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Distribution of heavy metals in sediments of the Gulf of Riga, Baltic Sea

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A large number of sediment samples (totally 138) were studied in 1991–1996 to clarify the role of sediments as a sink of heavy metals in the Gulf of Riga. The samples were analysed for total content of carbon, organic carbon, cadmium, lead, copper, zinc and mercury. Certain additional elements such as aluminium, lithium, iron, manganese, chromium, nickel, titanium and vanadium were also measured from some of the samples from the accumulation areas to enable combination with corresponding data from other parts of the Baltic Sea. The non-mineralogical portion of the heavy metals of some samples was estimated with nitric acid leaching. Heavy metal data for mean concentrations are shown separated into accumulation and non-deposition areas for 1, 2 and 5 cm sample intervals. Spatial distribution patterns are shown for the topmost 5 cm samples. The highest concentrations of metals are mainly found in the mud accumulation areas and in some specific cases, such as cadmium, in the near-shore areas. Lead, copper and zinc show a more widespread distribution over the whole Gulf. For copper and cadmium the presented vertical distributions of selected profiles show decreased accumulation trends during the past 30 years, while for other elements no similar pattern is identified. Comparisons with the Gulf of Bothnia and Gulf of Finland show that total concentrations of lead, copper and zinc are lower in the Gulf of Riga and cadmium and mercury are in the same range as those in the Gulf of Bothnia and Gulf of Finland.

Introduction

The ecosystem of the Gulf of Riga in the Baltic Sea was studied under the Nordic Environmental Research Programme 1993–1998. This was a co-operative multidisciplinary the Gulf of Riga project between Scandinavian, Latvian and Estonian scientists, divided into several sub-projects. Their aim was to investigate processes and fluxes involving contaminants and nutrients in the Gulf of Riga of importance for the ecosystem, thus enabling the modelling of the ecological system in the area. This research was made possible when the former Soviet territorial waters were opened for co-operation with the western science by the re-establishment of the Estonian and Latvian Republics. The present study presents the results of the sub-project dealing with sediment as a sink for heavy metals in the Gulf of Riga. One aim of the study was to clarify existing knowledge on sedimentation and to identify data on heavy metals and pollution. Such data can be found in archives and reports in difficult-to-access literature and publications in Russia, Estonia and Latvia. Other targets were to study the most recent distribution of heavy metals over the whole Gulf and compare the heavy metal content in the sediments with the Gulf of Bothnia and Gulf of Finland.

Organic and inorganic pollutants mostly enter the sea ecosystem either through atmospheric input, river inflow or as effluents from industrial or municipal sewage plants, combined with solid matter, dissolved in ionic and colloidal form or complexed with organic matter. Heavy metals and organic pollutants generally accumulate in sediments associated with organic matter, clay surfaces, sulphides and iron-manganese hydroxides. These compounds are mainly deposited together with the fine-grained sediment components, making knowledge of the distribution of sediment types on the seafloor an important part of the investigation when studying the distribution of heavy metals in the sediments. An estimation of sedimentation rates is also important in order to uncover the historical perspective for the accumulation of these elements, as well as discovering suitable sites for monitoring purposes.

In the countries around the Gulf of Riga, many studies have been made concerning sedimentation, heavy metal concentrations and pollution. In many cases the data of these studies were stored in records or reports in issues of literature in Russia, Estonia or Latvia which were not easily available. During the present study, at least a part of this knowledge has come to light and has given valuable background data for this research. The first studies of heavy metal concentrations in the ecosystem of the Gulf of Riga were started in 1977. In these studies, concentrations of various elements e.g. mercury, copper, zinc, lead, cadmium, nickel, iron, manganese, chromium and cobalt were investigated in biota i.e. plankton, molluscs, fish, crustaceans and macroalgae (Seisuma *et al.* 1984, 1996, Seisuma and Legzdina 1995, Kulikova 1995). These studies were started partly in order to make an assessment of the state of the marine environment. Studies of heavy metal concentrations in the water started at the beginning of 1985, and since 1986 the Institute of Aquatic Ecology of the University of Latvia (IAE) has carried out studies of the sediments of the Gulf (Seisuma and Legzdina 1991, 1995, Seisuma *et al.* 1990, 1993, 1995, 1996, Kulikova 1995). The aim of these studies was to follow the long-term changes of the anthropogenic impact of metal contents in the marine environment. Other researchers e.g. Jankovski *et al.* (1989) and Ott and Jankovski (1980), also studied the levels of heavy metals in the ecosystem of the Gulf of Riga. The results of many earlier studies were combined into a large-scale description of the ecosystem of the Gulf of Riga between 1920–1990 by Ojaveer (1995). Recently, Baraškovs *et al.* (1997) also combined the mapping of the deposition, transport and erosion areas with that of the benthos communities. They have also published maps of organic matter and the distribution of loosely-bound heavy metals (acetonic leaching) in the surface sediments from studies carried out since 1986.

Different sampling methods were used in the above-mentioned studies, sample pre-treatment and analytical methods, making comparability between the old and recent studies difficult. Attempts have been made by the Danish National Environmental Research Institute (NERI) during the present project to validate the older methods and data from same selected laboratories also involved in the present study. This was possible, as these laboratories still used the same methods as in their earlier investigations. The validation of

their methods (and hence older data) was carried out by comparing the performance of these laboratories and the methods used in an interlaboratory exercise utilising sediment samples. The interlaboratory study showed that the earlier data on lead and zinc are presumably acceptable. The values for copper may be too low in some cases, while there is a risk that low concentrations of cadmium and mercury are too high due to contamination. However, the data from earlier studies can be regarded as valid after assessing their quality.

During the Gulf of Riga project, a large database was established in Lithuania, in which 64 stations covering the whole Gulf were sampled by the Geological Survey of Latvia in 1991 (K. Jokšas, unpubl.). Selected elements were measured from sediment samples within the topmost 5 centimetres. The heavy metal analyses were carried out by the Lithuanian Institute of Geography (IG), and the data for mercury, cadmium, lead, copper and zinc from that study have been combined with that of the present study in order to have a data set as large as possible for the distribution studies.

This study presents the most recent results regarding the concentrations of selected heavy metals, such as mercury, cadmium, lead, copper and zinc in the topmost sediments (0–1, 0–2, 0–5 cm) of the Gulf of Riga as investigated in 1991–1996. Total concentrations of heavy metals are presented, as well as findings concerning the sedimentary environments i.e. mean, minimum and maximum concentrations of elements in the accumulation and transport/erosion areas of the Gulf. Heavy metals of the same sediments from the accumulation bottom areas were also measured with a nitric acid leaching technique. These data are also considered as an indication of the non-mineralogical portions of the metals. From samples taken from the accumulation areas in the present study, additional elements such as aluminium, lithium, iron, manganese, chromium, nickel, titanium and vanadium were also measured, but these are only commented upon when making a comparison with the rest of the Baltic Sea. The horizontal distributions of the metals in the Gulf of Riga are shown for the topmost (0–5 cm) part of the sediments, and a few examples of the vertical distributions of heavy metals from the mud accumulation bottoms are presented as examples of the development of accumulation. At the end of the paper, comparisons of the Gulf of Riga with the Gulf of Bothnia and Gulf of Finland are shortly discussed based on the total mean concentrations and annual accumulations of selected heavy metals in the surface sediments (0–1cm).

Study area

The Gulf of Riga is a semi-enclosed bay close to the central Baltic Sea. It is about 100 km wide and has an area of 19 000 km^2 (Fig.1). The maximum and mean depths are 62 and 20 m, respectively. It is connected to the Baltic Sea by two narrow sounds, the Irbe Sound and the Muhu Sound (Fig. 1). The sounds are so shallow (mean depths 8–14 m) that only the surface water of the Baltic can penetrate into the Gulf, and the water column is normally well mixed in the sounds. In the Gulf, the salinity varies between 4 and 7 PSU, except in the river estuaries were the salinity is lower (Yurkovskis *et al.* 1993). The water column is remarkably stable from the surface water to the bottom, and only the thermocline separates the upper well oxygenated water column from the bottom water.

The Gulf is surrounded by Latvia and Estonia, and its drainage area covers about 135 700 km^2, of which about 38% is forest, 28% arable land and 0.65% populated area (Sweitzer *et al.* 1996). Most of the surroundings are relatively sparsely populated, having a total of 4.6 million inhabitants in the two surrounding countries. The areas of Riga in Latvia and Pärnu in Estonia are the most heavily inhabited. Industry is mostly centred in these same areas in the northern and southern parts of the Gulf. The average annual freshwater inflow from rivers is about 31 km^3 (Pastors 1988) of which the rivers Gauja, Lielupe and Daugava, entering in the southern part of Gulf, contribute annually 25 km^3 (Fig. 1).

A bottom sediment map (1:200 000) covering the whole Gulf has been established through cooperation between the Geology Surveys of Latvia and Estonia (Striebrinš and Väling 1996). The bottom of the Gulf is composed of a mosaic of different types of sediments, with only about 30% of its area containing bottoms with a continuous deposition of fine material (Fig. 2). Areas with

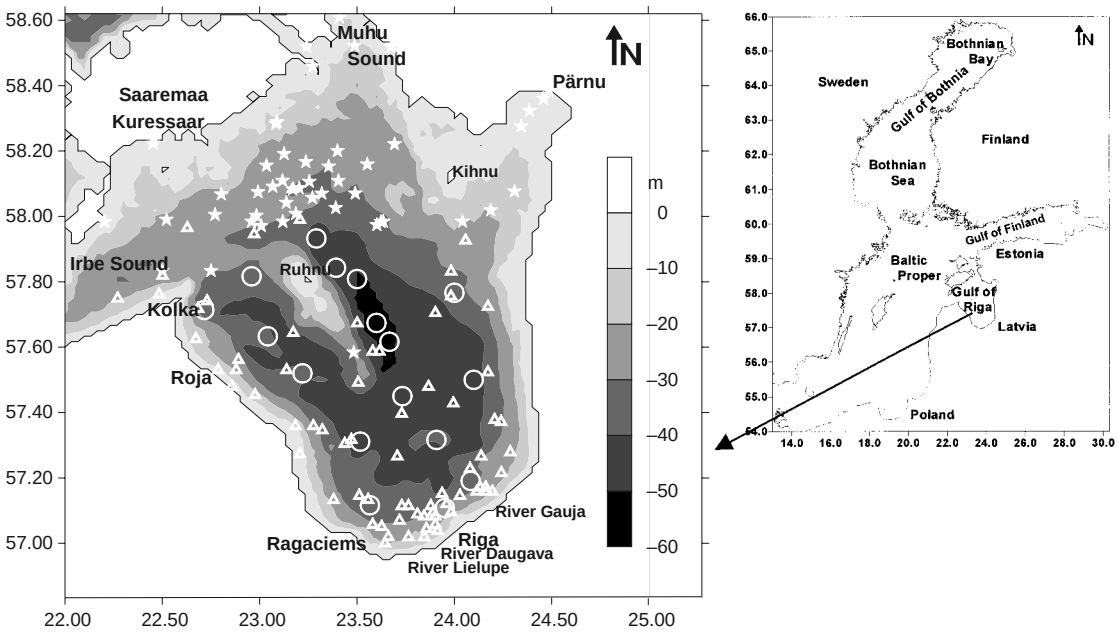

Fig. 1. Sampling stations in the Gulf of Riga in 1993–1996. Samples at locations marked with circles were taken and analysed by the Finnish Institute of Marine Research (FIMR) and the Institute of Aquatic Ecology of the University of Latvia (IEA)/the National Environmental Research Institute (NERI); samples at locations marked with triangles were taken and analysed by the Institute of Geography (IG); samples at locations marked with stars were taken and analysed by the Geological Survey of Estonia (GSE). For further information *see* Appendix. Bathymetry modified from Seifert and Kayser (1995).

continuous accumulation, the mud accumulation basins, are situated in the southern part of the Gulf and east of the island of Ruhnu (Fig.1) at water depths greater than 40 m, while westwards of Ruhnu small accumulation basins and non-deposition areas are to be found. The northern parts of the Gulf, with water depths of less than 25 m, are mainly slow deposition, transportation/erosion or non-deposition areas. In these areas, the bottoms are mainly composed of Glacial and Early Holocene clays or tills. From the Baltic Proper fine particles may enter the Gulf through the Irbe Sound. This material mainly settles in areas with water depths greater than 35 m. Partly terrigenous and other organic material that flows in from the rivers is first deposited in coastal areas and then slowly transported into the accumulation basins.

As the water in the Gulf is brackish, the fauna consists of comparitively few macrospecies e.g. *Monoporeia affinis* (550 ind. m^{-2}), *Pontoporeia femorata* and *Macoma balthica* (650 ind. m^{-2}, Cederwal *et al.* 1998). Recently some deeply bioturbating species e.g. *Marenzelleria viridis* (Polychaeta, on average 890 ind. m^{-2}) have populated the southern and south-eastern part of the Gulf, while their occupation of the deepest mud accumulation areas is far less (Jermakovs 1998, Jermakovs and Cederwall 1996). Based on this and recent studies of ^{210}Pb dating profiles, bioturbation seems to be low to moderate in the accumulation areas of the Gulf (Jensen and Larsen 1998).

Recent studies of the accumulation rates in the mud accumulation basins of the Gulf, based on ^{210}Pb and ^{137}Cs measurements, show rates between 500–2 000 g m^{-2} a^{-1}, corresponding to 2–10 mm a^{-1} (Larsen 1995). These rates are much higher than the earlier estimates, based on an average deposition over 7 800 years, of 285 g m^{-2} a^{-1}, indicating somewhat increased organic matter production in the Gulf in recent years. The last-mentioned rate is equal to an accumulation of dry matter of 1.3×10^6 ta^{-1} in the whole Gulf. However, an estimate of ca. 4.5×10^6 ta^{-1}, based on an average of the recent accumulation rates determined by ^{210}Pb and the area of the accumulation bottoms (data in Larsen 1995), is more realistic for the present-day accumulation. The accumulation rates vary a lot over the accumulation bottoms, showing an

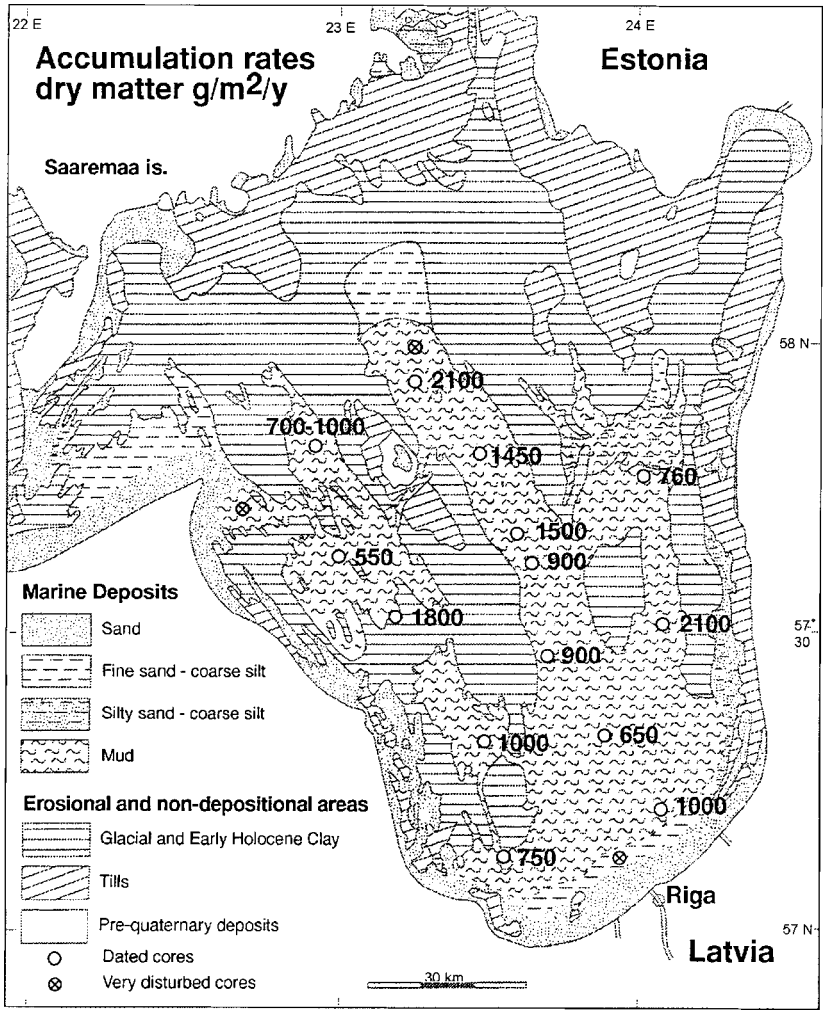

Fig. 2. Sedimentary environments in the Gulf of Riga, included some accumulation rates in g dry matter m^{-2} a^{-1} (redrawn from Larsen 1995).

incoherent distribution of accumulating material (Fig. 2).

Methods

Materials

In 1993–1996, sediment samplings were performed from the southern accumulation bottoms and the northern transportation/erosion bottoms of the Gulf of Riga (Fig. 1). Altogether 16 sites in the accumulation areas and surface sediments from 58 sites in the non-deposition areas north of 58°N were sampled. Information regarding the location of sediment stations, sampling depths, laboratories performing the analyses of this study and the additional samples from the earlier study (64 stations covering the whole Gulf) sampled by the Geological Survey of Latvia in 1991 (K. Jokšas, unpubl.) is shown in Appendix. Samples of the present study were collected during the international joint cruises of the Finnish research vessel R/V *Aranda*, but also other research vessels such as the R/V *Marina* from Estonia were used. Before sampling, the bottoms were checked by echosounding e.g. on board of *Aranda* with an Atlas Deso 12 kHz. A Gemini twin corer, with a diameter of 8 cm, was mainly used for the sampling, but different box corers were also used. Immediately after sampling the samples were dissected into 1, 2 or 5 cm sub-sample slices. These subsamples were sealed in plastic containers or bags and stored frozen until they were dried and later

analysed. Sediment sampling was usually performed to various deeper levels in the sediment cores, from the topmost layers down to 40 cm (Appendix), of which selected depths were taken for heavy metal analyses. For this study, data from various studies were collected into one data set, with the consequence that the sediment samples were prepared and analysed with different slice intervals in the different institutes (Appendix). Thus, the surface sediment concentrations are reported from surface layers of different thicknesses. 16 core samples were analysed down to 20/40 cm and from the surface an interval of 0–1 centimetres is reported. In 25 cases, the reported interval is 0–2 centimetres and from 138 cores the interval of 0–5 centimetres is reported.

Analysis

Cadmium, lead, copper, zinc and mercury were analysed at three laboratories: the Finnish Institute of Marine Research (FIMR), the Geological Survey of Estonia (GSE, no mercury) and the National Environmental Research Institute (NERI). At the NERI, the samples were analysed by the co-author Zinta Seisuma from IAE, as one target of the project was to train staff from eastern countries in the methods of western laboratories, and to try to solve analytical problems found in eastern laboratories. The drying, homogenisation and quantification methods used are listed in Table 1. Total metal contents were extracted using different acid combinations (Table 1) while metals were partly extracted with nitric acid. For mercury the nitric acid leaching used gives total amounts. Cadmium, lead, copper, zinc and mercury were determined using different AAS instruments. Other elements, i.e. aluminium, lithium, iron, manganese, chromium, nickel, titanium and vanadium, were measured at the FIMR after total extraction (Table 1) using an ICP-AES instrument. Total carbon (TC) was analysed using the coulonometric method in the IG and with a Leco element analyzer with an infrared sensor (Carman *et al.* 1996) at the Geological Survey of Denmark and Greenland (GEUS). Total organic carbon (TOC) was measured using the same method after dissolution of carbonate with H_2SO_4 and drying. Carbonate-C is given as $CaCO_3$ from the difference between TC and TOC. Sediment samples from the accumulation bottoms were dated by means of the ^{210}Pb method and accumulation rate estimates based on ^{137}Cs activity in the sediments (Kuzyurov *et al.* 1994, Pheiffer-Madsen and Sørensen 1979).

Data intercomparison and quality control

The NERI made an intercomparison of analytical quality between the IAE, the GSE and the Central laboratory of the Geological Survey of Latvia. Validation of the data in the present study was also carried out between the laboratories men-

Table 1. Analytical methods used for sample drying, homogenization and heavy metal analyses in the different laboratories.

Institute	Method	Reference
NERI/IAE	Freeze drying and homogenization in the GEUS, HNO_3 leaching with microwave oven, ET-AAS, FIMS for Hg.	Hewitt and Reynolds 1990
FIMR	Freeze drying, planetary mill homogenization, aqua reqia-HF–H_3BO_3 leaching with microwave oven, for Hg with HNO_3 in autoclave, ET-AAS, ICP-AES and FIAS + AAS for Hg.	Nordforsk 1975, Loring and Rantala 1992, Leivuori 1998
GSE	Room temperature + oven drying (105 °C), ceramic grinder/agate mortar homogenization, HF–HNO_3–$HClO_4$ leaching, FL- and ET-AAS.	Petersell *et al.* 1994
IG	Room temperature drying, mill homogenization, HF–$HClO_4$–HNO_3–HCl leaching, AAS, for Hg HNO_3–$HClO_4$–H_2SO_4 leaching and cold vapour-AAS	Jokšas 1994, 1996

NERI: the National Environmental Research Institute (Denmark); IAE: the Institute of Aquatic Ecology of the University of Latvia; GEUS: the Geological Survey of Denmark and Greenland; FIMR: the Finnish Institute of Marine Research; GSE: the Geological Survey of Estonia (GSE); IG: the Institute of Geography (Lithuania).

Table 2. Mean concentrations of measured commercial certified reference materials or corresponding materials with target values and standard deviations (standard deviation not available from the GSE, *see* text). Materials analysed in every sample batch. Units based on dry weights. Letters in subscript indicate from which reference materials the data were obtained.

Laboratory	Reference material	Cu (mg kg^{-1})		Zn (mg kg^{-1})		Cd (mg kg^{-1})		Pb (mg kg^{-1})		Hg (mg kg^{-1})	
		Target	Mean	Target	Mean	Target	Mean	Target	Mean	Target	Mean
FIMR*	SRM 2704	98.6±5.0	103±5	438±12	437±12	3.45±0.22	3.31±0.30	161±170	162±8	1.47±0.07	1.50±0.11
	MESS-1	25.1±3.8	27±1	191±17	181±8	0.59±0.10	0.58±0.09	34.0±6.1	33±1	0.092±0.009[a]	0.099±0.009
	BEST-1[a]										
NERI/IAE**	BCSS-1										
	BEST-1[a]	18.5±2.7	13.0±1.2	119±12	97±4	0.25±0.04	0.21±0.01	22.7±3.4	20.1±1.2	0.092±0.009[a]	0.099±0.007
GSE*	LB-A	25±1.5	20	117±9	101	0.25±0.07	0.88	30.5±1.5	30	–	–
	H-B	27±2.7	25	202±24	244	1.1±0.36	1.16	76.6±4.5	85	–	–
	ABSS-C	–	–	–	–	0.94±0.45	1.27	–	–	–	–
	MBSS-D	–	–	–	–	0.74±0.46	0.91	–	–	–	–
IG*	SDO-1, 2[b]	33±4[c]	30±2	130±10[b]	126±1	5±0.5	4.7±0.1	24±5	22.7±1.8	0.13±0.02[d]	0.14±2.4
	3[c] SDPS-2[d]										

* total extraction, ** partial leaching; FIMR: the Finnish Institute of Marine Research; NERI: the National Environmental Research Institute (Denmark); IAE: the Institute of Aquatic Ecology of the University of Latvia; GSE: the Geological Survey of Estonia (GSE); IG: the Institute of Geography (Lithuania).

tioned above, the FIMR and the NERI. From the intercomparison it was concluded that the quality of the present data was appropriate. The FIMR and the NERI have also participated since 1993 in an international quality performance QUASIMEME-program covering metals in sediment (Cofino and Wells 1994). The analytical quality of the laboratory of the Institute of Geography (IG) was checked under the Curonian Lagoon Project and noted as acceptable.

In each of the laboratories, different commercial certified reference materials or corresponding materials were analysed in every sample batch. At the FIMR, the commercial certified reference materials SRM 2704 (NIST, National Institute of Standards and Technology), MESS-1 (NRCC, National Research Council of Canada) and BEST-1 (for Hg, NRCC) were used, while at the NERI/IAE BCSS-1 (NRCC) and BEST-1 (for Hg, NRCC) were determined. In Estonia (GSE) various standards of international intercomparison exercises, e.g. LB-A (Lillebælt), H-B (Holland), ABSS-C (Brügmann and Niemistö 1987) and MBSS-D (Brügmann and Niemistö 1987)**,** were used. The Russian standards SDO-1, 2, 3 (Berkovits and Lukashin 1984) and SDPS-2 (Anon. 1987) were analysed for quality control in Lithuania (IG). A summary of the results is presented in Table 2. There it can be seen that the data for copper, zinc, cadmium, lead and mercury were acceptable. When a total leaching method was used, recoveries were between 80% (Cu in GSE) and 122% (Zn and Cd in GSE), while recoveries when a partial leaching method was used were between 70% and 89%. Unfortunately, standard deviations for the results of the GSE are not available, as different references were used in different analysis batches. For the other reported elements that were analysed at the FIMR, the recoveries were 80% (Cr)–109% (Ni) for MESS-1 and 84% (V)–143% (Li) for SRM 2704.

Results and discussion

In our study, the data from various studies were collected into one data set, and consequently sediment samples were prepared, analysed and the data handled with different slice intervals in the different institutes (Appendix); if the data for the whole

Gulf of Riga were considered, some simplifications of the data were made:

a. The results for heavy metals were presented for the sample intervals 0–1, 0–2 and 0–5 cm, as the original data were sampled incoherently. This kind of treatment is appropriate in order to get as much data as possible for the whole Gulf.
b. Data for partially-leached metals (nitric acid digestion) from the NERI/IAE were not included in the data set for the total concentration of heavy metals. They were only used as a verifying non-mineralogical portion of the heavy metals at certain stations in the Gulf of Riga.
c. Some very close inshore stations sampled by the GSE (16 stations, depth < 5 m, Appendix) were not included in the statistical treatment as they represent "local pollutants" caused by regional discharges; however, they were included in the distribution maps of the topmost 0–5 cm sediment samples.

The mean concentration data were handled in two groups: concentrations in accumulation (mud) basins and in transportation/erosion areas (sand, till, silt and clay). Samples were distinguished into these groups according to the description of sediment samples done on board (Appendix) and the mean concentrations referred to on a dry weight basis unless otherwise stated.

Carbon

The mean concentrations of TC and TOC were similar in the two first centimetres of samples in the accumulation bottoms (5.5 and 4.5/4.7 by wet weight, wt%, respectively (Table 3)). A significantly higher $CaCO_3$ content was measured in the 0–1 cm (7.0 wt%) than in the 0–2 cm samples (5.5 wt%). In the accumulation bottoms, mean concentrations of TC and TOC were about 30% higher than the values in the transport/erosion bottoms in the upper 2 cm (Table 3). This is due to the presence of more organic-rich material in the accumulation bottom as compared with the sandy-clay-like composition of material in the transport/erosion bottom, which is partly seen in the increased $CaCO_3$ content (10.2 wt%) in the non-deposition bottoms. In the 0–5 cm sample intervals, the mean TC concentration was almost five times higher in the accumulation than in the transport/erosion areas, the mean contents being 3.2 and 0.6 wt% with variations of 0.6–5.2 and 0.1–3.7 wt%, respectively (Table 3). Amounts of TOC seem to be higher in the accumulation areas and $CaCO_3$ in the transport bottoms, but unfortunately there were only two samples in the transport areas available for comparison.

Nitric acid extractable and total metal concentrations in the uppermost layers

There were nine stations (Fig. 1 and Appendix) from which the parallel sediment cores were analysed for heavy metal content with nitric acid at the NERI/IAE and total extraction at the FIMR. The results and the statistical descriptions of selected elements in the surface 0–1 cm and the topmost 0-5 cm sediments in the accumulation basins of the Gulf with partial (nitric acid) and total dissolution are given in Table 4. The table contains the percentage fractions of the selected elements dissolvable in nitric acid, P_{HNO3}%, which indicate the ratio between nitric acid extracted and the total concentration of elements.

The comparison between nitric acid extraction and total leaching showed similar mean concentrations of cadmium, lead and zinc with both techniques, whereas values for copper are one third lower in partial leaching than in total digestion. It is to be noted that the partial and total leaching were performed on samples from different cores. Nitric acid leaching is often used to give a rough estimate of the anthropogenic part of the selected heavy metal concentration, although it also partly dissolves loosely mineral-bounded heavy metals (Dolezal *et al.* 1968).

P_{HNO3}% varied between different stations, indicating differences in the sediment quality. Results from the sample interval 0–1 and 0–5 cm showed quite an even distribution of the partially-leached portion of metals. For the 0–5 cm interval P_{HNO3}% varied for zinc between 80 and 98 (mean 88, median 87), for cadmium between 69 and 101 (mean 81, median 77) and for lead between 80 and 103 (mean 92, median 93). In some cases i.e. the replicates for cadmium values at Riga

I and H, the P_{HNO3}% was over 100. This can partly be due to the fact that the parallel core samples were not good replicates, but also because of the analytical variability. These data have been excluded from the statistical calculations. It seems that mineralogical part of zinc and lead was somewhat higher than in the case of copper and cadmium. However, the natural concentrations of these metals based on the mineralogical composition of the sediments seem to be on average from 10% to 30%.

For total concentrations of heavy metals, the data was available for three sample intervals in the uppermost sediments in the accumulation and transport/erosion areas. Values presented in Table 3 are averages over all stations where measurements were made, and thus give an estimate of heavy metal concentrations in the Gulf. For copper and lead, the total mean concentrations in the 0–1, 0–2 and 0–5 cm samples in the accumula-

Table 3. Total concentrations of variables studied in the surface sediments (0–1, 0–2 and 0–5 cm) of the accumulation and transportation/erosion areas in the Gulf of Riga. Heavy metal units based on dry weights, carbon on wet weight.

	TC (wt%)	TOC (wt%)	$CaCO_3$ (wt%)	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	Pb (mg kg^{-1})	Hg (mg kg^{-1})
Accumulation area 0–1 cm								
Mean	5.5	4.5	7.0	31	146	0.73	39	0.103
Median	5.8	4.7	6.2	33	159	0.75	40	0.103
Standard Deviation	1.0	1.3	3.8	6	37	0.22	8	0.029
Minimum	2.3	0.9	1.8	13	44	0.21	17	0.054
Maximum	6.4	6.0	14.3	39	196	1.11	48	0.163
Number	16	14	14	16	16	16	16	16
Accumulation area 0–2 cm								
Mean	5.5	4.7	5.5	27	164	0.90	41	0.077
Median	5.5	4.7	4.3	33	161	0.76	41	0.084
Standard Deviation	0.5	0.6	3.2	9	84	0.52	12	0.040
Minimum	4.5	4.0	1.4	10	57	0.47	20	0.011
Maximum	6.2	6.0	13.0	41	475	2.83	80	0.130
Number	13	11	11	21	21	21	21	21
Transport/erosion area 0–2 cm								
Mean	3.9	2.7	10.2	22	89	0.56	25	0.094
Median	3.9	2.7	10.2	21	92	0.42	26	0.070
Standard Deviation	1.6	1.9	1.5	9	32	0.36	6	0.056
Minimum	2.2	0.8	8.7	13	47	0.30	18	0.054
Maximum	5.5	4.5	11.7	34	125	1.09	32	0.159
Number	3	3	3	4	4	4	4	3
Accumulation area 0–5 cm								
Mean	3.2	4.1	4.8	24	128	1.77	36	0.219
Median	3.3	4.2	4.3	25	132	1.97	38	0.190
Standard Deviation	1.3	0.4	2.5	10	45	0.71	12	0.104
Minimum	0.6	3.5	1.1	5	26	0.64	9	0.073
Maximum	5.2	4.7	10.4	38	225	3.20	62	0.400
Number	53	13	13	53	53	53	53	53
Transport/erosion area 0–5 cm								
Mean	0.6	1.7	12.4	10	47	0.72	20	0.085
Median	0.5	1.7	12.4	6	33	0.63	19	0.085
Standard Deviation	0.7	1.0	1.4	8	36	0.59	10	0.016
Minimum	0.1	1.0	11.4	1	5	0.05	0.2	0.050
Maximum	3.7	2.4	13.4	29	147	3.22	46	0.120
Number	34	2	2	69	69	54	69	34

tion areas were almost in the same range, while for cadmium and mercury the highest values were in the 0–5 cm interval. For zinc, the highest mean concentrations were in the 0–2 cm samples. The samples in the 0–2 and 0–5 cm interval were collected from different stations, which makes comparison between them uncertain (Appendix). The mean concentrations of elements seem to be higher in the samples from the accumulation bottoms than those from the transport/erosion bottoms, with the exception of mercury. In the sample interval 0–2 cm, the mean value of mercury (0.094 mg kg^{-1}) was almost 30% higher in the transport bottom areas than in the accumulation bottom areas (0.077 mg kg^{-1}). However, the median of the mercury concentration in the bottom areas (0.070 mg kg^{-1} in the transport/erosion and 0.084 mg kg^{-1} in the accumulation) showed that the high concentration (maximum 0.159 mg kg^{-1}) found at one site in the transportation areas explained this. However, it should be noted that there are only three stations in the transport bottom areas in the 0–2 cm samples making comparisons speculative. Also the maximum value of cadmium in the sample interval 0–5 cm in the transport/erosion bottoms was equal to that in the accumulation areas, which partly indicates that the transport bottoms include areas, which can occasionally act as accumulation areas. The concentrations of zinc were two times higher in the accumulation areas than in the transport/erosion bottoms, while lead was only 30% higher in the former. The concentrations of cop-

Table 4. Concentrations and descriptive statistics for heavy metals analysed with the total and partial leaching methods at nine stations in the accumulation bottoms. The dissolved fraction of metals in nitric acid, P_{HNO3}%, indicate the ratio between nitric acid extracted and the total concentration of elements. Units based on dry weights. (*See* stations in Appendix).

Station	Depth (cm)	Cu* (mg kg^{-1})	Cu** (mg kg^{-1})	Cu P_{HNO3}%	Zn* (mg kg^{-1})	Zn** (mg kg^{-1})	Zn P_{HNO3}%	Cd* (mg kg^{-1})	Cd** (mg kg^{-1})	Cd P_{HNO3}%	Pb* (mg kg^{-1})	Pb** (mg kg^{-1})	Pb P_{HNO3}%
RIGA B	0–1	33	21	63	158	115	73	0.89	0.60	68	39	34	87
Avg	0–5	32	22	69	161	128	80	0.97	0.67	69	39	34	88
RIGA D	0–1	34	26	76	165	143	87	0.66	0.70	105	38	37	96
Avg	0–5	34	26	76	173	148	85	0.76	0.76	101	42	41	97
RIGA E	0–1	38	30	80	162	154	95	0.77	0.80	104	40	41	102
Avg	0–5	37	33	88	164	161	98	1.01	0.93	92	44	46	103
RIGA G	0–1	34	24	69	123	116	94	1.05	0.67	64	32	28	89
Avg	0–5	35	27	77	135	127	94	1.00	0.85	86	33	32	96
RIGA H	0–1	32	25	79	161	153	95	(0.66)	(0.88)	(132)	44	40	90
Avg	0–5	37	29	77	179	154	86	(0.76)	(0.84)	(111)	47	41	87
RIGA I	0–1	33	21	63	152	145	95	(0.55)	(0.81)	(147)	43	37	87
Avg	0–5	36	23	65	177	154	87	(0.64)	(0.96)	(150)	47	44	93
RIGA J	0–1	28	18	66	146	118	81	0.85	0.57	68	35	30	84
Avg	0–5	32	21	64	152	127	84	0.93	0.66	71	38	37	96
RIGA M	0–1	30	22	75	122	127	105	0.85	0.59	69	40	25	62
Avg	0–5	33	23	71	156	142	91	0.85	0.65	77	41	33	80
RIGA K	0–1	39	29	75	196	153	78	1.11	0.75	67	48	43	90
Avg	0–5	36	31	84	180	158	87	1.14	0.86	76	52	45	87
Medium	0–1	34	24	72	154	136	89	0.88	0.67	78	40	35	87
	0–5	35	26	75	164	144	88	0.95	0.76	81	43	39	92
Median	0–1	33	24	75	158	143	94	0.85	0.67	67	40	37	89
	0–5	35	26	76	164	148	87	0.97	0.76	77	42	41	93
S.D.	0–1	3	4	7	23	17	10	0.16	0.09	18	5	6	11
	0–5	2	4	8	15	14	6	0.12	0.11	12	6	5	7

Data not included in the statistical treatment are given in parentheses; * total extraction at the FIMR; **nitric acid extraction at the NERI/IAE.

per (0–5 cm), mercury (0–5 cm) and cadmium were more than two times higher in the accumulation areas than in the transport/erosion bottoms.

Spatial distribution of metals

The spatial element distributions in the topmost five centimetres of sediments are presented in Fig 3. For the production of these graphs, the data were subjected to a geostatistical analysis (*see* e.g. Isaaks and Srivastava 1989) for optimal interpolation and a kriged distribution. In Fig. 3 the estimated parameters for sill variance, nugget effect and range are shown for each element.

For TC, the data from Carman *et al.* (1996) have also been included in the distribution map. In the transport areas, some carbon values were missing. Here these values were substituted with a value corresponding to 10× nitrogen concentrations (Carman *et al.* 1996). The highest amounts of carbon (4%) seem to have been transported to the deepest parts of the Gulf, with the exception of some enriched samples in the close inshore areas off Kuressaar (Fig.1).

Mercury was mainly concentrated in the mud accumulation basins of the Gulf (Fig. 3). The highest values (up to 0.400 mg kg^{-1}) were found in the deepest mud accumulation bottoms. The high concentrations found in the present study in the southern close inshore stations off the River Gauja (Fig. 1) and river sediments seem to be partly transported further north from these areas and spread out in the deeper parts of the open Gulf. The mercury distribution pattern presented by Kulikova (1995) has a similar shape, although some values are higher than in the present study.

The distribution of cadmium was very scattered, showing high concentrations in both the close inshore and the deeper areas of the Gulf. The highest concentrations were found in the transportation area in the vicinity of Ragaciems (3.22 mg kg^{-1}) and in the mouth area of the Irbe Sound to the southwest of Ruhnu (3.20 mg kg^{-1}, Fig. 1). High concentrations were also found (2.74 mg kg^{-1}) in the close inshore area of the Irbe Sound. Current measurements (Lips and Lilover 1995, Suursaar and Astok 1996) indicated that the water flows in from the Baltic Proper along the southern coast of the Irbe Sound in the bottom water layer and flows out in the surface layer along the northern part of the sound. Suursaar and Astok (1996) showed that in summer (May–October) water exchange occurs through both the Irbe and the Muhu Sounds; with inflows of water from the Muhu and outflows through the Irbe Sound dominating. In the ice-free winter period (November–April), very strong outflows occur only through the Muhu, and inflows from the Irbe are larger than outflows. During the ice-covered winter period (November–April) there are some outflows through the Muhu, while inflows and outflows are almost in balance in the Irbe Sound. The high cadmium concentrations found in the Sound and the mouth area can be partly explained by the water transportation in and out of the Gulf.

Of the metals considered, lead seems to be the most evenly distributed over the whole Gulf. Concentrations at a depth of 40–50 m in the mud accumulation bottom areas ranged from 30 to 50 mg kg^{-1}. The highest values were found in locations in the outer sea areas off Riga and Ragaciems (62 mg kg^{-1}), in the very close inshore area off Saaremaa, Kuressaar (80 mg kg^{-1}) and also in the Pärnu Bay (50 mg kg^{-1}) where local pollutants sources are situated.

Copper and zinc had quite even distributions in the mud accumulation areas, in a depth range of 30–60 m. The highest values for copper (80 mg kg^{-1}) and zinc (568 mg kg^{-1}) were found in the vicinity of Pärnu. High concentrations were also found in the sea area off Kuressaar. In both areas, the sediment contains high amounts of carbonate rock and clay mineral particles, which partly explain the elevated concentrations of copper and zinc. The stations are also located in close inshore areas, very close to local discharges, in some cases even in the vicinity of harbours.

Very few strong correlations between the concentrations of the elements were found in the data set (Table 5). Copper and zinc correlated strongly, and only copper correlated with total carbon. The inshore areas were enriched with elements, which is partly due to the presence of less degraded organic matter in the inshore zone. As the distribution of the metals showed incoherent patterns, it rather implies that the fluffy mud temporarily deposited in the non-deposition areas is the same as that in the deep basins, and this is eventually resuspended and transported into the accumula-

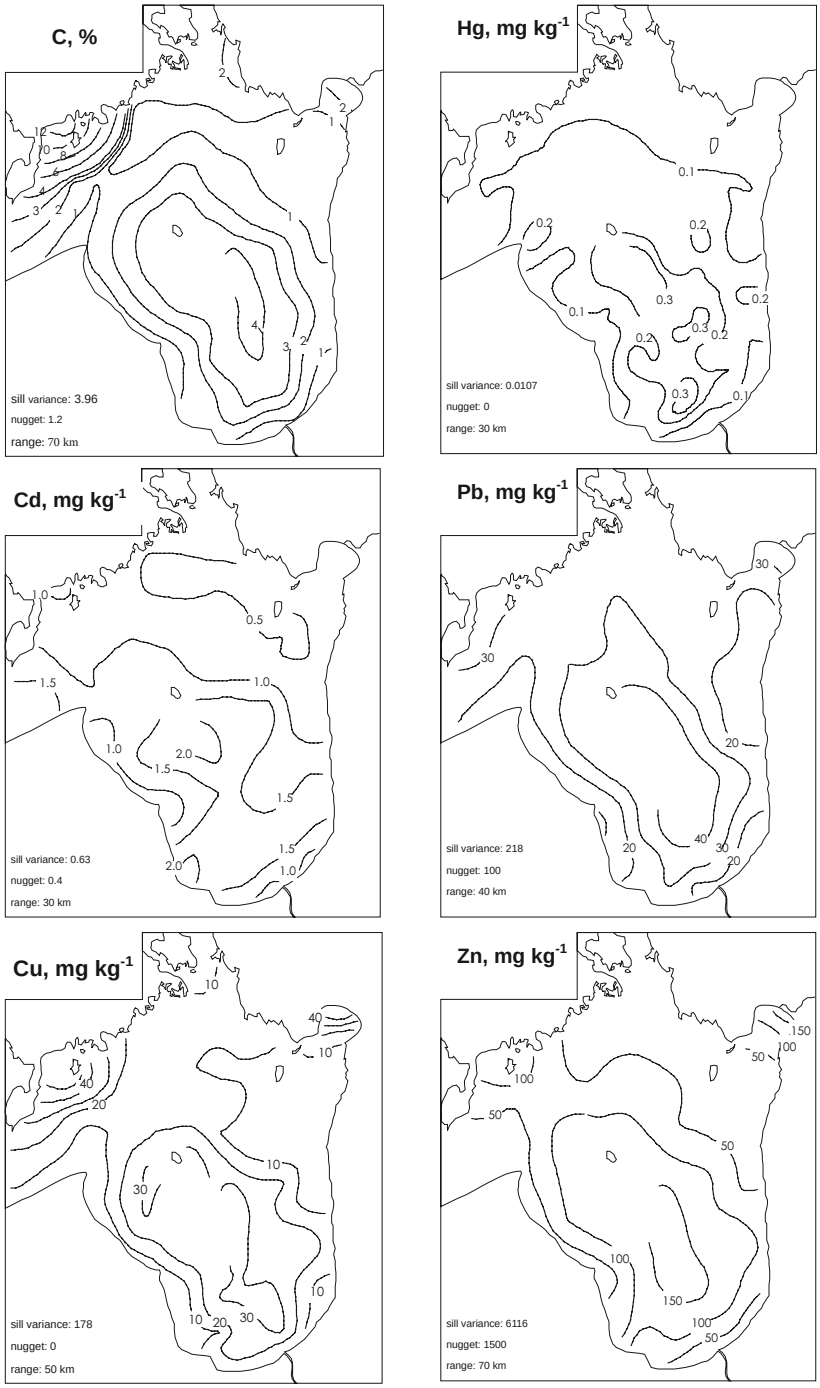

Fig. 3. Kriged distributions of selected elements in the topmost (0–5 cm) sediments of the Gulf of Riga. All krigings were ordinary and isotropic in 2 × 2 blocks, based on omnidirectionally modelled spherical variograms. Sill variance, nugget and range were selected manually as indicated specifically on each map. Heavy metal units based on dry weights, carbon on wet weight.

tion areas. It also implies that the loadings of the suspension feeders in the deep non-deposition areas and the mud accumulation areas are nearly the same. It is noted that resuspension is caused by strong winds, which remove particles from the shallow sea bottom and transport the resuspended matter to other locations (Floderus *et al.* 1999). The whole water current pattern in the Gulf strongly influences the distribution of elements, as discussed above. The distributions of the total

concentrations of zinc, lead and copper were similar, but the metal-to-carbon ratio indicates that the relative contents of these elements were slightly higher in the deep non-deposition areas than in the accumulation basins. In the non-deposition areas adsorption of metals into iron-manganese oxides and nodules is an additional mechanism operating to concentrate metals.

Vertical distribution of metals

Different segments in the sediment core represent different time periods, depending on the sedimentation rate in the area. Sixteen sediment cores from the accumulation bottoms were dated with the ^{210}Pb and ^{137}Cs methods finding the accumulation rates given in Fig. 2 (Larsen 1995). From the dated cores a typical examples of the vertical distribution of elements in a sediment core are shown in Fig. 4. At the station Riga C, the concentrations of copper and cadmium in the sediment were clearly decreasing during the past 30 years, while for the concentrations of lead, mercury and zinc, a decreasing trend was not identified. At the station Riga J, however, also the concentrations of mercury and lead have clearly decreased during the same period. In some cores, the vertical profiles of elements had quite an even distribution throughout the core, while in other cases only slightly decreased patterns, or even increased trends towards the surface layer were noticed for some metals. These may indicate that the sedimentation features in the active accumulation areas are heterogeneous. The fraction of the natural mineralogical composition also varied between the studied sediment cores (Table 4), which caused differences in the vertical profiles of the total concentrations of metals. In the surface layers of the cores, bioturbation can cause partial mixing of fresh metal deposits with older ones; however, there are not very many bottom animals present in the deep mud accumulation areas (Jermakovs 1998, Jermakovs and Cederwall 1996).

The background values of the various elements could only be measured in the core samples of few stations. On average, the following background values were obtained based on the dating results of sediment samples from the accumulation areas deposited before 1900: mercury 0.044 mg kg^{-1}, cadmium 0.20 mg kg^{-1}, lead 20 mg kg^{-1}, copper 20 mg kg^{-1} and zinc 90 mg kg^{-1}. The mean ratio of concentrations in the top sediments (0–1 cm) to the background concentrations were ca. 2 for lead, 3–6 for cadmium, ca. 1–2 for copper and zinc and 2–3 for mercury. These figures are, however, only examples, because the vertical profiles in the cores studied varied considerably. However, these values indicate that the sediments of the Gulf of Riga are not especially strongly polluted by heavy metals. This is in agreement with what has been earlier published by Seisuma and Legzdina (1991) and Seisuma *et al.* (1995), although the assessment of the quality of the older data through the intercomparison exercise revealed some uncertainties in the earlier data of some of the metals (e.g. cadmium and mercury).

Behaviour of additional elements

Only few data exist regarding the concentration of other elements such as aluminium, lithium, iron, manganese, chromium, nickel, titanium and vanadium in the accumulation areas and even less in the transport/erosion bottoms over the different sample intervals. Those data that do exist show, however, mainly similar pattern to those of mercury, cadmium, lead, zinc and copper the concentrations being highest in the accumulation bot-

Table 5. Correlation coefficients (significant set in boldface)for total carbon (TC) and heavy metals in the topmost sediments (0–5 cm) in the accumulation and transport/erosion bottoms of the Gulf of Riga. Number of samples in brackets.

	TC	Cu	Zn	Cd	Pb	Hg
Accumulation 0–5 cm						
TC (53)	1.00					
Cu (53)	**0.89**	1.00				
Zn (53)	0.72	**0.79**	1.00			
Cd (53)	–0.32	–0.28	–0.03	1.00		
Pb (53)	0.64	0.70	0.65	–0.06	1.00	
Hg (53)	–0.14	–0.13	–0.06	0.59	0.14	1.00
Transport/erosion 0–5 cm						
Cu (69)	**0.94**	1.00				
Zn (69)	0.63	**0.83**	1.00			
Cd (54)	0.10	–0.04	0.39	1.00		
Pb (69)	0.55	**0.81**	0.68	0.05	1.00	
Hg (34)	0.19	0.34	0.33	0.25	0.62	1.00

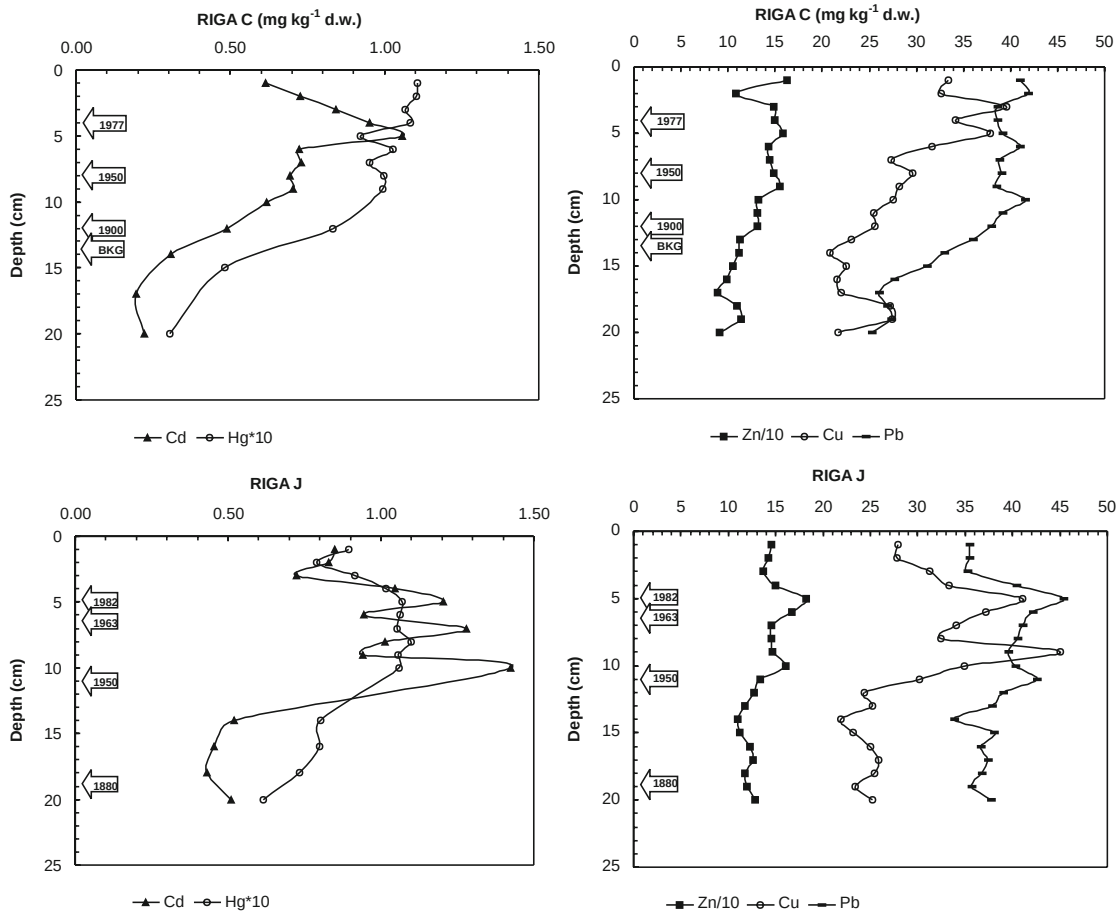

Fig. 4. Examples of vertical distributions of heavy metals in sediment cores from the Gulf of Riga. The arrows contain the estimated year for that depth. Bkg points indicating the background values are based on background values of ^{210}Pb (Riga C). *See* stations in Appendix.

toms (except manganese). An example of data on concentration levels for selected elements from 0–1 cm samples in the accumulation bottoms are shown in Table 6, where the data from other areas of the Baltic Sea are also given as a comparison.

Geochemical comparison with other Gulfs in the Baltic Sea

The mean concentrations (Table 6) show that e.g. lead, copper and zinc concentrations were lower in the Gulf of Riga while cadmium, mercury, chromium and vanadium were in the same range as in the Gulf of Bothnia and Gulf of Finland. The titanium concentration was the highest in the Gulf of Riga and aluminium, nickel and iron were in the same range in both the Gulf of Riga and Gulf of Finland (Leivuori 1998).

Another way of comparing the Gulf of Riga with the Gulf of Bothnia and Gulf of Finland is by comparing the annual accumulations of heavy metals related to the size of the accumulation area. Estimates of the annual accumulations of selected metals were calculated using the 0–1 cm data (Table 3) and a dry matter accumulation of 4.5×10^6 ta^{-1} for the sediments of the Gulf of Riga. A comparison of these to the values for the other Gulfs of the Baltic Sea is presented in Fig. 5. For the Bothnian Sea and Bothnian Bay (Fig. 1) the calculations were made using dry matter accumulation rates of 4.4×10^6 ta^{-1} (Niemistö *et al.* 1978)

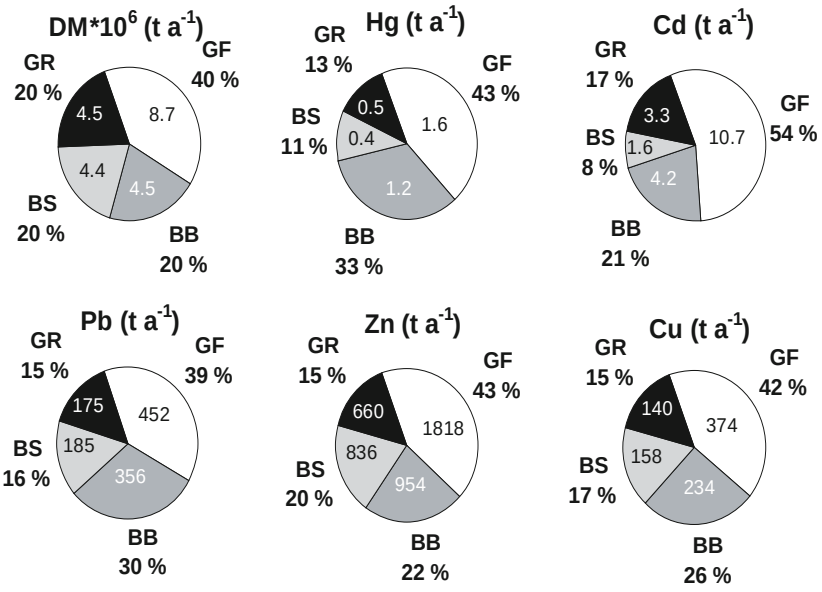

Fig. 5. Annual accumulations of dry matter (DM) and heavy metals in tonnes per year in the Gulf of Riga (GR) compared to other parts of the Baltic Sea. Data for the Gulf of Finland (GF) from Vallius and Leivuori (1999), for the Bothnian Bay (BB) and Bothnian Sea (BS) from Niemistö *et al.* (1983, 1978) and Leivuori (1998).

Table 6. Mean, median, minimum and maximum concentrations of selected elements in surface sediments (0–1 cm) in accumulation areas of the Gulf of Finland, Bothnian Bay, Bothnian Sea and Gulf of Riga. Units based on dry weights.

	Al (%)	Li (mg kg^{-1})	Fe (%)	Mn (mg g^{-1})	Cr (mg kg^{-1})	Ni (mg kg^{-1})	Ti (mg g^{-1})	V (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Cd (mg kg^{-1})	Hg (mg kg^{-1})
Gulf of Finland*, 20 samples													
Mean	7.6	62	4.5	5.07	85	42	3.94	76	175	43	50	1.06	0.13
Median	7.2	60	4.8	3.58	84	42	3.84	77	179	44	48	1.10	0.11
Minimum	5.9	49	3.0	0.56	53	25	2.42	57	107	27	26	0.34	0.05
Maximum	9.9	77	5.4	20.0	117	60	5.19	96	243	57	80	2.19	0.32
Bothnian Bay, depth > 60 m*, 8 samples													
Mean	5.6	33	6.2	8.96	73	48	3.42	73	212	52	79	0.94	0.27
Median	5.3	27	6.1	8.36	74	51	3.30	80	217	53	72	0.93	0.25
Minimum	4.7	13	3.2	1.87	56	27	3.00	40	50	18	19	0.23	0.06
Maximum	6.6	60	8.8	18.0	81	58	4.22	93	320	80	121	1.98	0.48
Bothnian Sea, depth > 60 m*, 13 samples													
Mean	6.2	59	6.0	3.55	80	53	3.88	89	190	36	42	0.37	0.09
Median	5.7	48	5.8	2.89	91	51	3.81	93	200	40	42	0.32	0.09
Minimum	4.4	26	2.9	2.03	48	32	2.33	49	90	19	17	0.14	0.01
Maximum	8.7	147	8.4	6.48	97	81	5.39	114	240	45	60	0.78	0.15
Gulf of Riga, 16 samples													
Mean	6.8	70	4.1	4.52	82	41	4.24	79	146	31	39	0.73	0.10
Median	7.1	73	4.5	2.20	84	42	4.29	81	159	33	40	0.75	0.10
Minimum	3.3	24	1.3	0.60	31	14	2.27	22	44	13	17	0.21	0.05
Maximum	8.4	83	5.5	14.9	105	57	5.74	113	196	39	48	1.11	0.16

* Leivuori 1998

and 4.5×10^6 ta^{-1} (Niemistö *et al.* 1983), respectively. For mean heavy metal concentrations, only surface sediment (0–1 cm) data in accumulation areas deeper than 60 m in the Gulf of Bothnia, as presented by Leivuori (1998), were used. According to these latest calculations, annual accumulations were somewhat higher for the whole Gulf of Bothnia than estimated earlier by Leivuori and Niemistö (1993, 1995), especially for lead and copper (2 and 1.5 times higher, respectively). This difference can partly be explained by the mean values used for the whole bottom area and the accumulation areas of the Gulf of Bothnia e.g. in Leivuori and Niemistö (1993). However, for a better comparison among the mud accumulation areas in the various parts of the Baltic Sea, new calculations are appropriate. It can clearly be seen from Fig. 5 that the highest annual accumulations of heavy metals were found in the Gulf of Finland, whereas accumulations in the Gulf of Riga were in many cases in the same range as those in the Bothnian Sea. The estimated annual accumulations of elements indicated low accumulations of these in the sediments of the Gulf of Riga.

Conclusion

The present study shows that the distribution and concentrations of heavy metals in the sediments of the Gulf of Riga are heterogenous. Various physical-geochemical features influence the horizontal and vertical distribution of elements in the area. The concentration levels of metals and the annual accumulations in the surface sediments of the off-shore areas in the Gulf of Riga are generally low and comparable to those found in the rest of the Baltic Sea in similar settings. However, more studies are needed for clarifying the role of the Gulf of Riga in the transport of trace elements to the rest of the Baltic Sea or the importance of the Baltic Sea as a source of heavy metals for inflow to the Gulf. This includes the levels of metals in the water phase, the role of annual in- and outflows, as well as the role of iron-manganese nodules in adsorbing metals from the biochemical cycle.

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Appendix. List and descriptions of sampling stations in the Gulf of Riga 1991–1996.

Station	Sampling year	Sampling and analyses	Sampling depths (cm)	Latitude	Longitude	Bottom depth (m)	Type
RIGA A	1994	FIMR	0–26	57°42.83´	22°42.94´	39	Sandy mud
RIGA B	1994	FIMR	0–20	57°49.01´	22°57.52´	38	Clayey mud
		NERI/IAE	0–25				
RIGA B1	1993	FIMR	0–29	57°31.20´	23°13.20´	45	Silty mud
RIGA B2	1993	FIMR	0–5	57°50.58´	23°23.53´	44	Silty sandy mud
RIGA B3	1993	FIMR	0–30	57°40.45´	23°36.00´	54	Mud
RIGA C	1994	FIMR	0–20	57°37.99´	23°02.51´	46	Clayey mud
RIGA D	1994	FIMR	0–20	57°18.66´	23°31.00´	44	Clayey mud
		NERI/IAE	0–30				
RIGA E	1994	FIMR	0–20	57°06.99´	23°33.97´	37	Mud
		NERI/IAE	0–35				
RIGA F	1994	FIMR	0–17	57°06.47´	23°57.07´	26	Sandy silt
RIGA G	1994	FIMR	0–21	57°11.47´	24°05.02´	34	Sandy mud
		NERI/IAE	0–35				
RIGA H	1994	FIMR	0–21	57°18.98´	23°54.47´	48	Mud
		NERI/IAE	0–50				
RIGA I	1994	FIMR	0–20	57°30.01´	24°05.96´	45	Mud
		NERI/IAE	0–40				
RIGA J	1994	FIMR	0–20	57°45.98´	24°00.01´	39	Mud
		NERI/IAE	0–40				
RIGA K	1994	FIMR	0–20	57°27.01´	23°44.00´	45	Mud
		NERI/IAE	0–40				
RIGA M	1994	FIMR	0–20	57°55.96´	23°17.47´	44	Mud
		NERI/IAE	0–35				
RIGA O	1994	FIMR	0–20	57°37.00´	23°40.00´	50	Mud
RIGAL	1994	IAE	0–35	57°48.51´	23°30.00´	52	Mud
105	1991	IG	0–5	57°01.14´	23°39.66´	27	Silty mud
106	1991	IG	0–5	57°06.84´	23°43.80´	36	Clayey mud
107	1991	IG	0–5	57°02.66´	23°51.39´	21	Clayey silt
108	1991	IG	0–5	57°03.42´	23°54.15´	21	Clayey silt
109	1991	IG	0–5	57°06.84´	23°52.77´	34	Clayey/pelitic mud
110	1991	IG	0–5	57°05.70´	23°58.98´	20	Fine sand
111	1991	IG	0–5	57°08.74´	24°01.72´	30	Clayey mud
112	1991	IG	0–5	57°09.12´	23°56.22´	36	Clayey/pelitic mud
113	1991	IG	0–5	57°13.68´	24°04.83´	36	Clayey/pelitic mud
114	1991	IG	0–5	57°10.26´	24°09.66´	22	Clayey silt
115	1991	IG	0–5	57°12.92´	24°14.49´	20	Clayey silt

Continued

Appendix. Continued.

Station	Sampling year	Sampling and analyses	Sampling depths (cm)	Latitude	Longitude	Bottom depth (m)	Type
116	1991	IG	0–5	57°16.72´	24°17.25´	19	Clayey silt
117	1991	IG	0–5	57°22.28´	24°14.39´	25	Silt
118	1991	IG	0–5	57°31.40´	24°10.35´	34	Mud
119	1991	IG	0–5	57°25.70´	23°59.67´	43	Mud
120	1991	IG	0–5	57°45.32´	23°58.98´	43	Clayey/pelitic mud
121	1991	IG	0–5	57°40.40´	23°30.07´	38	Clayey/pelitic mud
122	1991	IG	0–5	57°35.20´	23°34.83´	49	Clayey/pelitic mud
123	1991	IG	0–5	57°35.20´	23°36.90´	50	Clayey/pelitic mud
124	1991	IG	0–5	57°09.50´	24°11.73´	22	Clayey silt
125	1991	IG	0–5	57°38.62´	23°10.35´	41	Clayey/pelitic mud
126	1991	IG	0–5	57°29.50´	23°30.40´	41	Clayey/pelitic mud
127	1991	IG	0–5	57°44.94´	22°16.26´	29	Sandy silt
128	1991	IG	0–5	57°44.44´	22°43.80´	30	Clayey/pelitic mud
129	1991	IG	0–5	57°33.68´	22°53.46´	27	Clayey/pelitic mud
130	1991	IG	0–5	57°27.22´	22°58.58´	20	Fine sand
131	1991	IG	0–5	57°20.76´	23°19.32´	34	Fine sand
132	1991	IG	0–5	57°19.00´	23°28.29´	40	Clayey mud
133	1991	IG	0–5	57°15.96´	23°42.42´	41	Clayey mud
134	1991	IG	0–5	57°15.96´	24°08.27´	37	Silty mud-clayey
135	1991	IG	0–5	57°22.66´	24°12.42´	32	Silty mud-clayey
136	1991	IG	0–5	57°21.52´	23°16.56´	34	Fine sand
137	1991	IG	0–5	57°23.80´	23°43.80´	42	Clayey mud
138	1991	IG	0–5	57°18.24´	23°26.22´	40	Silty mud
139	1991	IG	0–5	57°08.74´	23°30.70´	35	Silty mud-clayey
140	1991	IG	0–5	57°03.04´	23°37.59´	31	Clayey mud
141	1991	IG	0–5	57°05.70´	23°53.46´	27	Coarse silt
142	1991	IG	0–5	57°04.94´	23°54.15´	25	Silty mud
143	1991	IG	0–5	57°09.50´	24°10.00´	21	Coarse silt
144	1991	IG	0–5	57°02.28´	23°54.84´	19	Coarse silt
145	1991	IG	0–5	57°01.14´	23°50.70´	16	Coarse silt
146	1991	IG	0–5	57°01.14´	23°45.87´	21	Coarse silt
147	1991	IG	0–5	57°00.00´	23°38.62´	21	Coarse silt
148	1991	IG	0–5	57°04.18´	23°43.11´	30	Clayey/pelitic mud
149	1991	IG	0–5	57°06.84´	23°45.87´	35	Clayey/pelitic mud
150	1991	IG	0–5	57°05.32´	23°48.63´	31	Clayey/pelitic mud
151	1991	IG	0–5	57°04.94´	23°50.70´	28	Silty mud
152	1991	IG	0–5	57°07.22´	23°57.60´	26	Silty mud
153	1991	IG	0–5	57°09.50´	24°06.90´	24	Silt
154	1991	IG	0–5	57°10.26´	24°07.93´	25	Silt
155	1991	IG	0–5	57°28.74´	23°52.04´	43	Mud
156	1991	IG	0–5	57°43.42´	24°10.35´	21	Silty sand
157	1991	IG	0–5	57°40.76´	24°09.66´	25	Fine sand
158	1991	IG	0–5	57°49.88´	23°58.98´	27	Clayey/pelitic mud
159	1991	IG	0–5	57°55.58´	24°03.45´	20	Sandy silt
160	1991	IG	0–5	57°42.28´	23°54.15´	40	Clayey/pelitic mud
161	1991	IG	0–5	57°59.38´	23°12.42´	39	Clayey/pelitic mud
162	1991	IG	0–5	57°56.72´	22°58.29´	31	Clayey/pelitic mud
163	1991	IG	0–5	57°57.86´	22°37.70´	28	Clayey/pelitic mud
164	1991	IG	0–5	57°49.12´	22°30.07´	27	Clayey silt
165	1991	IG	0–5	57°45.70´	22°29.03´	16	Clayey silt
166	1991	IG	0–5	57°43.04´	22°41.04´	42	Clayey/pelitic mud
167	1991	IG	0–5	57°37.48´	22°40.35´	21	Fine sand

Continued

Appendix. Continued.

Station	Sampling year	Sampling and analyses	Sampling depths (cm)	Latitude	Longitude	Bottom depth (m)	Type
168	1991	IG	0–5	57°31.78´	22°47.25´	21	Fine sand
169	1991	IG	0–5	57°28.74´	22°51.39´	20	Fine sand
170	1991	IG	0–5	57°31.78´	22°52.77´	37	Clayey/pelitic mud
171	1991	IG	0–5	57°31.78´	23°08.28´	41	Clayey/pelitic mud
172	1991	IG	0–5	57°21.52´	23°11.04´	22	Silty sand
173	1991	IG	0–5	57°16.34´	23°12.42´	12	Fine sand
174	1991	IG	0–5	57°07.98´	23°22.77´	31	Fine sand
175	1991	IG	0–5	57°07.98´	23°33.45´	37	Fine sand
176	1991	IG	0–5	57°03.42´	23°34.83´	31	Silty mud
SMAA1	1996	IG	0–20	58°05.00´	23°10.19´	31	–
R03-05	1993	GSE	0–5	58°31.32´	23°29.24´	17	Sandy silt
R03-07	1993	GSE	0–5	58°36.51´	23°24.60´	19	Sandy silt
R05-02	1993	GSE	0–5	58°03.40´	23°16.25´	42	Mud
R05-03	1993	GSE	0–5	58°06.39´	23°15.28´	37	Clayey silt
R05-04	1993	GSE	0–5	58°10.00´	23°14.25´	33	Silt
R05-05	1993	GSE	0–5	58°06.56´	23°07.06´	33	Silt
R05-06	1993	GSE	0–5	58°05.48´	23°04.06´	36	Silt
R05-07	1993	GSE	0–5	58°02.51´	23°08.23´	34	Silt
R05-08	1993	GSE	0–5	58°00.51´	23°11.16´	41	Silty mud
R05-10	1993	GSE	0–5	58°04.21´	23°19.15´	41	Mud
R05-13	1993	GSE	0–5	58°09.57´	23°33.18´	33	Silty mud
R05-14	1993	GSE	0–5	58°13.28´	23°41.57´	30	Silty sand
R06-01	1993	GSE	0–5	58°17.33´	23°05.35´	21	Fine sand
R06-02	1993	GSE	0–5	58°09.34´	23°02.10´	27	Silty mud
R06-03	1993	GSE	0–5	58°04.47´	22°59.49´	32	Silty mud
R06-04	1993	GSE	0–5	57°59.06´	22°57.51´	34	Fine sand
R06-05	1993	GSE	0–5	57°59.04´	23°07.15´	40	Silty mud
R07-04	1993	GSE	0–5	57°59.00´	23°37.36´	39	Silty mud
R07-05	1993	GSE	0–5	57°58.45´	23°36.10´	39	Silt
R07-07	1993	GSE	0–5	58°06.52´	23°24.27´	33	Silty sand
R08-04	1993	GSE	0–5	58°01.12´	24°11.20´	24	Fine sand
R08-07	1993	GSE	0–5	58°16.56´	24°20.57´	8	Sand
R08-08	1993	GSE	0–5	58°19.40´	24°23.13´	7	Sand
R08-17	1993	GSE	0–5	58°04.60´	24°18.54´	15	Sand
R08-20	1993	GSE	0–5	57°59.05´	24°02.52´	26	Fine sand
R09-01	1993	GSE	0–5	57°59.07´	23°38.08´	40	Silt
R10-06	1993	GSE	0–5	58°04.22´	23°29.45´	36	Silty sand
R10-07	1993	GSE	0–5	58°01.57´	23°23.44´	43	Mud
R11-01	1993	GSE	0–5	58°00.14´	22°59.00´	35	Silt
R11-02	1993	GSE	0–5	58°05.19´	23°12.17´	38	Silt
R11-03	1993	GSE	0–5	58°09.18´	23°21.26´	33	Silt
R12-02	1993	GSE	0–5	58°00.31´	22°46.25´	32	Fine sand, clay
R15-15	1993	GSE	0–5	58°04.07´	22°48.18´	28	Clay
R19-01	1993	GSE	0–5	57°59.41´	22°31.29´	27	Clay
P-94-1-1	1994	GSE	0–5	58°23.12´	24°29.05´	3	Mud
P-94-1-3	1994	GSE	0–5	58°23.12´	24°29.05´	3	Mud
P-94-1-5	1994	GSE	0–5	58°23.12´	24°29.05´	3	Mud
P-94-2-1	1994	GSE	0–5	58°23.09´	24°29.09´	4	Mud
P-P4-2-3	1994	GSE	0–5	58°23.09´	24°29.09´	4	Mud
UN-88-20-1	1994	GSE	0–5	58°27.54´	23°16.36´	2	Silty mud
P-48-1	1994	GSE	0–5	58°21.60´	24°27.42´	4	Mud
KÄ-90-9-1	1994	GSE	0–5	58°31.18´	23°40.48´	1	Silty mud

Continued

Appendix. Continued.

Station	Sampling year	Sampling and analyses	Sampling depths (cm)	Latitude	Longitude	Bottom depth (m)	Type
KÄ-90-59-1	1994	GSE	0–5	58°31.33´	23°41.09´	1	Silty mud
K-89-11	1994	GSE	0–5	58°14.18´	22°27.33´	2	Silty mud
K-89-12	1994	GSE	0–5	58°13.39´	22°27.18´	2	Mud
SM	1994	GSE	0–5	58°31.15´	23°14.48´	1	Silty mud
M-94-32-1	1994	GSE	0–5	57°59.00´	22°12.18´	5	Silty mud
M-94-32-2	1994	GSE	0–5	57°59.00´	22°12.18´	5	Silty mud
M-94-32-5	1994	GSE	0–5	57°59.00´	22°12.18´	5	Mud
M-95-32-7	1994	GSE	0–5	57°59.00´	22°12.18´	7	Silty mud
IB-1	1996	GSE	0–2, 4–6.5	57°50.01´	22°30.00´	29	Mud
IB-2	1996	GSE	0–1.5, 2–10	57°50.02´	22°45.02´	28	Mud, clay
R-1-1	1996	GSE	0–2	57°35.04´	23°28.98´	33	Mud, clay
R-4-1	1996	GSE	0–2, 7–10	57°58.23´	23°00.51´	31	Mud, clay
Sm-1-1	1996	GSE	0–2, 12,14, 24–26	58°04.98´	23°10.20´	31	Mud, clay
Sm-2-1	1996	GSE	0–2, 2–7	58°11.49´	23°07.52´	24	Clay, mud
Sm-3-1	1996	GSE	0–2, 2–5	58°17.01´	23°04.94´	17	Mud, clay
Sm-5-1	1996	GSE	0–2, 10–12	58°12.01´	23°23.98´	28	Mud, clay

FIMR: the Finnish Institute of Marine Research, IAE: the Institute of Aquatic Ecology of the University of Latvia, NERI: the National Environmental Research Institute (Denmark), IG: the Institute of Geography (Lithuania), GSE: the Geological Survey of Estonia (GSE).

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