EKOLOGIJA. 2005. Nr. 2. P. 6–10

Spatial and temporal distribution of metals in sediment of the Gulf of Riga (the Baltic Sea)

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Spatial and temporal variability of metal concentrations (Hg, Cd, Pb, Cu, Zn, Ni, Mn, Fe) in sediments was investigated in the Gulf of Riga. Surface layers of sediments (first three centimeters) were taken during different seasons at three locations of different depth. To identify related variables (metals) and samples (stations), principal component analysis (PCA) with Varimax Rotation was used. The results showed that the spatial variability was important for all the metals studied. Two expressive behaviors were observed for the metals: sediment texture and bathymetry had a high influence on the metal distribution in sediments of the gulf, and variations of some metals in three seasons (spring, summer, autumn) were significant. A good correlation between metal concentrations and organic matter content in sediments was found. Metals were more concentrated in the muddy sediment cores of the open part of the Gulf of Riga and less in the Daugava River mouth and in the dam-lake of the Daugava sediment cores.

Key words: metals, sediment, the Gulf of Riga (Baltic Sea)

INTRODUCTION

The Gulf of Riga is a semi-enclosed basin of the Baltic Sea. It has a surface area of 16.330 km^2 (3.9% of the Baltic Sea area) and a volume of 420 km^3 (2.1% of the Baltic Sea volume), giving a mean depth of 26 m (max depth > 60 m) (Berzinsh, Zaharchenko, 1996). The drainage area is relatively large, 134.000 km^2 (8% of the drainage area of the Baltic Sea) and freshwater inflow from the rivers is high compared to other sub-regions of the Baltic Sea. The Daugava River (total length is 1005 km, 39% of the total area belongs to Latvia) is the 3rd largest river discharging into the Baltic Sea, and it alone gives 65% of runoff (Пасторс, 1988). The influence of freshwater is most remarkable in the southern and eastern parts of the gulf.

The bottom of the gulf constitutes a mosaic of different bottom types, with only on 30% of its area continuous deposition of fine material is observed (mainly at a depth of 40–50 m) (Emelyanov, 1988). These accumulation bottoms are mostly situated in the south and southwestern part of the Gulf of Riga.

In 1997, about 327 million m^3 of wastewater from registered point sources were discharged into Latvia's water bodies. Of them 60% was treated, but of this amount 61% only partially. The municipalities discharge most of wastewater (177 million m^3), of which 74% is partly treated and 26% untreated, half of the latter being relatively clean discharges. Server systems in large towns collect wastewater from household and small industry. The second largest producer of wastewater is industry (98 million m^3), of which 56% is treated, about 1% untreated and the rest is relatively clean water (cooling water, rain water, etc). Agriculture is the third with 52 million m^3. Since 1990 the use of fertilizers has decreased by more than 85%. Since the early 90s, the generation and discharge of wastewater have fallen significantly, mainly due to the economic recession. Wastewater discharges fell by 41% between 1990 and 1997. The proportion of untreated wastewater also dropped, because the capacity of the facilities was no longer exceeded (Environmental…, 1999).

Metal pollutants discharged to the Daugava River and to the Gulf of Riga are not uniformly distributed to bottom sediments.

The main objective of this study is to describe the spatial and temporal distribution of metals (Hg, Cd, Cu, Zn, Ni, Fe and Mn) in the sediments of the Gulf of Riga and Daugava River, investigate metal interrelations, and determine the factors that affect their distribution. Investigation of metal concentrations in the subsurface layer was also made to see if there have been any changes over the core of sediments.

MATERIALS AND METHODS

Sediments in the Gulf of Riga were collected from the research ship "Antonija" in the Gulf of Riga, and in the mouth of the Daugava River and in the dam-

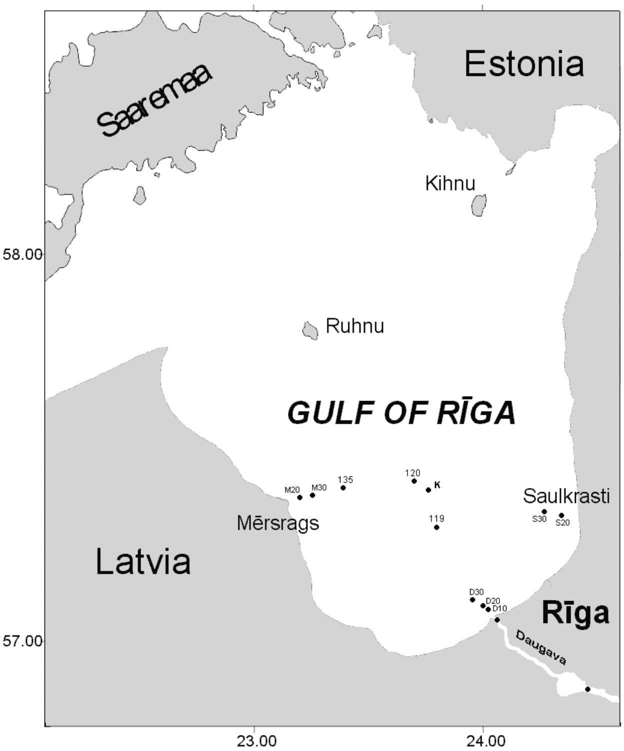


Fig. 1. Location of sampling stations in the Gulf of Riga and in the Daugava River

lake of the Daugava Hydro-Power Station from a boat (Fig. 1).

A Van Veen grab, Kajak corer and a special corer for river sediments were used. The surface layer (first three centimeters) was taken during different three seasons at three locations of the Gulf of Riga: the western part (Mersrags) at a depth of 20, 30, 40 m the eastern part of the Gulf (Saulkrasti) 10, 20, 30 m, and along the consecutive transect of the Daugava River forwards to the central part of the gulf at a depth of 10, 20, 30 and 40 m in 1996–1999. Sediment cores (integrated samples from 3–8 cores) were collected from deep sampling stations of the gulf (119, depth 43, m, 120, depth, 44 m, and K, depth 45, m), from the mouth of Daugava River (depth 12 m, middle part) and from the dam-lake (depth 12 m) of the Daugava Hydro-Power Station, which is the third and the last one on the River Daugava and lies approximately 30 km from the mouth. The cores were sliced. All sediment samples were stored frozen until they were dried at 80 °C for 48 h and homogenized. The mouth-bed of the Daugava consists of gravel and varied grained sand with mud, the sediments of the dam-lake are heterogeneous and in the central part are formed mainly by silt.

The texture of sediments in the Gulf of Riga stations was determined. The grain-size analysis of sediments (granulometric composition, %) was carried out using the sieve method.

Cd, Pb, Cu, Zn, Ni, Mn and Fe were extracted from sediment samples with concentrated HNO_3. Sediment samples were assessed by atomic absorption spectrophotometry (AAS-1, Carl Zeiss, Jena and Perkin Elmer 403) (Seisuma, Legzdina, 1995).

Hg was extracted from sediments by a mixture of conc. H_2SO_4, HNO_3, HCI in the presence of $KMnO_4$ and $K_2S_2O_8$. The equipments used for determination of total mercury were AAS-1 (Carl Zeiss, Jena) and a Flow Injection Mercury system (FIMS–Perkin Elmer). The blank and standard reference material was analyzed in the same way (Kulikova, 1995).

For accuracy of result control, the internationally accepted standard samples from the National Research Council of Canada were used (BEST-1 for marine sediments MESS-2-for mercury, HISS-1, MESS-2 for other metals). For elements the recoveries varied between 90–95%.

To identify the related variables (chemical elements) and samples (stations), principal component analysis (PCA) of the correlation matrix was performed using a programme package (Seisuma, Kulikova, 2000). The Varimax method was used to rotate the initial factors. This method was used to derive the components that represent groups of related variables or samples. Loadings and scores on the components indicated the level of correlation of variables and samples, respectively, with each component. PCA was used also to classify the sampling stations into groups with regard to principal component.

RESULTS AND DISCUSSION

The stations Daugava (depth 10 m), Saulkrasti and Mersrags (20 m) are located in an abrasion accumulation plain formed by sand. The stations Daugava (20 m) and Saulkrasti (30 m) are in the zone of accumulation plain formed by silt, the station Mer-

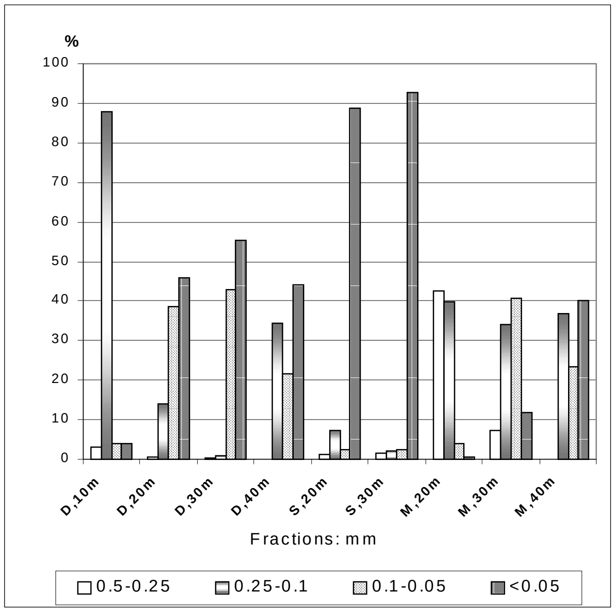


Fig. 2. Grain-size composition (%) of the bottom sediments in the Gulf of Riga (D – Daugava, S – Saulkrasti, M – Mersrags)

srags (30 m) is located in the zone between the accumulation-erosion plain formed by sand and clay, and the station Mersrags (depth 40 m) is in the zone of an accumulation erosion plain formed by clay (covered by a thin layer of sand or silt). At the same time, the station Daugava (30 m) is located in an accumulation plain formed by mud and silty mud, and the station Dauguva (depth 40 m) is in an accumulation plain formed by mud and silty mud (Barashkovs et al., 1997). The granulometric composition of sediments is shown in Fig. 2. At stations Daugava, Saulkrasti and Mersrags at a depth of 20, 30, 40 m, sediments were finer in texture in comparison with those in shallow waters.

The levels of metals in 1997–1999 in the sediment of the Gulf of Riga were similar and were found to range within 0.023–0.151 mg Hg kg^{-1}, 0.06–1.6 mg Cd kg^{-1}, 0.78–42.4 mg Pb kg^{-1}, 1.6–31.7 mg Ni kg^{-1}, 0.38–99.7 mg Cu kg^{-1}, 5–130 mg Zn kg^{-1}, 62–25000 mg Fe kg^{-1}, and 1311–48660 mg Mn kg^{-1} of sediment dry weight. This is below the concentration range of marine unpolluted sediments.

Relationships between Hg, Cd, Pb, Cu, Ni, Zn, Mn, Fe and C_{org} variables in sediments were explored using Principal Components Analysis (PCA) with Varimax rotation (Tables 1, 2 and Fig. 3). When doing a PCA with Varimax rotation, two components (eigenvalues >1) explained 96% of variance. In Table 1 the factor loadings for the components are shown.

Cu, Pb, Zn, Ni, Hg, Cd, and C_{org}, Fe were positively intercorrelated and had the highest loading (0.996, 0.995, 0.938, 0.937, 0.931, 0.903, 0.783 and 0.709, respectively) on Component 1, which described 80% of the total variation. This component distinguished between more polluted stations (Mersrags, 40 m, Daugava, 30 m, Mersrags, 30 m and Saulkrasti, 30 m) with high concentrations of the above-mentioned variables and stations with low concentrations of the variables (Daugava, 20 m, Saulkrasti, 20 m, Daugava, 10 m, and Mersrags, 20 m) (Table 2). Component 2, which described 16% of the total variation, had a high loading for Mn, and this component distinguished Mn as an outlier.

At a depth of 30 and 40 m of all three transects, the concentrations of metals were essentially higher than at a depth of 20 and 10 m; the finer texture of sediment is associated with raised concentrations. The distribution of organic carbon in the gulf is a result of the introduction of sediment from the river flow and remains of micro and macro fauna and flora. Organic carbon as an active sorbent accumulates metals. The maximum content of C_{org} was found in the deeper water (30, 40 m in all transects) and varied from

Table 1. **PCA loadings of variables of metals and C_{org} in sediments (values less than 0.5 are omitted). Data from May 1997**

	Component 1 80%	Component 2 16%
Cu	0.996	
Pb	0.995	
Zn	0.938	
Ni	0.937	
Hg	0.931	
Cd	0.903	
C_{org}	0.783	
Fe	0.709	0.678
Mn		0.975

Table 2. **PCA component scores for stations. Data from May 1997**

Station	Component 1 80%	Component 2 16%
Mersrags, 40m	3.56	–1.23
Daugava, 30 m	2.08	–0.92
Mersrags, 30 m	1.99	2.34
Saulkrasti, 30 m	1.40	–0.04
Daugava, 20 m	–1.75	–0.32
Saulkrasti, 20 m	–2.03	–0.17
Daugava, 10 m	–2.98	–0.08
Mersrags, 20 m	–3.26	–0.18

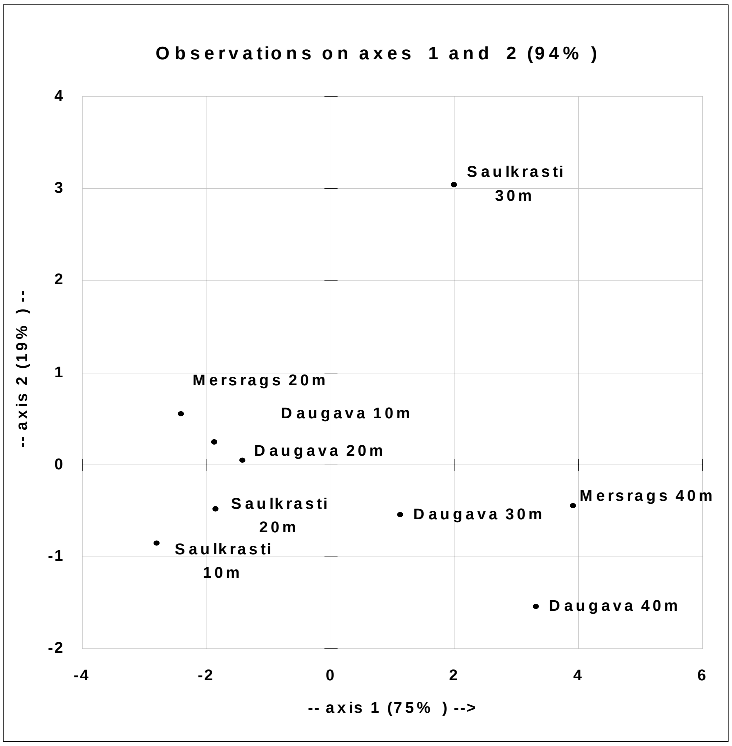


Fig. 3. Plot of scores for the Daugava transect (depth 10, 20, 30, 40 m), Saulkrasti (10, 20, 30 m) and Mersrags (20 and 40 m). Data from May 1999

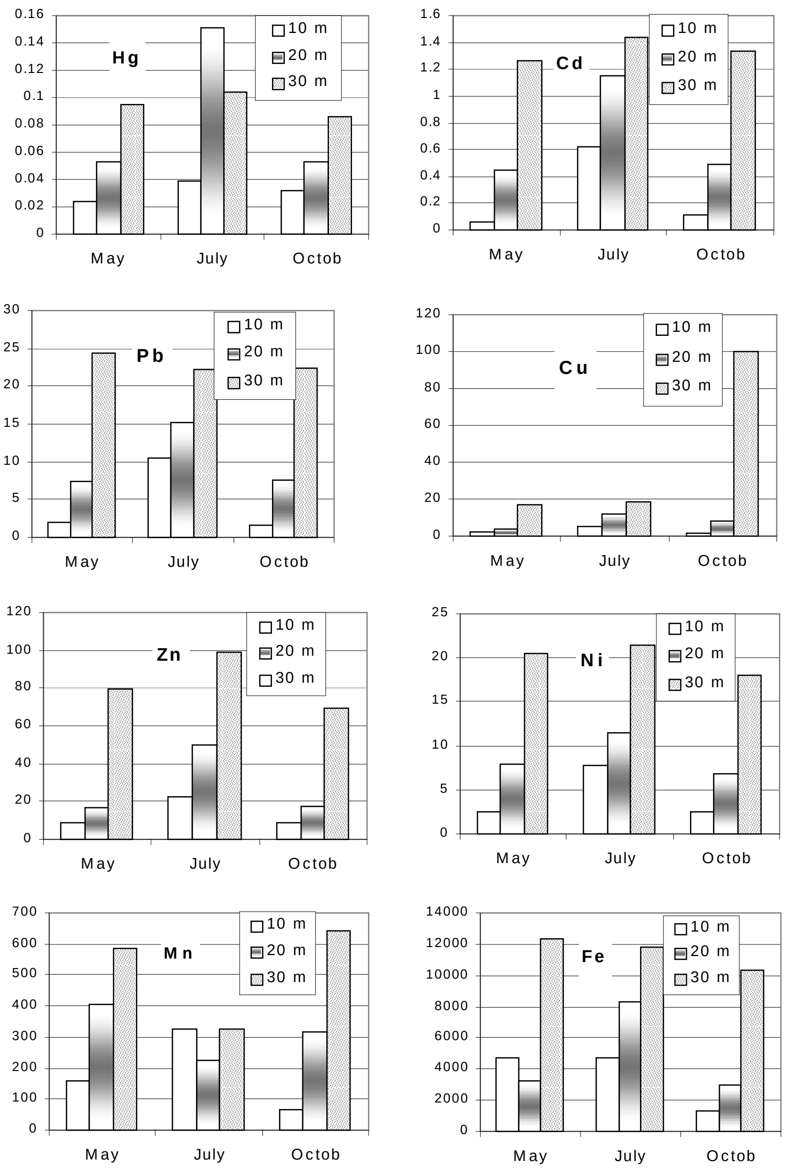


Fig. 4. Concentrations of metals (mg · kg^{-1} dry wt) in sediment (Daugava transect, 10, 20, 30 m). Data from May, July and October 1997

12% to 18.1%. The content of C_{org} diminished in shallow water (20 and 10 m) to 0.53–5.93%. The factor scores of all the sampling stations in 1999 were determined and presented graphically in Fig. 3. The PCA of concentrations in sediment in 1999 showed the same situation as in 1997. In Component 1, Daugava (30, 40 m), Saulkrasti (30 m), and Daugava (40 m) with the highest concentrations of variables had the highest positive loadings, but on the opposite side of the component, Saulkrasti, Daugava, Mersrags (20 m) and Saulkrasti, Daugava (10 m) had the highest negative scores.

The results indicate that concentrations of metals increase with depth towards the open part of the gulf, and metals were present in elevated levels at the stations Mersrags (30, 40 m) and Daugava, Saulkrasti (30, 40 m). Thus, metal concentrations generally increase with decreasing the sediment particle size.

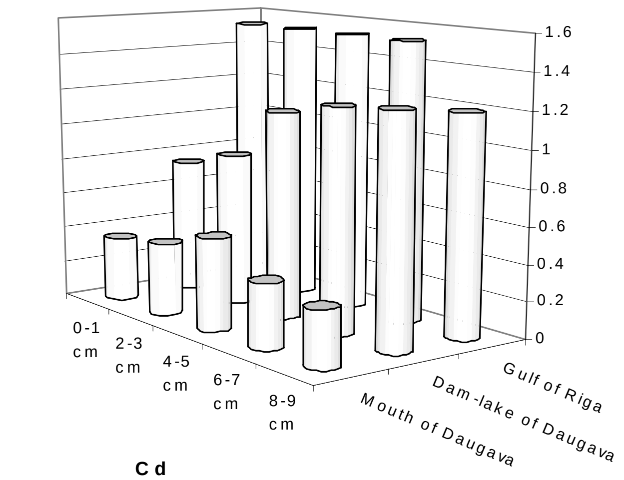
Essential seasonal variations (spring, summer, autumn) of metals were observed in the surface layer of sediments at three transects at a depth of 10 and 20 m, where most active biological processes occur (Fig. 4). At the Daugava and Mersrags transect the maximum concentration of metals was stated in July when we observed also the most active biological processes. A possible explanation is that the action of benthic organisms (bioturbation change the original geochemistry of sediment) was higher in comparison with May and October. But at a depth of 20 m of the Saulkrasti transect in July was observed the minimum of the concentrations of metals in sediments, implying differences in the course of biological processes at all three transects. The seasonal changes of the concentrations of metals at a depth of 30 m at all three transects were insignificant, except Mn, a metal of natural origin.

Comparing the vertical distribution of metals in sediment cores at stations 119 and 120 in spring (May), we observed a pronounced tendency that the maximum concentrations of all metals in the top layer of the sediment core (0–1 cm) were at station 119, *i.e.* closer to the mouth of the Daugava River.

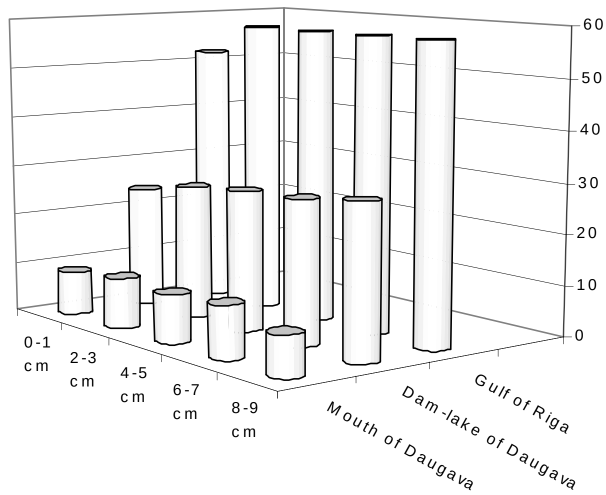
The concentrations of metals (mg · kg^{-1} dry wt) in the surface and deep layers of the core at the station 119 in the Gulf of Riga (May, 1997) were as follows:

Depth, cm	Hg	Cd	Pb	Cu	Zn	Ni	Mn	Fe
0–1	0..226	1.2	52	30	184	47	3400	27000
23–24	0.097	0.6	28	19	106	34	890	25200

As a result of biological activity in summer and autumn there was an alignment of concentrations of metals, and the differences in the concentrations of Hg, Cd, Pb, Cu, Zn, Ni and Fe at both stations in the top (0–1 cm) and bottom (23–24 cm) layers of the cores were insignificant. Only the concentration of Mn considerably differed from that at the station 120, possibly because these two stations essentially differ in their natural mineralogical structure, and Mn brought in by the Daugava River is deposited at the station 119, closest to the runoff of the river.



Cd



Pb

Fig. 5. Vertical distribution of selected metals (mg · kg^{-1} dry wt) in the sediment cores from the Gulf of Riga (K station), mouth and dam-lake of the Daugava River, May 1996

The mouth-bed of the Daugava consists of gravel and varied grained sand with mud. The sediments of the dam-lake are heterogeneous, in the central part formed mainly by silt. The vertical distribution of metals in sediments of the Gulf of Riga and Daugava River was different (Fig. 5). The marine sediments showed higher metal levels than the river sediment. Metals were more concentrated in the muddy sediment cores of the open part of the Gulf of Riga (station K) and less in the Daugava River mouth and in the dam-lake of the Daugava sediment cores. The distribution of metals was almost even throughout the sediment profiles.

Application of the Principal Component Analysis has shown that this method allows to group different stations according to chemical composition. The obtained results revealed spatial variability to be important for all the metals studied. Sediment texture and bathymetry had a strong influence on the metal distribution in sediments of the gulf, and variations of some metals among three seasons (spring, summer, autumn) were significant. The distribution of metals in the depth profile of sediments of the sampling stations was different.

Received 7 September 2004
Accepted 22 November 2004

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METALØ PASISKIRSTYMAS RYGOS ÁLANKOS (BALTIJOS JÛRA) DUGNO NUOSËDOSE LAIKE IR ERDVËJE

S a n t r a u k a

Atlikti metalø (Hg, Cd, Pb, Cu, Zn, Ni, Mn, Fe) koncentracijø kaitos Rygos álankos dugno nuosëdose tyrimai. Skirtingais metø sezonais trijuose pjûviuose skirtingame gylyje buvo paimti dugno nuosëdø bandiniai ið pavirðinio sluoksnio (pirmieji trys centimetrai). Kintamøjø (metalø) ir bandiniø (stoèiø) ryðiui nustatyti buvo taikomas pagrindiniø komponenèiø metodas su varimakso posûkiu. Nustatyta, kad erdvinis pasiskirstymas yra bûdingas visiems tirtiems metalams. Metalø pasiskirstymui didelës reikðmës turëjo dugno nuosëdø sudëtis ir batimetrija. Nustatyta metalø koncentracijos ir organinës medþiagos kiekio gera koreliacija.