Baltic is given in Figs. 3–7, Table 1.

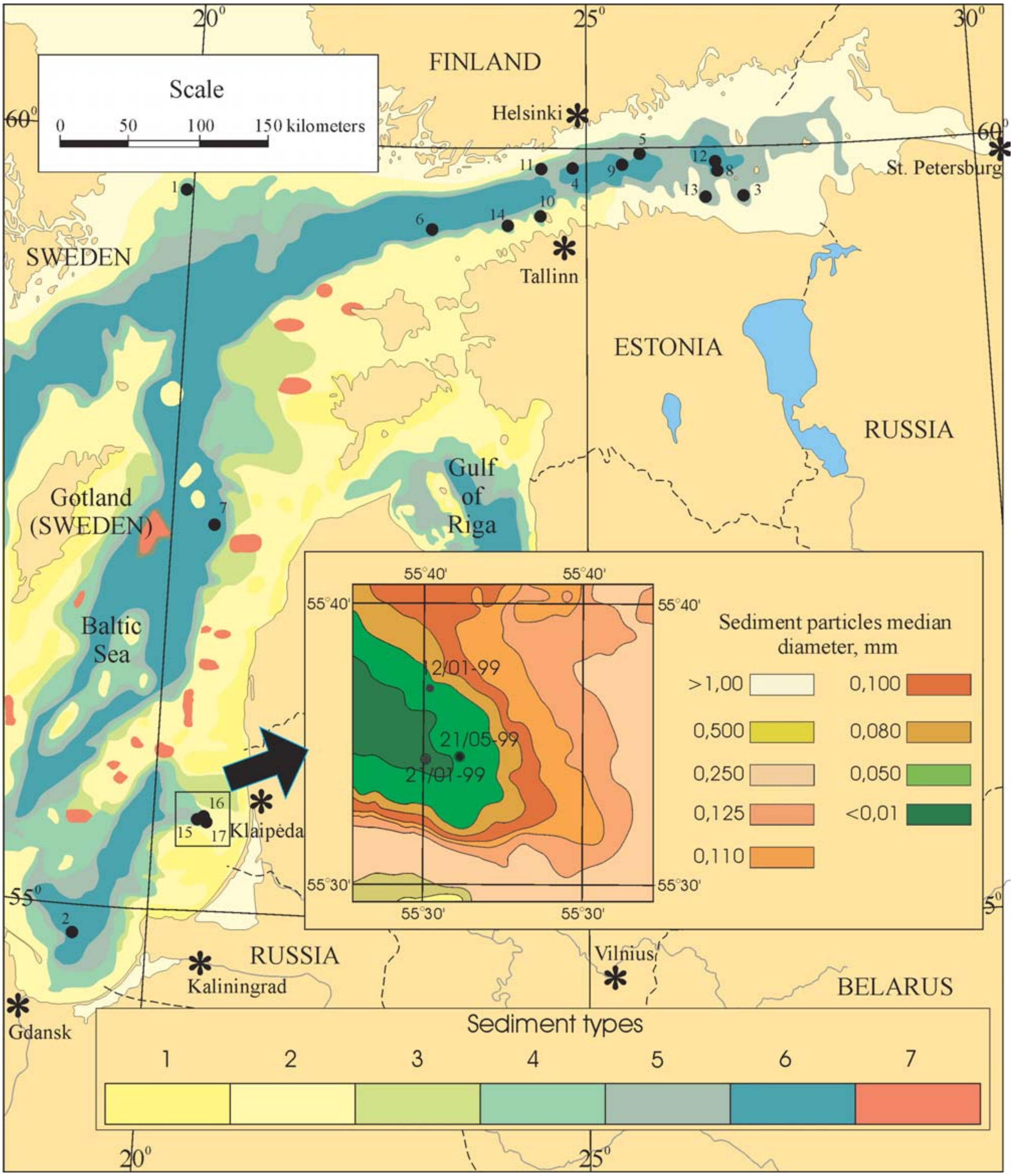

Fig. 2. The bottom sediments of the eastern Baltic Sea. (Winterhalter *et al*. 1981, Repečka and Cato 1998). Situation around sampling sites close to Lithuanian coast is shown in detail. Note: 1 - boulders, gravel, pebble, 2 -sand, 3 -coarse aleurite, 4 - fine aleuritic mud, 5 - aleuritic-pelitic mud, 6 - pelitic mud, 7 - relictic (till, clay) deposits.

Many cores displayed regular decreasing of $^{210}$Pb activity with increasing core profile depth to activity corresponding to radioactive equilibrium with parent radioisotope $^{226}$Ra and changing in relatively narrow interval. The lowest $^{210}$Pb activity close to the sediment–water interface equalled to 60 Bq/kg, the highest – to about 500 Bq/kg. The smallest depth of sediments, where $^{210}$Pb activity reached its radioactive equilibrium with $^{226}$Ra, was, in some cores, 4–5 cm, the largest – about 40 cm. Analysis of distribution patterns of the total $^{210}$Pb revealed that the activity of supported $^{210}$Pb in sediments tends to range from 10 to 50 Bq/kg. It is evident that the highest activity of the total $^{210}$Pb and especially unsupported $^{210}$Pb are observed in the cores from the Gulf of Finland (stations 13/1998, 17/1998), where the input of terrigenous matter is associated with the crystalline rocks of higher natural radioactivity (Figs. 8–9). The smallest values of mentioned indices were characteristic of cores from the southerner parts of the east Baltic, where the input of particulate matter is associated with sedimentary rocks of low radioactivity (stations 33/1978, 07/1987). Yet this trend was not characteristic of all cores. It depends on the sorption capacity of particulate matter, rates of sedimentation, dilution, anthropogenic loads, etc.

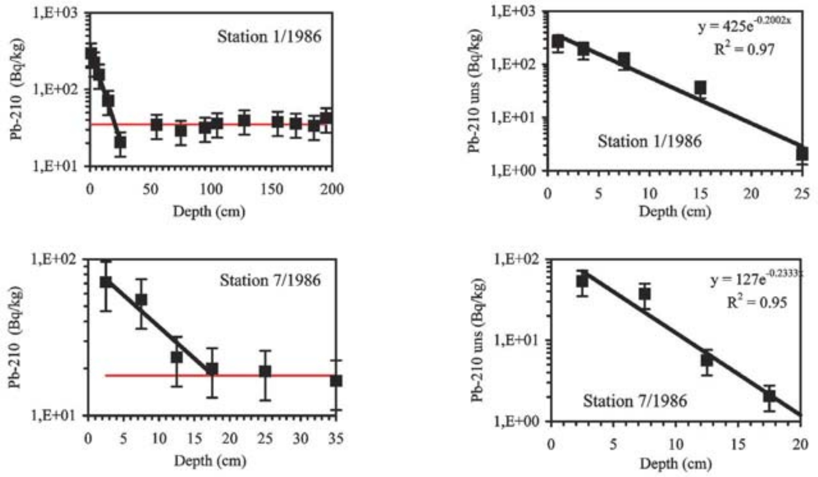

Fig. 3. Total $^{210}$Pb, supported $^{210}$Pb (red line) and unsupported $^{210}$Pb versus depth for short gravity cores taken in 1986.

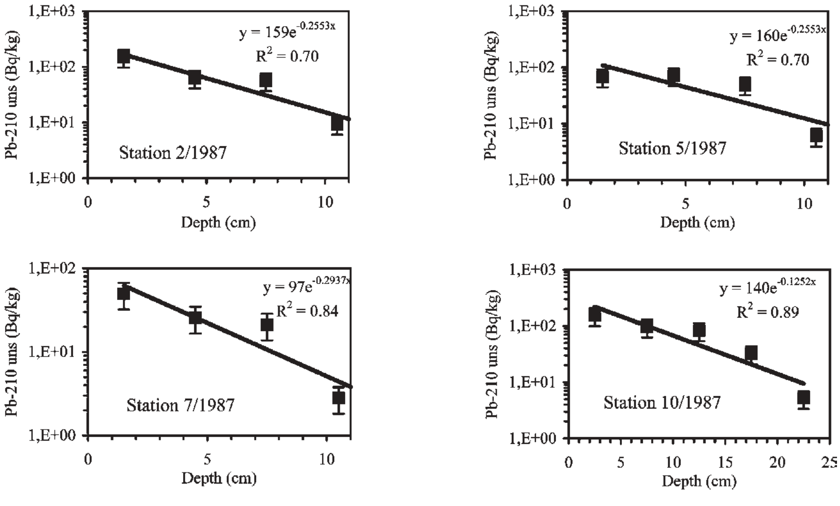

Fig. 4. Unsupported $^{210}$Pb versus depth for short gravity cores taken in 1987.

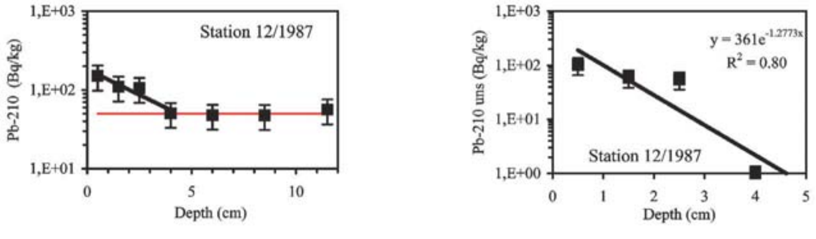

Fig. 5. Total $^{210}$Pb, supported $^{210}$Pb (red line), and unsupported $^{210}$Pb versus depth for short gravity core taken in 1987.

Two cores were taken from the mud area closest to the Lithuanian coast (Fig. 10). They were sampled (2 cm slices) and dated with high resolution. $^{210}$Pb, $^{226}$Ra and its daughter fission products and anthropogenic $^{137}$Cs (Figs 8–9) were determined by gamma spectrometric methods. The highest values of unsupported $^{210}$Pb in these cores were 180 Bq/kg (station 12/01) and 200 Bq/kg (station 21/01), whereas the mean values of supported $^{210}$Pb were 10 Bq/kg (station 12/01) and 18 Bq/kg (station 21/01). Sedimentation rates determined by CRS model for core 12/01 were 1.0 mm/year and for core 21/01 – 1.3 mm/year. These data are in good correlation with the distribution pattern of $^{137}$Cs with the maximum in around 1986 determined by the sediment $^{210}$Pb age model. The generalised rates of sedimentation for all sediment cores are given in Table 1.

The highest rates of sedimentation (2.5–6.5 mm/year) were found in the cores 1, 2, 8, 10, and 12. The lowest values are typical of core 9. In most of the rest cores the rates of sedimentation range within a very narrow – 1.0–1.5 mm/year – interval notwithstanding that the cores were collected in different years, were sliced into segments of different thickness and examined by different methods. This implies good application perspective for this method.

A large association of trace elements was assessed in cores (stations 21/01 and 21/05), taken from the mud area closest to the Lithuanian coast. The main primary statistical

Table 1. Sedimentation rates estimated by lead-210 dating for short gravity cores.

| Numbers in Figs 1-2 | Station (original number) | Latitude | Longitude | Sea depth (m) | Core length (cm) | Slice number in core | Prevailing lithology of mud | Mean sedimentation rate (mm/a) |
|---|---|---|---|---|---|---|---|---|
| 1 | 17/1978 | 56°42'N | 19°52'E | 130 | 40 | 4 | Fine aleuritic | 2.7 |
| 2 | 33/1978 | 54°45'N | 19°16'E | 96 | 60 | 6 | Pelitic | 4.3 |
| 3 | 01/1986 | 59°37'N | 27°05'E | 70 | 200 | 14 | Aleuritic-pelitic | 1.5 |
| 4 | 07/1986 | 59°50'N | 24°50'E | 68 | 40 | 6 | Pelitic | 1.3 |
| 5 | 02/1987 | 59°50'N | 25°38'E | 77 | 24 | 6 | Pelitic | 1.2 |
| 6 | 05/1987 | 59°28'N | 23°00'E | 90 | 21 | 7 | Pelitic | 1.2 |
| 7 | 07/1987 | 57°31'N | 20°34'E | 145 | 20 | 6 | Pelitic | 1.2 |
| 8 | 10/1987 | 59°41'N | 26°38'E | 70 | 30 | 7 | Pelitic | 2.5 |
| 9 | 12/1987 | 59°40'N | 25°24'E | 93 | 13 | 7 | Pelitic | 0.3 |
| 10 | 14/1987 | 59°31'N | 24°23'E | 60 | 35 | 7 | Fine aleuritic | 2.5 |
| 11 | 13/1988 | 59°44'N | 24°24'E | 72 | 50 | 13 | Aleuritic-pelitic | 1.0 |
| 12 | 17/1988 | 59°54'N | 26°37'E | 64 | 70 | 9 | Aleuritic-pelitic | 6.5 |
| 13 | 13/1992 | 59°39'N | 26°26'E | 45 | 15 | 5 | Aleuritic-pelitic | 1.5 |
| 14 | 16/1992 | 59°28'N | 23°57'E | 75 | 17 | 6 | Fine aleuritic | 2.0 |
| 15 | 21/01-99* | 55°34'520N | 20°30'400E | 68 | 41 | 20 | Fine aleuritic | 1.3 |
| 16 | 12/01-99* | 55°36'970N | 20°30'390E | 64 | 33 | 16 | Fine aleuritic | 1.0 |

* $^{210}$Pb dating results adjusted to $^{137}$Cs markers

data on trace element concentrations are summarised in Table 2.

The average of element concentrations in the two sediment cores shows the same rank of elements sorted by their mean concentrations:

Al>Ti>P>Ba>Zr>Mn>Rb>Sr>V>
>Cr>B>Zn>Ni>Pb>La>Li>Y>Cu>
>Nb>Sc>Ga>Co>(Sn>Mo)>Yb>Ag.

Only Sn and Mo have different ranks in two sediment cores. The average values of elements in the core from the station 21/01-99 are slightly higher than in the core from the station 21/05-99 (Fig. 11). This is due to the grain-size composition of sediments. The sediment core 21/01–99 has been collected from the aleuritic–pelitic mud (Md=0.05-0.001 mm) area while the core 21/05-99 – from the fine-aleuritic (Md=0.01-0.05 mm) mud area (Fig. 2).

Variation coefficients of elements rank as well and might reflect different intensity of their accumulation in sediment core profile or contribution of various factors (such as grain-size composition, organic matter content, sedimentation rates etc.). In comparison, variation coefficients of Ag>Pb>Mo>Zn>Y>Sc>La>P in the core 21/01-99 and of Ag>Pb>Zn>Mo>Sc>Cu>P>Ni>Co>Y in the core 21/05-99 are higher than 0.30, thus showing very uneven distribution of elements. The variation coefficients of

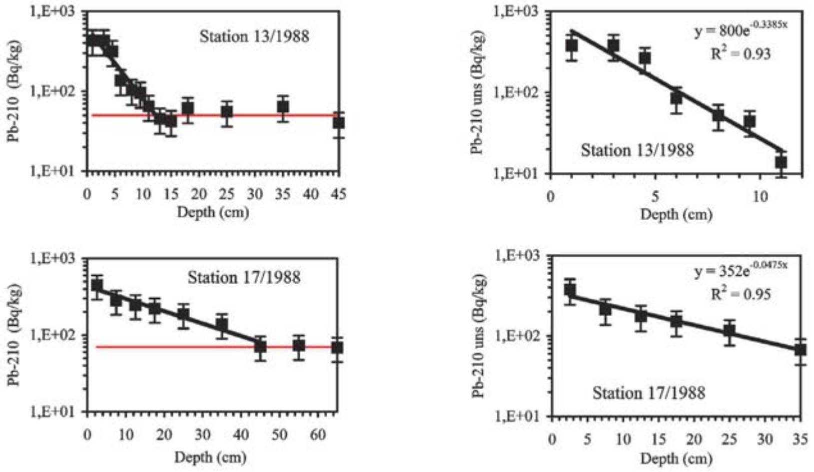

Fig. 6. Total $^{210}$Pb, supported $^{210}$Pb (red line), and unsupported $^{210}$Pb versus depth for short gravity cores taken in 1988.

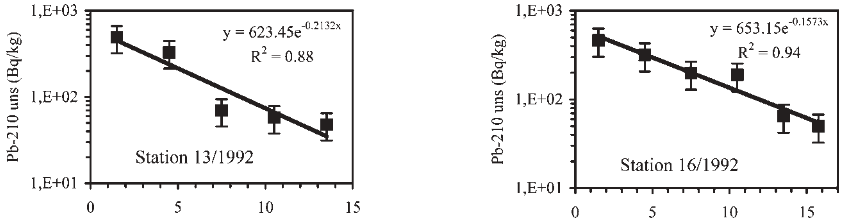

Fig. 7. Unsupported $^{210}$Pb versus depth for short gravity cores taken in 1992.

other elements are lower than 0.30 and indicate more even distribution in sediment core profiles.

A more complicated situation was revealed by comparison of variation coefficients of elements between two cores. Only Al, Ti, Zr, B, La, Y, Nb, Mo and Yb variation coefficients are slightly (in average 1.15 times) higher in the core 21/01–99 than in the core 21/05-99 while other variation coefficients of elements are higher (1.25 times on the average) in the core 21/05-99. The factor analysis was applied for finding out which factor influences such uneven distribution of elements in the sediment cores.

## DISCUSSION

Sedimentation rates estimated vary between 0.3-2 mm/a and tends to increase (3-7 mm/a) mainly after 1960. The similar values in adjacent areas are given by H. Kunzendorf *et al.* (1998) (1-2 mm/a, sometimes 4-6 mm/a) and by A. Ilus (2000) (0.2-4 mm/a, sometimes up to 29 mm/a). Recent sedimentation is mainly determined by basement topography, the flux of material from rivers, coastal and submarine erosion of old sediments, plankton production, and by the hydrography (waves and currents) as the driving force of sediment transport. The spatial distribution of bed sediment types reflects the temporal integration of the various environmental influences. The fine-grained and light material (silt, clay, organic matter) is being deposited under low energy conditions, which are in the major basins. This context follows from the available sediment maps of the Baltic Sea (Emelyanov et al. 1994, Repečka and Cato 1998).

Only in 6 cores of the total 16 of lead-210 dated the rates of sedimentation were higher or lower than the dominant rate interval – 1–2 mm/year. Only two cores taken close to the Lithuanian coast were examined with high resolution. Nevertheless, the growth of the rates of sedimentation after 1960 is notable. This might be associated with intensified river erosion and seacoast erosion (Žilinskas 2004) driven by climate (increased frequency of extreme storms) and anthropogenic changes in the region.

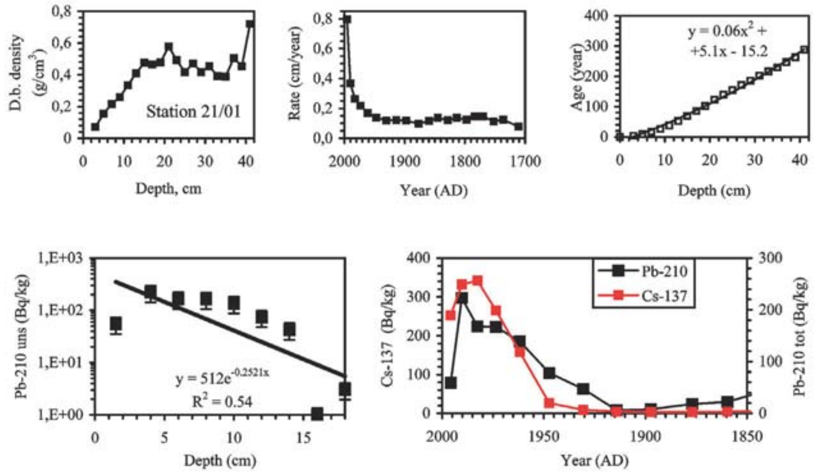

Fig. 8. Depth profile of dry bulk density, CRS age model for gravity core, sedimentation rate versus calendar years, unsupported $^{210}$Pb versus depth and $^{137}$Cs and total $^{210}$Pb versus calendar years for core 21/01 taken in 1999.

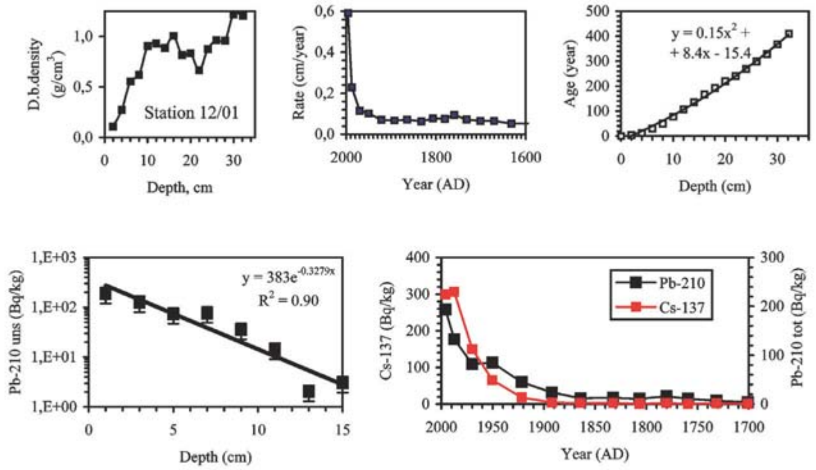

Fig. 9. Depth profile of dry bulk density, CRS age model for gravity core, sedimentation rate versus calendar years, unsupported $^{210}$Pb versus depth and $^{137}$Cs and total $^{210}$Pb versus calendar years for core 12/01 taken in 1999.

A more detailed chronological assessment of the mentioned cores contributed to a more reliable interpretation of trace elements data based on PCA. By applying this technique, one or more factors can be extracted by analysing the data set in greater detail. In our case, trace elements associate into groups due to similar ionic charge and radius that show similar geochemical affinity for certain mineral phases. Trace elements associated in groups or associations can be distinguished. They may be discharged from the same sources or different sources but confined to fine grained sediment phase such as adsorption complexes, organic matter, Fe- and Mn-oxyhydroxides and aluminosilicates minerals. We grouped elements and element associations according to their occurrences in various mineral and non-mineral phases: allothigenous trace elements (Li, Ga, Sc, B, V, Cr, Ni, Co, partly Cu) in main allothigenous minerals such as feldspars, mica, clay minerals; allothigenous–accessory elements (Ti, Zr, Nb, Y, Yb, La) related to weathering resistant minerals such as ilmenite, leucoxene, rutile, zircon; biogenous-technogenous elements (Ag, Pb, Zn, Sn, Mo, partly Cu, Cr, Ni); authigenous trace elements (Sr, partly Ba, Mn, P) being mayor

Table 2. Statistical results on geochemical data for 21/01-99 and 21/05-99 sediment cores.

| | Core 21/01-99<br>(n = 27) | | | | | Core 21/05-99<br>(n = 26) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Min | Max | Mean | SD | V | Min | Max | Mean | SD | V |
| LOI | 4.99 | 17.18 | 11.43 | 3.47 | 0.30 | 4.38 | 12.87 | 7.87 | 2.85 | 0.36 |
| Al | 4.2 | 10.0 | 6.6 | 1.73 | 0.26 | 3.5 | 8.6 | 5.9 | 1.44 | 0.24 |
| Ti | 2400 | 5000 | 3537 | 664.6 | 0.19 | 2400 | 4300 | 3204 | 480.0 | 0.15 |
| P | 450 | 1200 | 652 | 198.3 | 0.30 | 350 | 1100 | 592 | 181.0 | 0.31 |
| Ba | 280 | 530 | 434 | 52.3 | 0.12 | 330 | 600 | 455 | 53.8 | 0.12 |
| Zr | 227 | 388 | 284 | 43.5 | 0.15 | 222 | 366 | 294 | 38.7 | 0.13 |
| Mn | 190 | 270 | 229 | 24.4 | 0.11 | 150 | 260 | 210 | 27.8 | 0.13 |
| Rb | 93 | 169 | 134 | 23.1 | 0.17 | 79 | 162 | 118 | 27.4 | 0.23 |
| Sr | 79 | 120 | 99 | 10.8 | 0.11 | 68 | 106 | 89 | 10.0 | 0.11 |
| V | 66 | 125 | 99 | 18.2 | 0.18 | 54 | 135 | 85 | 21.3 | 0.25 |
| Cr | 64 | 105 | 82 | 12.5 | 0.15 | 50 | 94 | 73 | 13.0 | 0.18 |
| B | 52 | 105 | 78 | 13.8 | 0.18 | 51 | 92 | 69 | 11.8 | 0.17 |
| Zn | 30 | 145 | 66 | 28.8 | 0.44 | 25 | 110 | 49 | 23.0 | 0.47 |
| Ni | 21 | 54 | 39 | 8.4 | 0.22 | 16 | 52 | 33 | 9.9 | 0.30 |
| Pb | 11 | 74 | 34 | 17.3 | 0.52 | 7 | 60 | 25 | 15.9 | 0.63 |
| La | 16.5 | 44.0 | 26.8 | 8.22 | 0.31 | 16.0 | 34.0 | 24.2 | 5.62 | 0.23 |
| Li | 17.0 | 35.0 | 26.2 | 5.26 | 0.20 | 13.0 | 33.0 | 24.0 | 6.26 | 0.26 |
| Y | 13.0 | 45.0 | 22.0 | 7.66 | 0.35 | 9.6 | 33.0 | 19.2 | 5.73 | 0.30 |
| Cu | 11.0 | 27.0 | 19.0 | 3.51 | 0.19 | 11.0 | 38.0 | 18.3 | 5.86 | 0.32 |
| Nb | 9.4 | 21.0 | 13.9 | 3.14 | 0.23 | 6.4 | 19.0 | 13.8 | 2.67 | 0.19 |
| Sc | 7.0 | 22.0 | 12.8 | 4.16 | 0.33 | 5.0 | 21.0 | 11.0 | 3.80 | 0.35 |
| Ga | 7.2 | 13.5 | 10.1 | 1.71 | 0.17 | 4.7 | 13.0 | 8.9 | 2.17 | 0.24 |
| Co | 4.9 | 10.0 | 7.2 | 1.53 | 0.21 | 3.9 | 12.5 | 7.4 | 2.22 | 0.30 |
| Sn | 2.4 | 6.0 | 3.7 | 0.83 | 0.22 | 1.9 | 4.8 | 3.3 | 0.80 | 0.24 |
| Mo | 1.3 | 6.6 | 3.2 | 1.48 | 0.47 | 1.5 | 6.6 | 3.6 | 1.26 | 0.35 |
| Yb | 1.8 | 4.6 | 2.7 | 0.65 | 0.24 | 1.4 | 3.5 | 2.4 | 0.54 | 0.22 |
| Ag | 0.05 | 0.66 | 0.19 | 0.16 | 0.84 | 0.05 | 0.54 | 0.14 | 0.13 | 0.93 |

Note: LOI and Al concentrations in %, other elements in ppm; Min – minimum, Max – maximum, SD- standard deviation, V – coefficient of variation; n – number of samples in each core.

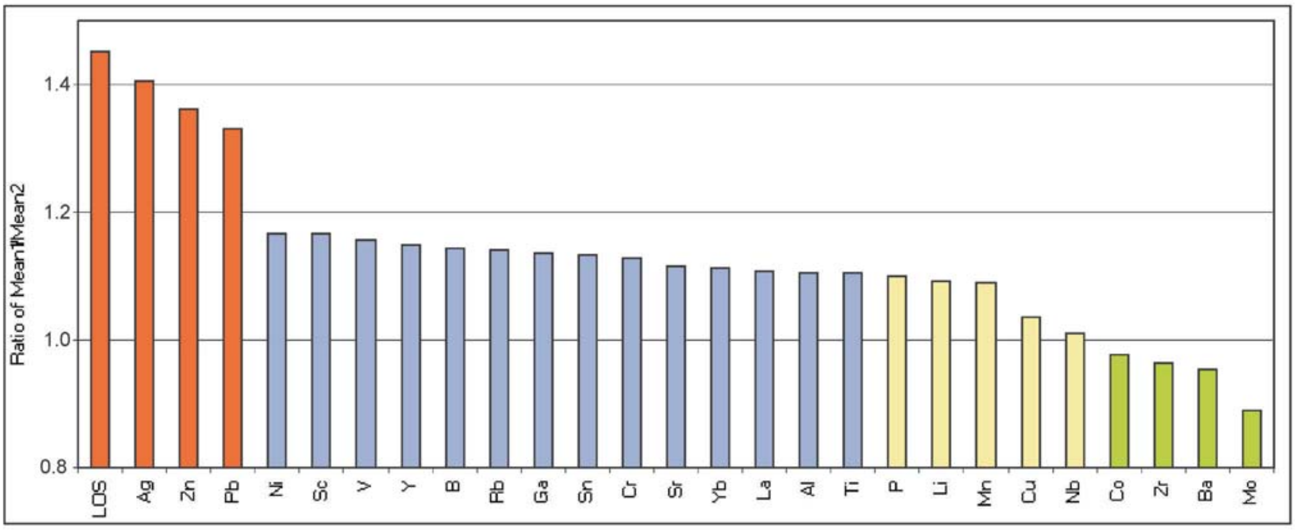

Fig. 10. Comparison of average values of element concentrations for two sediment cores. Note: Mean1 – element average value from core 21/01-99, Mean2 – average value from core 21/05-99. Colors: foxy – ratio more than 1.2, blue – between 1.2 and 1.1, yellow – between 1.1 and 1.0 and green – lower than 1.0.

Table 3. Principal component matrix[1] for 21/01-99 sediment core.

| Elements | Factor 1 | Factor 2 | Factor 3 | Factor 4 | Factor 5 |
|---|---|---|---|---|---|
| Li | 0.95 | -0.20 | 0.12 | -0.01 | 0.09 |
| Co | 0.95 | 0.04 | 0.01 | 0.11 | -0.04 |
| Ga | 0.90 | -0.17 | 0.04 | 0.25 | 0.00 |
| Rb | 0.85 | 0.33 | -0.12 | 0.07 | 0.26 |
| Ni | 0.74 | -0.05 | 0.42 | 0.44 | 0.13 |
| V | 0.73 | 0.38 | -0.03 | 0.49 | -0.01 |
| Zr | -0.63 | -0.19 | -0.31 | -0.24 | -0.53 |
| Cr | 0.59 | -0.36 | 0.44 | 0.44 | -0.14 |
| Al | 0.18 | 0.94 | -0.08 | -0.09 | 0.03 |
| Yb | -0.20 | 0.93 | -0.04 | -0.19 | 0.15 |
| La | -0.09 | 0.92 | -0.29 | 0.02 | -0.04 |
| Y | -0.06 | 0.90 | -0.04 | -0.12 | 0.28 |
| Sc | 0.32 | 0.87 | 0.03 | -0.19 | 0.16 |
| Ti | -0.10 | 0.83 | -0.24 | 0.12 | -0.15 |
| Mn | 0.28 | 0.45 | 0.12 | 0.38 | -0.35 |
| Pb | 0.24 | -0.10 | 0.84 | 0.24 | 0.38 |
| Ag | 0.02 | -0.15 | 0.84 | 0.29 | 0.36 |
| Mo | 0.28 | -0.15 | -0.83 | 0.25 | -0.16 |
| Zn | 0.34 | -0.06 | 0.79 | 0.40 | 0.07 |
| Sn | 0.40 | -0.14 | 0.78 | 0.37 | 0.15 |
| Nb | -0.02 | 0.53 | -0.69 | 0.29 | -0.14 |
| P | 0.00 | -0.20 | 0.61 | 0.02 | -0.17 |
| B | 0.33 | -0.02 | 0.13 | 0.88 | 0.10 |
| Ba | -0.21 | 0.39 | -0.19 | -0.79 | 0.08 |
| Sr | 0.09 | 0.18 | 0.28 | -0.09 | 0.85 |
| Cu | 0.55 | 0.07 | 0.19 | 0.12 | 0.59 |
|  |  |  |  |  |  |
| Eigenvalue | 6.32 | 6.14 | 5.01 | 3.03 | 2.13 |
| % of var. | 24.3 | 23.6 | 19.2 | 11.7 | 8.2 |
| Cum. % var. | 24.3 | 47.9 | 67.2 | 78.8 | 87.0 |

Note[1]: Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization.

constituents or significant admixtures of authigenous minerals (Mn in Mn-Fe oxyhydroxides and rhodochrosite, P in phosphates, Sr, also partly Ba, in carbonates) (Budavičius 2003, Gregorauskienė, Kadūnas 2000).

The principal component analysis extracted five factors (Table 3) accounting for the 87% of the variance in the 21/01-99-sediment core. All factor loadings in the matrix were considered to be significant and the elements were accordingly grouped under the respective factors for the given sediment core. Factor analysis highlights five groupings among the variables. Factor 1 accounts for more than 24% of the variance. Li, Co, Ga, Rb, Ni, V, Cr (partly Sn, Cu) are grouped under this factor. Zr is an antipodal element to this group and has negative loading on Factor 1. Factor 2, describing 23.6% of the variance, has high factor loadings for the elements Al, Yb, La, Y, Sc Ti, Mn and Nb. Factor 3, which explains 19.2% of the total variance, shows association of the elements Pb, Ag, Zn, Sn, P, (partly Cr, Ni) but Nb and Mo are antipodes to this group. Factor 4 explains 11.7% of the variance and groups B, (partly Ni, Cr, V, Zn), with antipodal Ba. Finally, Factor 5 explains 8.2% of variance and groups only Sr, Cu, and an antipodal element to this group is Zr. The three first factor scores of all the samples for this core (station 21/01-99) were calculated and illustrated in Fig. 11.

The Factor 1, loaded by Li (0.95), Co (0.95), Ga (0.90), Rb (0.85), Ni (0.74), V (0.73), Cr (0.59), Cu (0.55), shows high scores (>0) between 20 and 42 cm in the sediment core. In the upper and lower parts of sediment core, Factor 1 scores are low (i.e. below zero). The elements grouped under this factor form an allotigenous association, which is related to clay minerals, i.e. due to their sorption or/and isomorphic admixture. We can refer to the typical elements (Li, Ga and Rb) of clay minerals (Degens 1967, Chester 1990, Brügmann 1992, Baltakis 1993, Ward *et al.* 1995, Kadūnas 1998).

The Factor 2, loaded by Al (0.94), Yb (0.93), La (0.92), Y (0.90), Sc (0.87), Ti (0.83), Nb (0.53), and Mn (0.45), shows very changeable scores along the sediment core but loadings of this factor are very close to zero. Factor 2 groups elements related with allotigenous minerals such as micas, clay minerals, pyroxene and feldspar. Some of them (Al, Ti, Mn) are major constituents of allotigenous minerals; other elements (Yb, La, Nb) are isomorphic admixtures (Degens 1967, Kadūnas 1998).

The Factor 3, which consists of Pb (0.84), Ag (0.84), Zn (0.79), Sn (0.78) and P (0.61), has low scores in the lower and high in the upper (over 30 cm) part of the sediment core. Based on radioisotope dating this part of the sediment core could have been formed during an anthropogenic epoch (last 100

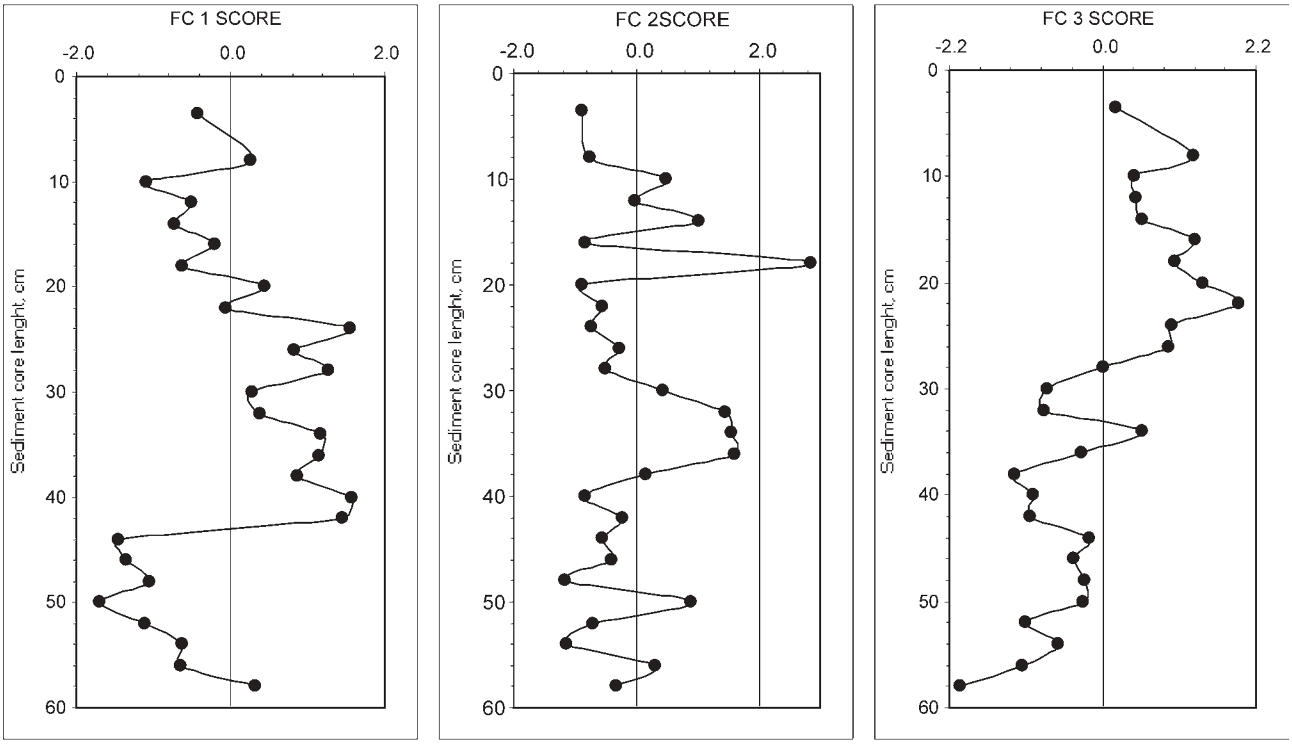

Fig. 11. Factor scores for geochemical data along sediment core 21/01-99.

years). In general, the third factor scores gradually increase from the lower part to the upper part of the sediment core. This tendency may be explained by the contamination from various pollution sources and in any case reflects evidence of contamination. The last two factors (Factor 4 and Factor 5) are grouping one or two elements and it is difficult to explain this grouping.

Principal component analysis extracted four factors (Table 4) accounting for 83.5% of the variance in the sediment core from station 21/05-99. Factor 1 explains 45.1%, Factor 2 – 20.8%, Factor 3 – 10.1% and Factor 4 – 7.3% of the total variance. The factor analysis shows that Factor 1 has the highest influence among others factors. The elements Ni, Li, Sn, Ga, Cr, B, Pb, Rb, Zn, V, Co, Sr, Cu, Ag, (partly Al, Sc) are grouped under Factor 1 and Zr is their antipode. The factor loadings are gradually increasing from the lower part to the upper part of the sediment core (Fig. 12).

We may also distinguish two sediment intervals: the lower one at the depths between 30 and 51 cm with factor loadings smaller then zero and the upper one at depth 0-30 cm. Interpretation of Factor 1 can be explained in two ways. Firstly, Li, Ga and partly Al, Sc are grouped under this factor as these elements are associated with clay minerals, particularly with clay minerals crystal lattice (Degens 1967) while Rb, B, V are related to a sorption complex. Secondly, the presence of Pb, Zn and Ag may be related to anthropogenic activity and reflect contamination influence (Kadūnas 1998). So, associations related to this factor are mixed and formed by natural allotigenous and technogenous-biogenous elements.

Factor 2 groups La, Yb, Ti, Y, Al, Nb, Sc and Ba. The factor scores are very changeable in the sediment core. Low and high factor scores are change frequently. Nevertheless, we may distinguish three sediment column divisions: the first one is at the depths between 0 and 14 cm with dominating negative factor scores, the second one at the depths between 14 and 46 cm with prevailing positive scores and third the one – between 46 and 51cm with low factor loadings. Allotigenous minerals such as mica and clay minerals can explain associations related to this factor. It refers to Al and Sc, which are grouped under this factor. These elements are forming crystal lattice or occur as isomorphic admixtures (Degens 1967). Also allotigenous minerals of sand-silt size (for example feldspars, pyroxene) may have influence on grouping of elements under this factor. First of all Ba is resident in feldspar as an isomorphic admixture (Kadūnas 1998). Referring to the fact that Ba is grouped under the factor 2 together with Al, we may conclude that the content of minerals such as feldspars of sandy-silty size increases in the middle part of the sediment core. Also, Al groups under the Factor 2 but has high loadings on the first factor as well. Al is one of the major constituents in alumosilicates minerals such as feldspars, micas, and clay minerals. Al loadings in Factor 1 and Factor 2 indicate an increase of feldspar content in the sediment.

Associations of the past two factors are small as regards elements and it is difficult to interpret them. Factor 3 includes only Mo and Mn, and in factor 4 the only element (P) has a high negative factor loading.

Table 4. Principal component matrix[1] for 21/05-99 sediment core.

| Elements | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|---|---|---|---|---|
| Ni | 0.96 | 0.12 | -0.03 | 0.06 |
| Li | 0.92 | -0.09 | -0.04 | 0.23 |
| Sn | 0.90 | -0.13 | -0.29 | -0.10 |
| Ga | 0.89 | -0.14 | 0.07 | 0.08 |
| Cr | 0.88 | -0.26 | 0.05 | -0.14 |
| B | 0.88 | 0.04 | -0.03 | -0.31 |
| Pb | 0.85 | -0.06 | -0.42 | -0.12 |
| Rb | 0.85 | 0.29 | 0.04 | 0.40 |
| Zn | 0.85 | 0.02 | -0.44 | -0.21 |
| V | 0.84 | 0.42 | 0.06 | 0.12 |
| Zr | -0.84 | -0.10 | 0.11 | 0.20 |
| Co | 0.83 | 0.26 | 0.17 | 0.26 |
| Sr | 0.80 | 0.20 | -0.08 | 0.28 |
| Cu | 0.76 | -0.24 | -0.41 | -0.09 |
| Ag | 0.64 | -0.25 | -0.58 | -0.24 |
| La | 0.01 | 0.89 | 0.09 | -0.10 |
| Yb | -0.03 | 0.86 | 0.06 | 0.26 |
| Ti | -0.16 | 0.84 | -0.03 | -0.05 |
| Y | 0.24 | 0.84 | 0.05 | 0.19 |
| Al | 0.53 | 0.80 | 0.06 | 0.14 |
| Nb | -0.24 | 0.64 | 0.06 | -0.32 |
| Sc | 0.52 | 0.61 | 0.01 | 0.28 |
| Ba | -0.34 | 0.54 | 0.42 | 0.15 |
| Mo | -0.18 | -0.12 | 0.84 | 0.18 |
| Mn | 0.21 | 0.29 | 0.83 | -0.25 |
| P | 0.03 | -0.11 | -0.08 | -0.89 |
|  |  |  |  |  |
| Eigenvalue | 11.75 | 5.41 | 2.62 | 1.90 |
| % of var. | 45.1 | 20.8 | 10.1 | 7.3 |
| Cum. % var. | 45.1 | 65.9 | 76.0 | 83.3 |

Note[1]: Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization.

## CONCLUSIONS

Sediment cores collected from fourteen stations along the eastern coast of the Baltic Sea were dated radiometrically using natural $^{210}$Pb; two additional cores collected close to Lithuanian coast were dated using natural $^{210}$Pb and artificial fallout radionuclide $^{137}$Cs. For most sites the sedimentation rates were relatively uniform – between 1.0 and 2.0 mm/year. In four sites the sedimentation rates were relatively high – between 2.5 and 6.5 mm/year. One site showed low sedimentation rate (0.3 mm/year). For most sites the $^{210}$Pb activity versus depth profile was regular, and in consequence the $^{210}$Pb dates were relatively unambiguous. Some sites, however, were notable for irregularities in $^{210}$Pb activity versus depth profiles, indicating significant variations in sedimentation rate during the past 120 years and especially after 1960.

High-resolution dated cores were also analysed for trace elements and based on multivariate statistical analysis this has led to determination and classification of different sources of elements in the sites under investigations. The influence of clay minerals on element occurrence in the studied sediments was obvious. Some of the elements are forming sorption complexes of clay minerals; others act as an isomorphic admixture. Factor analysis showed that the anthropogenic load was more intensive in the sediment core 21/05–99 than in the core 21/01–99 despite that both cores were located close to each other. On the other hand, the trace element concentrations in sediments from the core 21/01–99 were more evenly distributed and might be explained by a low sedimentation rate or better sorting of sediments.

The data obtained by radioisotope dating and trace elements methods showed to be in sufficiently good agreement with those from the eastern part of the Baltic Sea.

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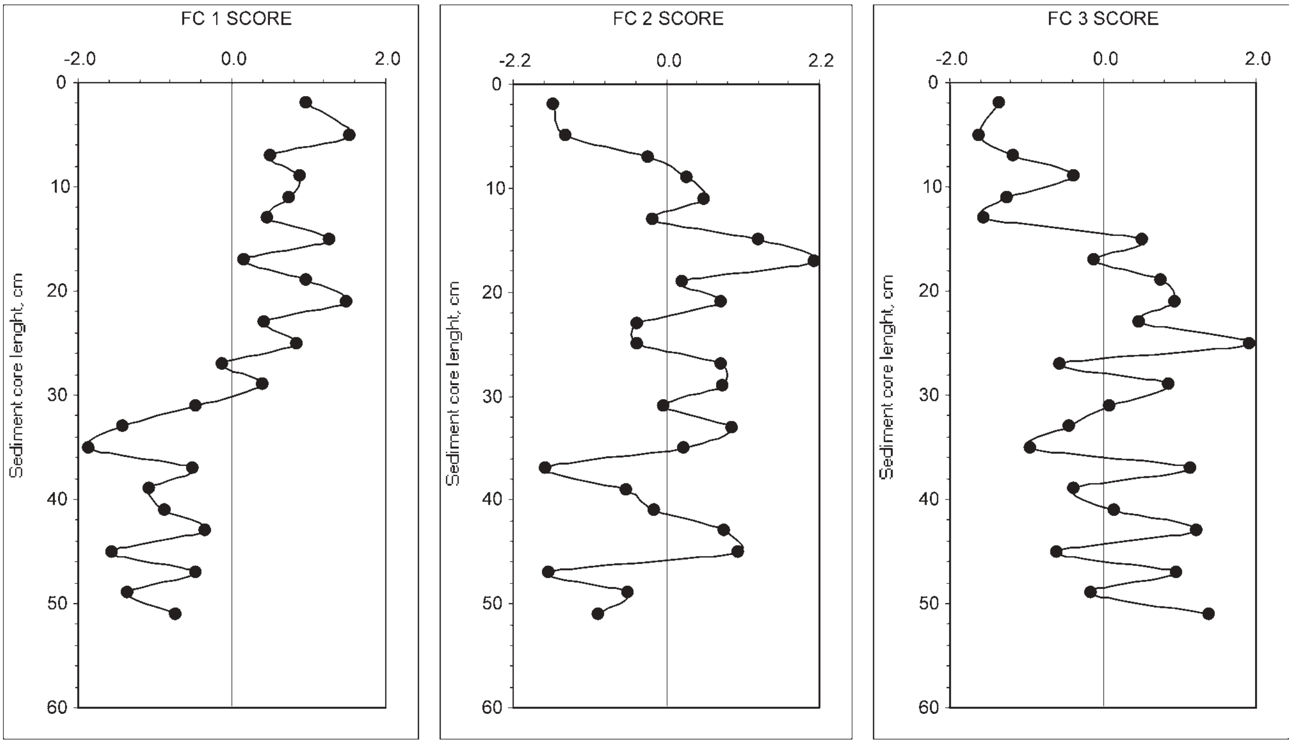

Fig. 12. Factor scores for geochemical data along sediment core21/05-99.

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