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**Holocene sedimentary environment and sediment geochemistry
of the Eastern Gulf of Finland, Baltic Sea**



Edited by Henry Vallius

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Espoo 2007

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This report is a product of common efforts of not only the writers of the articles but also of the staffs of the vessels and office staff of GTK and VSEGEI. The included papers were reviewed by Professors Reijo Salminen and Georgy Cherkashov. Their contribution is gratefully acknowledged. Roy Siddall kindly revised the language of the articles. Finally the authors express their gratitude to the financing agencies and to the Geological Survey of Finland (GTK) for supporting the publication of this report.

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Vallius, H. (ed.) 2007. Holocene sedimentary environment and sediment geochemistry of the Eastern Gulf of Finland, Baltic Sea, *Geological Survey of Finland, Special Paper 45*. 70 pages, 48 figures, 14 tables and one appendix.

The joint Finnish-Russian project *Sediment geochemistry and natural and anthropogenic hazards in the marine environment of the Gulf of Finland* (SAMAGOL) aimed at filling a gap in knowledge of the environmental situation of the seafloor in the Eastern Gulf of Finland. This publication contains five peer-reviewed papers based partly on old existing data combined with new data collected during the time-frame of the SAMAGOL project.

The Quaternary deposits of the seafloor of the Eastern Gulf of Finland are described in the paper by Spiridonov et al. based on numerous data concerning the structure, distribution, and lithology of the sediments. Also problems of correlation with Quaternary deposits on land are discussed.

Different aspects of the environmental conditions in the study area are discussed in the remaining 4 papers. Zhamoida et al. have investigated the possible influence of the ferromanganese concretion formation processes on environmental conditions in the Eastern Gulf of Finland. The concretion fields were mapped and high concretion growth rates were measured. It is very likely that the concretion fields play an important role as a buffer system in the near-bottom and pore waters. In two papers (Vallius et al. and Vallius) the geochemistry of the soft surface sediments in the vicinity of cities Kotka and Hamina are described, with focus on heavy-metal concentrations and distribution. Also, background levels of 12 trace metals are presented as a baseline for future studies and for sediment guidelines. Kotilainen et al. discuss an overall shallowing of anoxia since 1950's in the coastal area of the eastern Gulf of Finland, as towards the present, laminated sediments have developed also in the shallower basins. Extended and prolonged seafloor anoxia could enhance the environmental problems by releasing metals and nutrients, like P, from the seafloor sediments.

Key words (Georef Thesaurus AGI): anoxia, marine geology, marine sediments, ferromanganese concretions, geochemistry, heavy metals, Baltic Sea, Gulf of Finland, Russian Federation, Finland, Holocene.

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INTRODUCTION

The Geological Survey of Finland (GTK) and A. P. Karpinsky Russian Geological Research Institute (VSEGEI) are the national geoscience institutes of their countries. Both institutes have very long traditions in geological research. Also co-operation between the institutes have long traditions. This has involved many aspects of geology, not the least marine geology. As a natural consequence of this co-operation the management of both institutes decided in early 2004 to start a common project in the field of marine geology. It was decided that the area on both sides of the national border between the participating countries would be the best area for common research. The work was coordinated under a joint project called "*Sediment geochemistry and natural and anthropogenic hazards in the marine environment of the Gulf of Finland, SAMAGOL*". The project started with a workshop in St. Petersburg on June 6th 2003. It was agreed that the already available seafloor data of both institutes would be the basis of the co-operation. That data has been complemented during cruises to the study area in summers 2004 and 2006. The area of interest is situated in the eastern Gulf of Finland between longitudes 26° 27,5'E and ~28° 30 E and between latitudes 60° 00,0'N and 60° 30,0'N. The western part of this area to longitude 27° 10,8'E was chosen to be of first order of importance. During the project altogether 6 workshops have been arranged for participating scientists in both St. Petersburg and Espoo. Two major cruises have been arranged with GTK's vessels R/V *Geola* and R/V *Geomari* and one cruise from St. Petersburg with R/V *Aurora*. Additionally some data have been collected during two cruises of Finnish Institute of Marine Research's R/V *Aranda*. Altogether some 800 kilometres of survey lines have been surveyed during the different cruises. Depending on which vessel was used different equipment was operating. In all cases a *pinger* sub-bottom profiler was used. On different ships different frequencies were used but in all cases it provides good penetration in soft sediments and gives a good picture of the sediment stratigraphy of the seafloor. In some cases also a side scan sonar and shallow seismic equipment was used. The acoustic data was primarily used in order to find best suitable sampling locations for sediment cores and grab samples and secondly in order to gather as good data as possible for seafloor map production. Altogether 47 surface samples were collected, of which 21 van Veen grabs and 26 GEMAX gravity cores. The grab samples were used for description of coarser and harder bottoms, with special emphasis on studies of Fe/Mn concretions. The GEMAX gravity cores were used for description of soft bottoms, usually muddy clays, as well as for geochemical sampling. Geochemical analyses were performed in the Geolaboratory of the GTK and all interpretation, writing and map production on the basis of geochemical and acoustic data were done with joint effort in Espoo and St. Petersburg. This report is a synthesis of three years of collaborative work between staffs of GTK and VSEGEI and is filling a gap in knowledge of the environmental situation of the sea and seafloor in the North-eastern Gulf of Finland.

THE QUATERNARY DEPOSITS OF THE EASTERN GULF OF FINLAND

by

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Henry Vallius², Elena Nesterova¹ and Vladimir Zhamoida¹

Spiridonov, M., Ryabchuk, D., Kotilainen, A., Vallius, H., Nesterova, E. & Zhamoida, V. 2007. The Quaternary deposits of the Eastern Gulf of Finland. *Geological Survey of Finland, Special Paper 45, 7–19, 12 figures and one appendix.*

The systematic geological survey carried out by the Russian Research Geological Institute (VSEGEI) during the period from 1984–2004 has enabled collection of data regarding the distribution, composition, structure, and thickness of the Quaternary deposits of the northern–western area of the Russian part of the Gulf of Finland. The main aim of this paper is to summarize these abundant data. The problems of the origin and correlation of the Quaternary deposits described on land and at the sea bottom are discussed.

Key words (Georef Thesaurus AGI): Marine geology, marine sediments, stratigraphy, grain size, mineral composition, heavy minerals, pollen analysis, Quaternary, Russian Federation, Baltic Sea, Gulf of Finland

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INTRODUCTION

The seafloor of the eastern Gulf of Finland is almost completely covered by Quaternary deposits. The importance of investigations of the Quaternary deposits within the study area is extremely high for several reasons. First of all, these deposits are the basis for different types of underwater constructions such as pipelines and cables, while at the same time they accumulate many kinds of pollutants. All mineral resources of economic interest, such as sand, gravel, or Fe–Mn concretions, in the sea floor of the study area are connected with the Quaternary deposits. New data on the Quaternary deposits of the eastern Gulf of Finland also allow extension of our knowledge about the paleogeography of the whole region and a greater understanding of the

processes of its development. The main aim of this paper is to summarize the numerous data concerning the structure, distribution, and lithology of the Quaternary sediments, which were obtained during a geological survey of the Russian part of the eastern Gulf of Finland adjacent to the Russian–Finnish border (Figure 1). In addition, Finnish marine geologists also collected a large amount of data and knowledge about the structure of some areas of the bottom of the Gulf of Finland. Therefore, comparison and harmonization of the methods, views, and outputs can make an important contribution to our knowledge of the geology of the Baltic Sea and allows production of joint map of the Quaternary deposits of the near border area of both countries.

METHODS

The structure of the Quaternary sediment sequence within the study area was investigated using an echo-sounding survey (about 2600 km). The sediments were sampled using grab-samplers (more than 1000 sampling sites including 632 stations in 1999–2000) and gravity-corers (more than 600 sampling sites, including 420 in 1999–2000) up to 3 meters long. The frequency of sampling was

about 1 station per 1–4 km². Detailed descriptions of the sediment cores were carried out on the ship. A portion of sediment samples from the cores was analyzed in VSEGEI laboratories using standard methods of grain-size analysis, optical mineralogy, X-ray diffractometry, and spectroscopy. For two cores, palynological investigations were carried out.

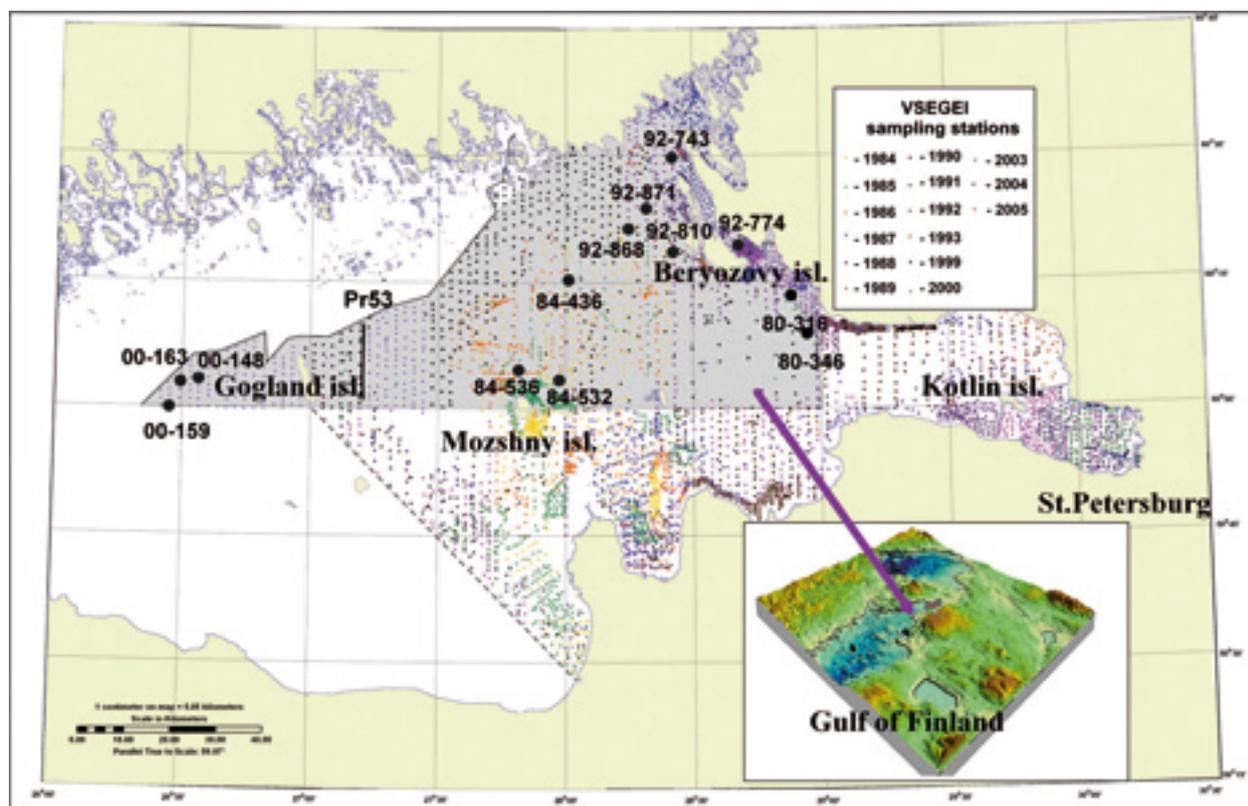


Figure 1. Map of sampling stations made by VSEGEI in 1984–2000. Shaded areas are described in the article.

RESULTS

Lithology and stratigraphy of the Quaternary deposits

Dense deposits interpreted as a glacial till form the lowermost part of the Quaternary sequence. Till is very well identified on the echo-sounding profiles of the gulf bottom (Figure 2), but it could be verified by coring in some locations only. Grain-size analyses of the till deposits show that they are practically unsorted. The brownish sandy-clays (clayey-sands) contain up to 15–20% of silt, while the quantity of coarse material (including boulders with traces of glacial striation) reaches 30%. In the coarse material debris, rapakivi granite predominates. The mineral association of till sediments includes quartz, feldspar, muscovite, and biotite. Illite, kaolinite, and chlorite are prevailing clay minerals.

Among the heavy minerals (1.3–1.6% of the sandy fraction), limonite and hematite (37.0–39.3% of the heavy mineral fraction), amphiboles (30.4–37.4%), epidote (11.0–12.0%), garnets (9.6–9.5%), and zircon (4.2–8.8%) are worth mention. As accessory minerals, sphene, rutile, leucoxene, and apatite can be observed. Sometimes authigenic carbonate aggregates occur.

In some areas, coarse- and medium-grained sands with well-rounded gravel and cobbles (up to 30–35%) form submarine risings (sunken oozes, kame terraces, and hills), and deltas are to be found, as well. These bottom relief forms can be interpreted as glaciofluvial deposits. The thickness of such deposits varies from 3–5 to 10–12 meters.

The next sedimentological unit is represented by glaciolacustrine deposits formed in the ice marginal lakes. In most sequences, till is covered by the rhythmic couplets of grey clays and brown silt layers (Figure 3). These deposits are very distinct in the echo-sounding profiles because of a laminated structure.

Facies of glaciolacustrine deposits change in a wide spectrum from thin-laminated clays to sandy clays with gravel and cobbles. The most widespread type of glaciolacustrine deposits consists of rhythmic, varved horizontal alteration of brown clays and grey silty layers. Clay layers are 2–5 times thicker than the silty ones (4–10 mm and 1–2 mm, respectively). The thickness of the layers and sand particle content decrease from the bottom of the unit to the top. At the lower part of the unit, sandy layers, gravel grains of crystalline rocks, and lenses of dry dense silt can be observed. Grain-size analyses

Core	99-T-305F	60° 00,491 N	27° 07,176 E
Description			
0.00 – 0.07			
At the surface remains of concretion layer. 0 – 7 cm – brown-grey unsorted (mainly middle-grained) sand without silty-clay. Some pebbles. Downward contact is sharp.			
0.07 – 0.50			
7 – 50 cm – varved horizontal alteration of brown clays (4–5 mm) and grey silts (2–3 mm). 33 – 34 cm – layer of badly sorted medium-fine grained sand, at 45 – 50 cm – a small boulder (5 cm in diameter).			
0.50 – 0.68			
50 – 68 cm – varved horizontal alteration of brown clays (5–6 mm) and grey silts (4–5 mm), with some sand particles and rare pebbles.			
99-305			

Core	99-T-409F	60° 10,782 N	27° 13,860 E
Description			
0.00 – 0.28			
At the surface – small diskoidal Fe-Mn concretions. 0 – 1 cm – brown grey unsorted sand (mainly fine-grained) with high water content. Lower contact is sharp.			
0.28 – 0.52			
1 – 28 cm – brownish grey dense varved alteration of brown clay (1–1.5 cm) and grey sandy-silt (2–3 mm) layers			
0.52 – 0.52			
28 – 52 cm – brownish grey dense varved alteration of brown clay (1–1.5 cm) and grey sandy-silt (2–3 mm) layers. At interval 30 cm – layer of coarse-grained badly sorted sand			
99-409			

Figure 3. Cores of varved clays of the marginal ice lakes.

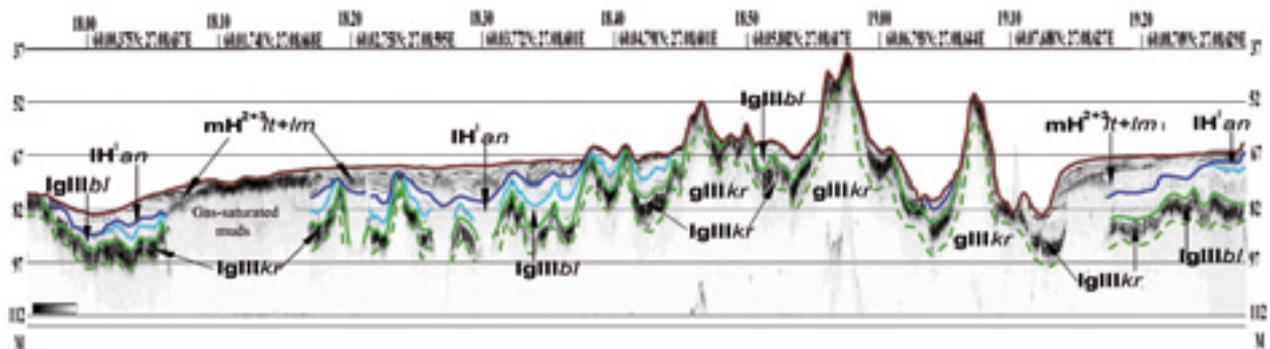


Figure 2. Echo-sounding profile across the sampled area (profile 53): $mH^{2+3}t+lm$ – Marine Litorina and Limnea silty-clayey muds; IH^{an} – Ancylus Lake clays; $IgIIIbl$ – Baltic Ice Lake deposits; $IgIIIkr$ – Glaciolacustrine deposits (varved clays) of the marginal ice lakes; $gIIIkr$ – Glacial deposits (till).

of varved clays show that the finer layers consist of clay (median grain-size (Md) varies from 0.0008 mm to 0.004 mm), while the coarser layers are silt. The average content of clay particles (less than 0.005 mm) is about 50%; silt fraction (0.05–0.005 mm) varies from 10% to 30%; and sand amounts vary by more than 20% (Figure 4).

The main components of the sandy fraction of the lake–glacial deposits are quartz (75–89%), feldspar (10–20%), and fragments of crystalline rocks (up to 3%). The predominant clay minerals are illite (60–80%), kaolinite (10–20%), and chlorite (9–15%).

The heavy mineral content in these sediments is very low ($n \times 10^{-2}\%$). A major part of the heavy minerals (30–100%) is made up of authigenic barite concretions. The allogenic heavy mineral association of the sandy fraction of varved clays consists of amphiboles (30–70% of allogenic minerals in the 0.1–0.25 mm fraction and 25–50% in the 0.01–0.1 mm fraction); epidote (10–20%); garnets (5–30%), biotite (0–60%); zircon (up to 10%); and ilmenite (up to 4%). As accessory minerals, sphene, apatite, tourmaline, and pyroxene can be observed.

The amount of pollen of periglacial flora (*Betula nana*+*Betula* sect *Fruticosae*, *Alnaster fruticosus*, *Ephedra*, *Selinella selaginoides*) is low in these sediments (Raikova 1989). There are some pollen of *Artemisia* and *Chenopodiaceae*. Additionally, a lot of redeposited pollen of alder, hazel, and other deciduous trees can be found.

The next unit of sediments is characterized by essential transformation of its structure from the bottom of the layer to its upper part. At the lower part of the unit, there is alternation of brown clays and grey silty layers (the thickness of the rhythm (couplet) is 3–8 mm). This part of the unit looks like varved clay but is characterized by lower density. Silty layers become less distinct and transform into silt lenses toward the upper part of the succession. Clays of very homogeneous grain-size composition form the upper part of the unit. Characteristic features of this part of the unit are the alternating brown, red-brown, and grey bands (Figure 5). The whole unit is interpreted as Baltic Ice Lake deposits.

The grain-size fraction of these sediments is the finest of all Quaternary sequences and represented by clays (Md = 0.0005–0.005 mm) with 80–95% of particles less than 0.01 mm and 40–60% of particles less than 0.001 mm. The percentage of fine fractions increases from the bottom of the horizon to its top (Figure 6).

The predominant clay minerals are illite (70–85%), kaolinite (5–20%), and chlorite (7–15%). The major allogenic minerals of the sandy fraction

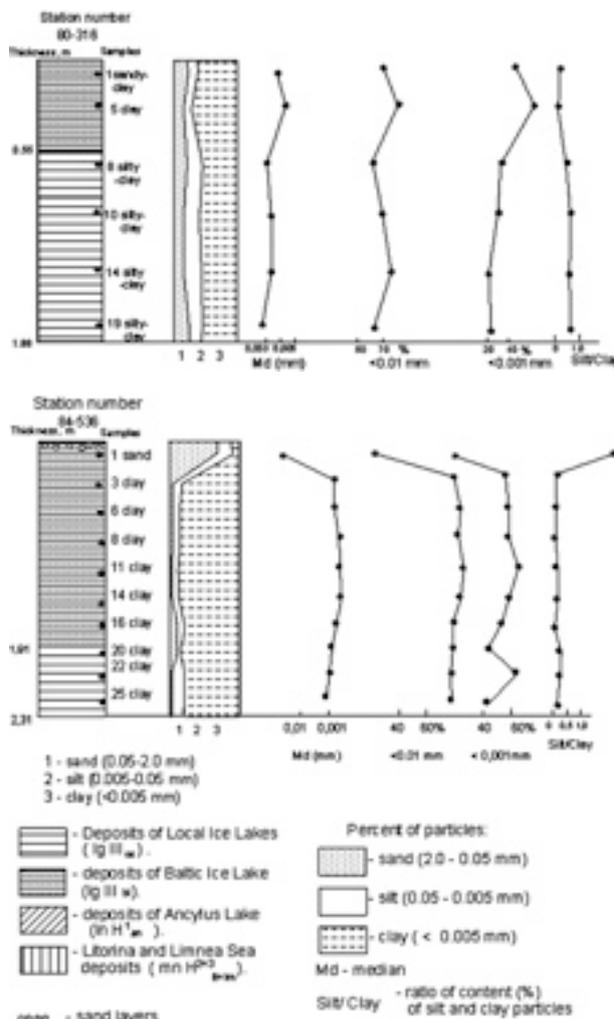


Figure 4. Grain-size parameters of the marginal ice lake deposits.

are quartz (70–85%), feldspar (15–30%), and fragments of crystalline rocks (up to 6%). The amount of heavy minerals reaches 0.8–1.2% of the sandy fraction, reaching in some samples up to 3–20%. The relatively high quantity of heavy minerals is caused by an increasing amount of authigenic barite micro-concretions. In the upper part of the sequence, rare pyrite micro-concretions also can be observed. Among the allogenic heavy minerals, amphiboles (25–45%), epidote (0–20%), and garnets (6–20%) predominate. Additionally, there are some zircon, sphene, apatite, and pyroxene grains.

The Baltic Ice Lake unit is characterized by two pollen complexes. In the lower part of the unit tree pollens dominate (*Pinus sylvestris*, *Betula*, sometimes *Picea*). Among the herbs there is pollen of *Artemisia*, *Cyperaceae*, or *Chenopodiaceae*. In the upper part of the horizon, another complex of tree pollens was discovered (*Betula nana*, *B. sect. Fruticosae*, *B. sect. Albae*, and *Alnus*). These pollens are typical for Alleröd and Younger Dryas chronozones.

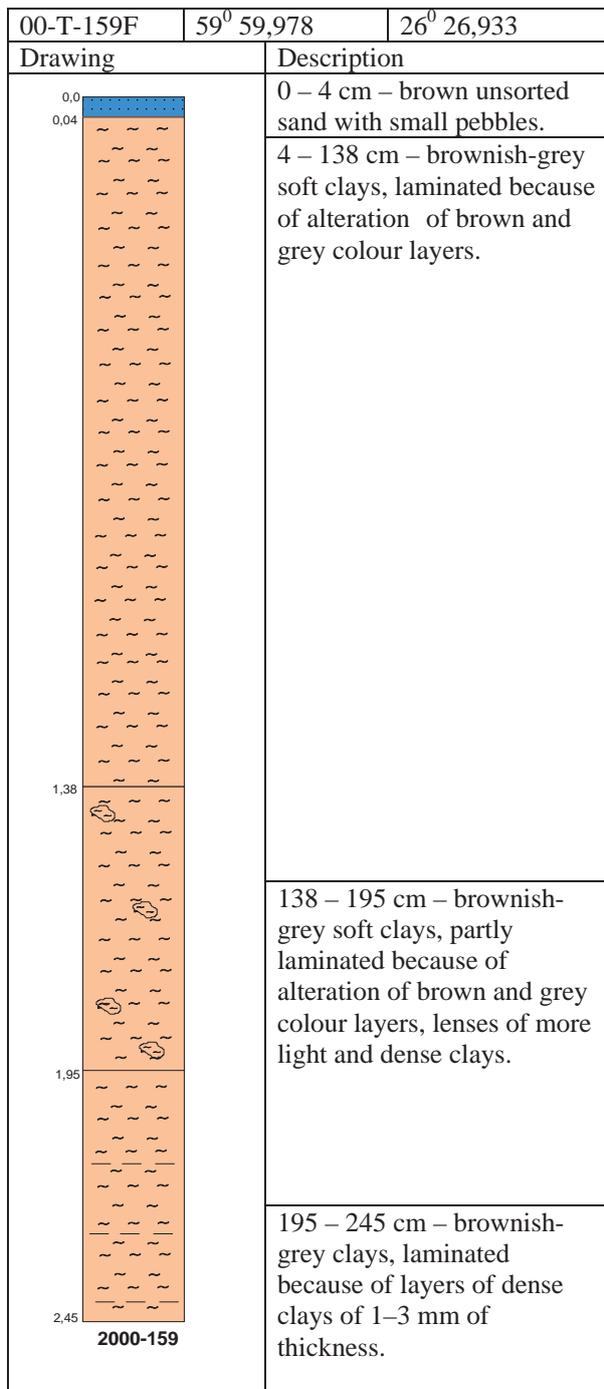


Figure 5. Typical core of Baltic Ice Lake deposits.

The next unit consists of grey (brownish-grey) soft clays and is interpreted and named as Ancylus Lake sediments. There are no reliable features for distinguishing Yoldia and Ancylus sediments in the eastern Gulf of Finland. Therefore, sediments deposited during the Yoldia phase of the Baltic Sea might also be included in this unit. These sediments are characterized by the presence of black hydrotroilite inclusions, which group into "chains" (0.1–1.5 cm thick) and form so-called "hydrotroilite horizons," enriched with these inclusions. An-

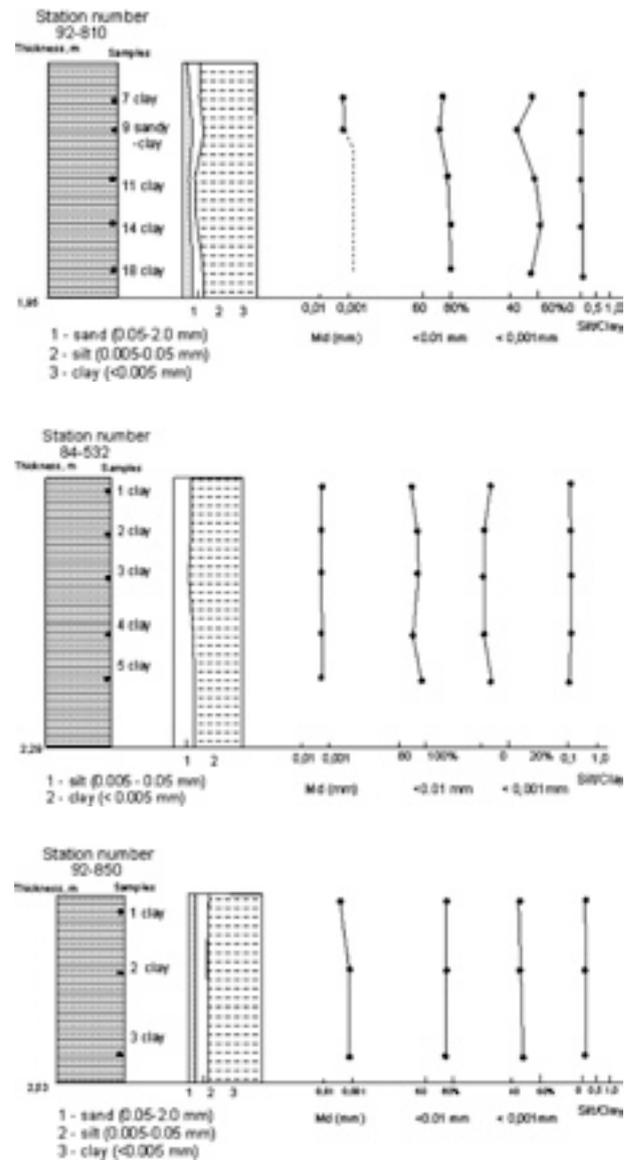


Figure 6. Grain-size parameters of the Baltic Ice Lake deposits.

other important feature of these sediments is the great amount of very small (less than 1 mm in diameter) spots and microlenses of silt (Figure 7). In acoustic profiles, it is usually difficult to distinguish confidently the layer of Ancylus sediments from overlying Litorina marine mud.

The sediments of this unit are characterized by rather high content of silty particles (up to 25%). Md of these sediments is about 0.01 mm. The quantity of particles less than 0.01 mm in diameter varies from 40% to 70%, while the share of particles of

size less than 0.001 mm is 30%. Grain-size parameters are much more variable in comparison to the Baltic Ice Lake deposits (Figure 8).

The mineral association of this unit is very similar to the Baltic Ice Lake unit. Clay minerals are represented by illite (75–80%), kaolinite (5–18%), and chlorite (5–10%). Allogenic minerals of the sandy fraction include quartz (75–80%), feldspar (10–20%), and fragments of crystalline rocks (up to 8%).

The sediments of Ancylyus Lake are characterized by a high amount of heavy minerals (20–25% of the grain-size fraction 0.1–0.25 mm and 10–12% of the grain-size fraction 0.01–0.1 mm), represented mainly by authigenic sulphides. The presence of hydrotroilite (an amorphous monosulphide of Fe) is one of the most important diagnostic features for these sediments. In the layers of so-called "hydrotroilite horizons," its content is about 100% of the heavy minerals fraction. Some micro-concretions of pyrite can be detected in the upper part of the unit, which is often represented by blue-gray clays up to 10 cm thick.

The allogenic heavy mineral association of the sandy fraction includes amphiboles (30–50% of allogenic minerals in the grain-size fraction 0.1–0.25 mm; and 40–60% in the grain-size fraction 0.01–0.1 mm) and garnets (10–20%). In the fine fraction, there is up to 30% of epidote, and in the coarse fraction, biotite (up to 10%) and ilmenite (10–25%).

In the palynological spectrum, tree pollens dominate, birch in the lower part of the interval and pine in the upper part; additionally, some particles of deciduous tree pollens can be found. Among the herbs, Cyperaceae and Artemisia prevail, evidence of birch–pine forests with irregular herb cover. Such conditions were very common at the end of the Dryas and beginning of the Boreal.

In the erosion zones located on the tops and slopes of submarine risings, islands and coastal slopes of mainland sands and gravel sediments are observed. In sedimentation basins, silty-clayey mud was formed during the late Holocene. Both facial varieties are interpreted as marine sediments of Litorina and Post-Litorina seas, which usually are interpreted as one unit.

Marine mud deposits are normally represented by olive-grey, silty clayey mud with a high content of black dispersed organic material. Depending on the quantity and distribution of organic matter, these sediments can have a spotted or laminated texture. In the anoxic conditions of the deep basins, mud sediments have a black color and sometimes high gas content (H₂S) (Figure 9). In acoustic profiles, this clayey mud is usually well identified by the laminated structure and its position within depressions of bottom relief. However, if the gas con-

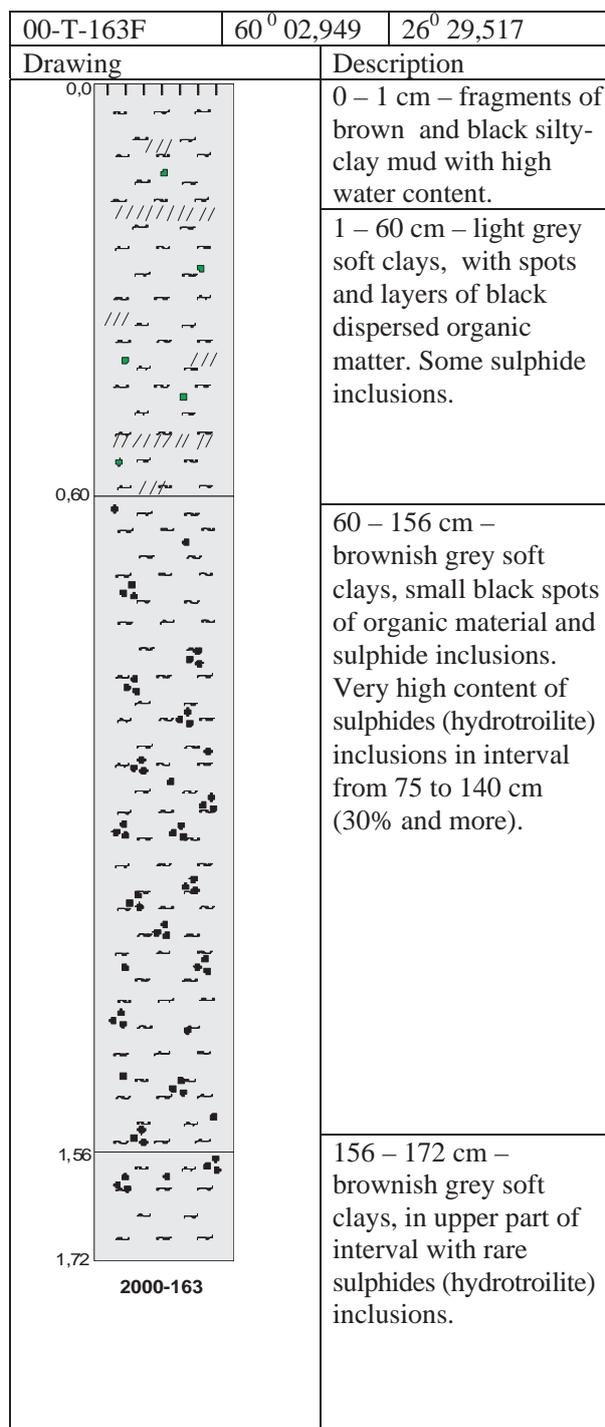


Figure 7. Core of Ancylyus Lake deposits.

tent in sediment is high, it might form an acoustically impenetrable horizon in the seafloor.

Grain-size distributions of these sediments are variable and correspond to changes of hydrodynamic conditions; transgression and regression phases alternate. Clay and silt fractions dominate, but in some cases the mud has relatively high sand (particles) content. Median-size and other grain-size parameters vary from the bottom of the horizon to the

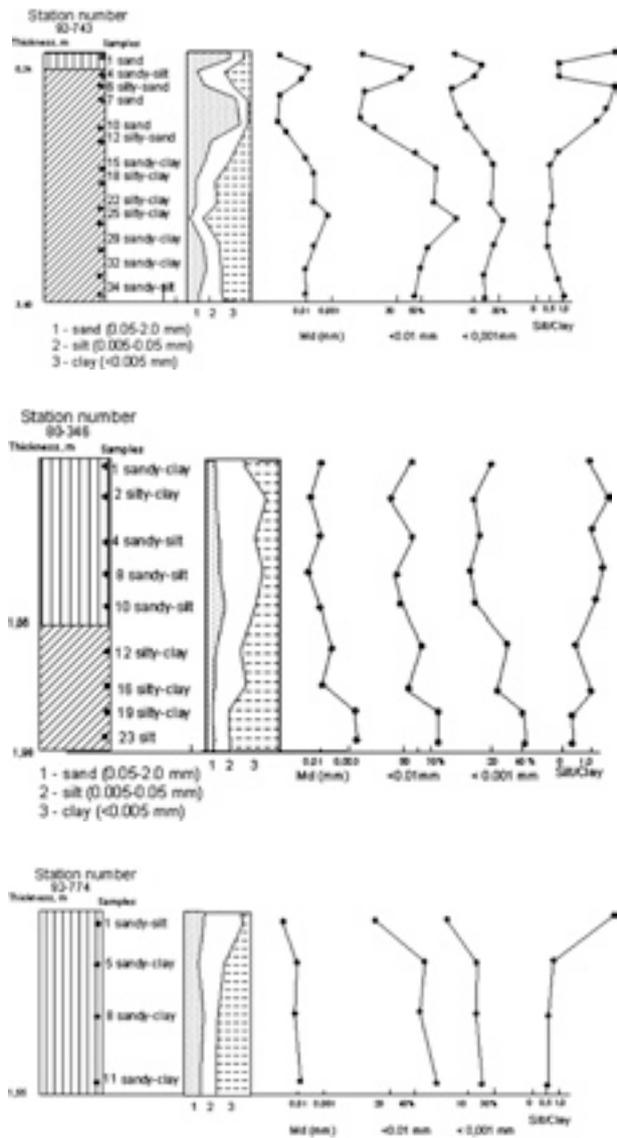


Figure 8. Grain-size parameters of Ancylus Lake deposits.

top. Md changes from 0.001 mm to 0.05 mm, the weight of the fraction less than 0.01 mm in diameter varies from 80% to 30%, and the fraction less than 0.001 mm in diameter varies from 40% to 10% (Figure 10).

The clay mineral association includes illite (65–82%), kaolinite (10–20%), and chlorite (5–10%). Terrigenous minerals are represented by quartz (75–90%), feldspar (10–20%), and fragments of crystalline rocks (up to 10%). Weight-percent of the heavy minerals is 0.3–0.7%, and the main authigenic

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Drawing		Description	
0.0		0 – 1 cm – brown silty-clay mud with high water content.	
0.01		1 – 88 cm – olive-grey silty-clay, partly laminated because of dark and light layers alteration	
0.88		88 – 134 cm – dark olive-grey silty-clay, partly laminated because of dark and light layers alteration. Thickness of black layers is 1–2 mm.	
1.34		134 – 154 cm – dark olive-grey silty-clay without lamination.	
1.54		154 – 201 cm – dark dense olive-grey silty-clay, partly laminated because of dark and light layers alteration. Thickness of black layers is 1–2 mm.	
2.01			
2000-148			

Figure 9. Core of Litorina Sea deposits.

mineral is pyrite (20–70% of all heavy mineral weight). The allogenic heavy mineral association is similar: amphiboles (50–75% of allogenic minerals in the grain-size fraction 0.1–0.25 mm; 40–55% in the grain-size fraction 0.01–0.1 mm), epidote (5–15% of allogenic minerals in the grain-size fraction 0.1–0.25 mm; 15–20% in the grain-size fraction 0.01–0.1 mm), biotite (10–20%), and ilmenite (up to 15%). As accessory minerals, zircon, apatite, sphene, muscovite, rutile, aegirine, and leucoxene can be found.

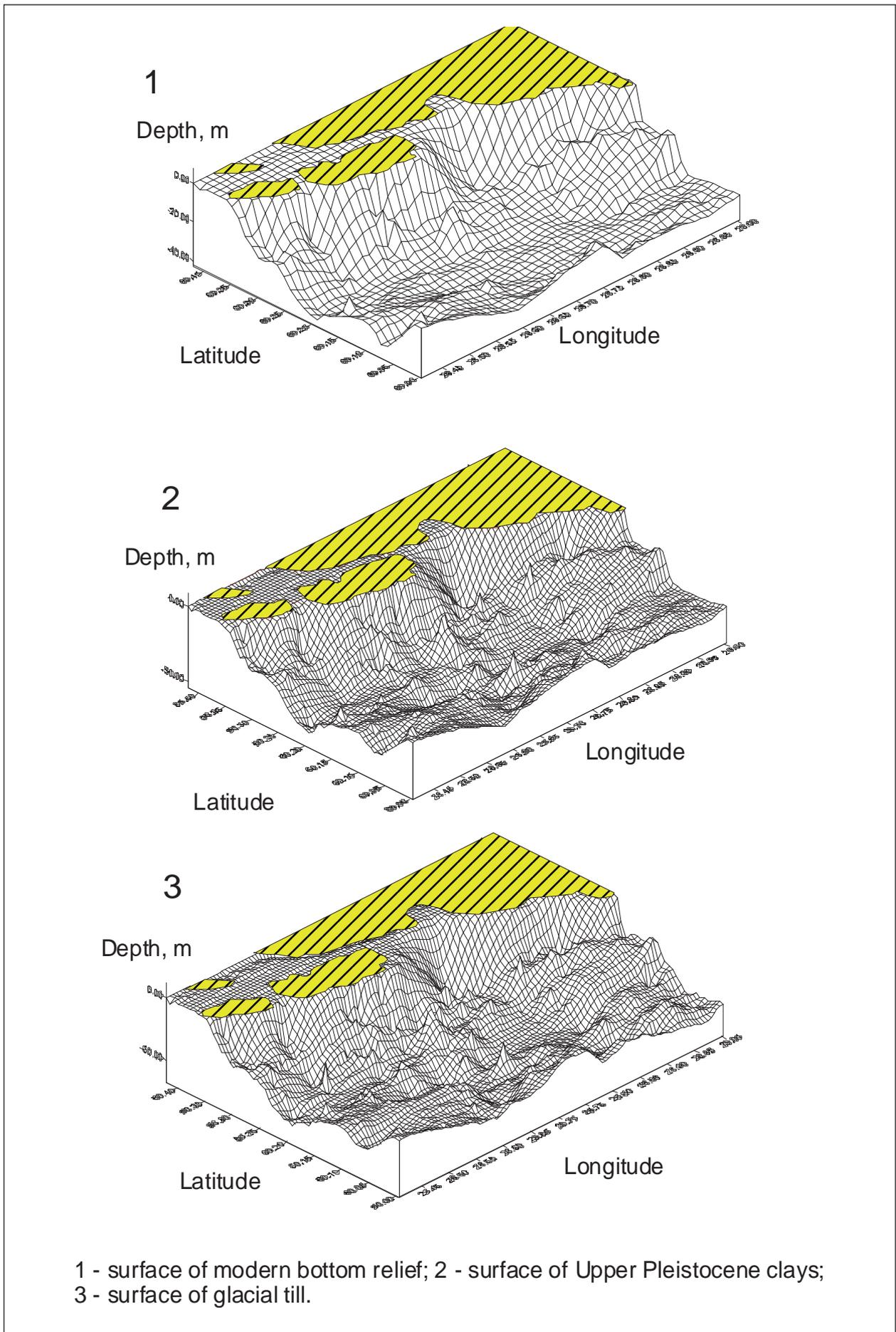


Figure 11. Evolution of the bottom relief during Upper Pleistocene–Holocene. Area to the south of Beryozovy Island.

varies from 0 to 70 meters, and its thickness varies in a range of 3–10 meters.

The Holocene sediments usually have a thickness of about 1–2 meters, but in the main sedimentation basins, their thickness can reach 20–25 meters.

The Ancylus Lake unit is the first clearly established sedimentary unit of the Holocene sequence within the investigated area. These sediments are found mainly in the basins of modern mud deposition underlying Litorina Sea sediments and outcropping at the slopes of these basins. Their thickness is usually 1–3 meters.

Marine sediments (Litorina and Limnea sea) of wave activity origin are represented by sands, which cover the tops of small submarine risings and the surface of the near-shore zone of Gogland Island at depths less than 15 meters.

Marine mud sediments have formed in the bottom depressions through active hydrodynamic influence. Their thickness reaches up to 6–8 m. Stable silty-clay mud accumulation in this part of the Gulf takes place in local basins, usually deeper than 30 m.

Samples of correlations of the cores are shown in Figure 12.

DISCUSSION: ORIGIN AND CORRELATION OF THE QUATERNARY DEPOSITS

The discovered units of submarine sediments can be correlated with Quaternary deposits on land, which have a long history of investigation within the area around St. Petersburg, including Karelian Isthmus (Malyasova & Spiridonova 1965; Jinoridze & Kleimenova 1965; Serebryanny & Raukas 1967), as well as with the Quaternary sequence of the western part of the Gulf of Finland and Baltic proper (Heinsalu et al. 2000; Ignatius et al. 1981; Repechka 2001; Emelyanov 1995).

The investigated area has undergone several glaciations during the Late Pliocene and Pleistocene; thus, the sediments formed during interglacial intervals have mainly been destroyed. The oldest Quaternary deposits exposed in the bottom of the Gulf of Finland were formed during the last stage of the late Weichselian glaciation. At the same time, there are arguments suggesting the possibility of the occurrence of layers of Quaternary deposits in the buried paleovalleys (Auslender et al. 2002).

On land, the glacial till deposits have been studied by drilling at many places. Its age is determined as being of the Luga stage of the Weichselian glaciation (Pandivera) (Spiridonov et al. 1988). Investigations of the Quaternary deposits within the Lahta depression (Usikova et al. 1963) and in valleys of the rivers Neva and Mga (Usikova & Malyasova 1965; Usikova et al. 1967) suggest the division of the horizon into two layers and allowed extraction of a so-called Neva stage till (Palivera till), with layers of glaciolacustrine and glacio-fluvial deposits between two till horizons. Comparison of the echo-sounding profiles with the land drilling data provides the basis for the assumption that these deposits have an unsteady character (Usikova et al. 1967; Krasnov 1995). However, there is still no real

evidence of such deposits in the bottom of the Gulf of Finland.

Glaciolacustrine varved deposits have been formed in the local ice-dammed lakes, which existed near the ice-sheet margin. Stratigraphic identification of these deposits (as Neva stage and Ohta interstadial) are based on palynological analyses (Spiridonova 1983) and are determined as Younger Dryas–Alleröd (Spiridonov et al. 1988).

As a result of the melting of the ice sheet, the water level rose and the local ice lakes near the ice-sheet margin were united to form the Baltic Ice Lake. There is only one ^{14}C -dating of the Baltic Ice Lake deposits from the Russian part of the Gulf (in the Neva Bay), where it is represented by laminae of peat interlayered between thinly laminated silts and fine sands. It was analyzed in the laboratory of St. Petersburg University, and the age was defined as 11050 ± 760 calendar years BP, which probably corresponds to Alleröd (Auslender, 2002). In the land sections of the Baltic Ice Lake sediments, salt and brackish water diatoms (*Thalassiosira gravida* Cl. and *Diploneis smithii f. rhombica* Mer.) were found in the Karelian Isthmus, at Vasilievsky island (St. Petersburg), near the Neva lowland, and in Privetninskoye village (Jinoridze & Kleimenova 1965; Usikova et al. 1963; 1967). But the problem of increasing salinity during the Baltic Ice Lake stage is open to discussion (Vyshnevskaya & Kleimenova 1970; Kvasov et al. 1970). Kvasov (1979); however, it clearly demonstrates that the so-called I-st Yoldia Sea never existed in the outskirts of the eastern Gulf of Finland (Kvasov 1979).

The Holocene deposits are lacustrine, and marine sediments formed since the time of ice-sheet recession from Second Salpausselka zone. ^{14}C -datings from buried peat near Gorelovo village show

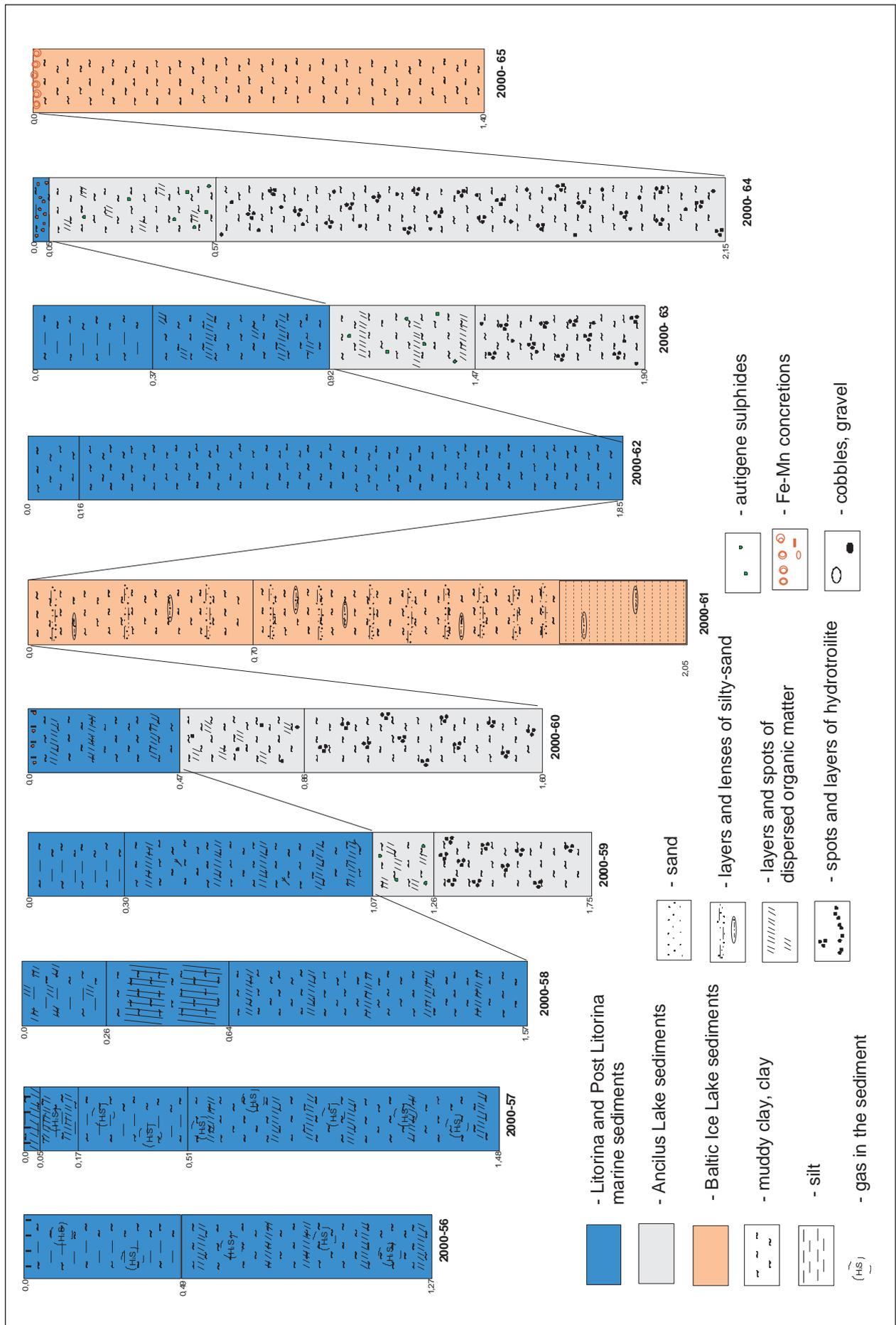


Figure 12. Sample of correlation of the cores.

that the boundary between the Baltic Ice Lake deposits and the Holocene deposits lies in the interval from 9600–9800 calendar years BP (Malakhovsky et al. 1969). But V. G. Auslender et al. (2002) proposed that an age of 10200 calendar years BP is more reliable. The genesis of the Holocene sediments is connected with the lake and marine environment of the Postglacial Baltic. It is possible to distinguish some lithological–stratigraphical units of Holocene sediments formed during several phases of the Baltic Sea development: these include the Yoldia Sea and Ancylus Lake (Preboreal), Litorina Sea (Atlantic), Limnea Sea (Subboreal), and the modern Baltic Sea (since the Subatlantic time).

Deposits of the Yoldia Sea can exist in the investigated area only as small fragments. The key section of the Yoldia Sea deposits on land was discovered at the Lahta depression (Biske 1963; Usikova et al. 1963), the Primorsk area and the center of St. Petersburg (Znamenskaya & Theremisina 1974), and in the Vyborg area (Vishnevskaya & Kleimenova 1970). In the section near Vyborg, the quantity of brackish water diatoms reached 80% (Vishnevskaya & Kleimenova 1970). On the other hand, in later publications by the same authors (Dzhinoridze 1992, Kleimenova & Vishnevskaya 1992), the eastern part of Yoldia Sea was characterized by freshwater conditions. It is probable that Yoldia deposits cannot be found in the Holocene sequence because of the small thickness and lithological homogeneity, and thus they can be extracted only by diatomic data. According to detailed studies of the Yoldia Sea (shorelines, litho- and biostratigraphy, and ecological conditions) carried out by A. Raukas (1994), the area of our investigation belongs to the outmost eastern part of the

Yoldia Sea. The shoreline was located between Cape Stirsudden and Cape Shepelevo. Thus, that part of the sea could have been practically fresh. Unfortunately, during our study, diatomic analyses of Pleistocene and early Holocene sediments were not made. Thus, no evidence of seawater intrusion into the Baltic Ice Lake was discovered in the bottom sediments of the Gulf of Finland. However, in the western Gulf of Finland, the brackish phase of the Yoldia Sea has been documented (Heinsalu et al. 2000).

Ancylus Lake sediments are the first clearly established sediment unit of the Holocene sequence. Diatoms are very rare in Ancylus Lake sediments in the investigated area, which can be an indicator of the relatively deep-water conditions of the lake. In the land sections (near Chernaya River and Lahta Depression), the end of Ancylus regression dates as 8180 ± 160 and 8190 ± 70 yrs BP (Auslender et al. 2002).

Marine Litorina deposits sampled in the borehole of the northern coast of the gulf (near Privetninskoye village) were dated with the ^{14}C -method. These analyses showed that the age of these sediments is 4620 ± 60 yrs BP, which after calibration corresponds to an interval of 5000–5300 calendar years BP (Auslender et al. 2002).

Subdivision of the Limnea Sea deposits from the marine sequence is very difficult, and in the investigated area, such studies were not carried out. However, there are data suggesting that these deposits have been discovered in the modern northern underwater coastal slope of the gulf, where they form a narrow (0.1–0.6 km) ribbon of sands, sandy-clay, and clay deposits up to 3.6 m thick (Auslender et al. 2002).

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THE INFLUENCE OF FERROMANGANESE CONCRETIONS-FORMING PROCESSES IN THE EASTERN GULF OF FINLAND ON THE MARINE ENVIRONMENT

by

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and Daria Ryabchuk

Zhamoida, V., Grigoriev, A., Gruzdov, K. & Ryabchuk, D. 2007. The influence of ferromanganese concretions-forming processes in the eastern Gulf of Finland on the marine environment. The Quaternary deposits of the Eastern Gulf of Finland. *Geological Survey of Finland, Special Paper 45, 21–32, 10 figures and 5 tables.*

We investigated the possible influence of the processes of ferromanganese concretion formation on environmental conditions in the eastern Gulf of Finland based on field observations of concretion occurrence and numerous chemical and isotopic analyses. We found that concretions are not only the principle concentrators of Mn and Fe, as well as PO₄ – one of the main pollutants in the region, but they also concentrate some radioactive elements (e.g., ²²⁶Ra) and trace elements (primarily As). Some new data were obtained using ²¹⁰Pb and regarding the rate of spheroidal concretions radial growth in the range 0.013–0.042 mm/yr. The concretion fields situated in the border area between oxidized and reduced conditions in the sediments appear to play an important role as a buffer system, partially smoothing changes in redox conditions in the near-bottom and pore waters. Some indirect evidence suggests dependence on the processes of concretion growth and biological activity to achieve this role.

Key words (Georef Thesaurus AGI): Marine geology, marine sediments, modules, ferromanganese concretions, chemical composition, radioactive isotopes, growth rates, marine environment, Russian Federation, Baltic Sea, Gulf of Finland

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INTRODUCTION

The processes of ferromanganese concretion growth are extremely active in the eastern Gulf of Finland. The concretions are found at 30% of the sampling sites in the Russian part of the gulf at depths from 3 to 100 m, where the frequency of sampling was about 1 station per 1–4 km² (Butylin & Zhamoida 1989, Zhamoida et al. 2004). In most of this area, only occasional concretions were found; however, in some places, the abundance of concretions reaches 50 kg/m² (Figure 1). The total area of the fields abundant in concretions make up 10% of the Russian part of the SAMAGOL project area (Figure 2). The distribution and composition of the various morphological types of concretions of

the eastern Gulf of Finland appear to be related to the bottom relief and sediment characteristics (Zhamoida et al. 1996; Zhamoida et al. 2004). The most abundant fields are situated on the margins of basins containing recent silty-clayey mud (Figure 3). Accordingly, the water depth at which these fields occur depends on the position of the silty-clayey mud zones with which they are associated. The underlying sediments are represented mainly by early Holocene lacustrine or the upper part of the limno-glacial clays (for a detailed description of the sediments, see Spiridonov et al. in this volume). Rarely, the concretions are found on Holocene marine silty-clayey muds.

MATERIALS AND METHODS

Sampling was carried out mainly during geological surveys of the Russian sector of the Gulf of Finland in 1984–2000 from different Russian research vessels. The concretions in the Finnish part of the Gulf of Finland were sampled during a 2004 cruise from the research vessel *Geola* as part of the SAMAGOL project. Samples were collected using different types of grab samplers and box-corers. The concretions and crusts were separated from the hosted sediments onboard. The samples for bulk analysis were then dried at 105–110°C and ground

prior to analysis. More than 250 samples of different morphological types of concretions were analyzed.

The major elements were analyzed by wet chemistry methods and X-ray fluorescence spectroscopy at the VSEGEI laboratories. Trace elements were determined by atomic emission and atomic absorption spectrometry.

The natural (²²⁶Ra, ²³²Th, ⁴⁰K) and anthropogenic (¹³⁷Cs) radionuclides in the concretions and crusts were determined in VSEGEI using a



Figure 1. Underwater photograph of an abundant concretion field on the sea floor of the eastern Gulf of Finland.

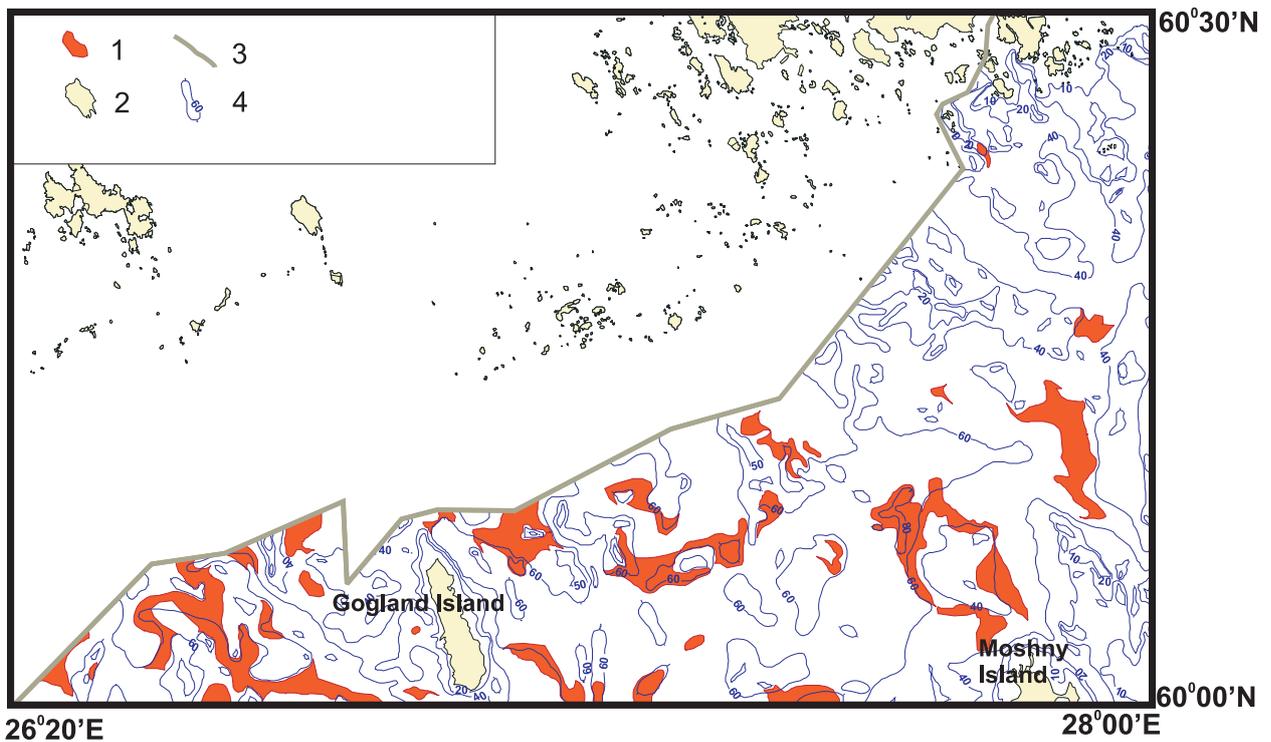


Figure 2. Schematic map of relatively abundant concretion fields in the Russian part of the SAMAGOL project area in the eastern Gulf of Finland: 1 = concretion fields; 2 = islands; 3 = Russian–Finnish borderline; 4 = isobath.

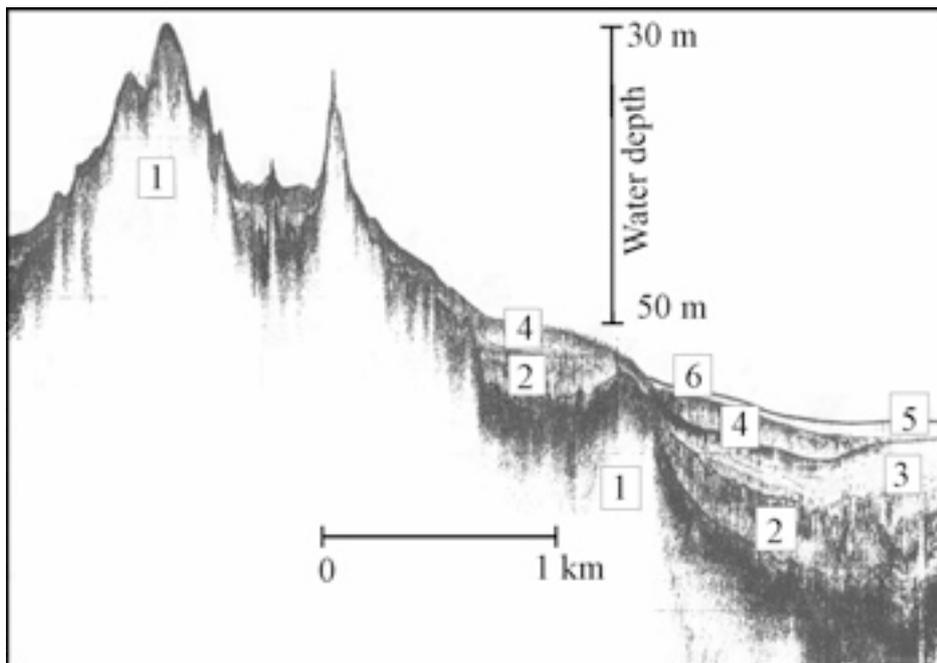


Figure 3. Geo-acoustic section across the concretion field near Moshny Island: 1 = glacial till; 2 = limno-glacial deposits (lower part, mainly varved clays); 3 = limno-glacial deposits (upper part); 4 = lacustrine deposits; 5 = recent marine muds; 6 = abundant concretion field.

RADEK gamma-ray scintillation spectrometer. The scintillation detector contained an 80- \times -80 mm NaI(Tl) crystal. The resolution of the detector was better than 8%–10% on the ^{137}Cs line at 661.7 keV. Minimum measuring activity was 37 Bq for ^{40}K , 2.8 Bq for ^{137}Cs , 8.2 Bq for ^{226}Ra , 5.6 Bq for ^{232}Th , and 3.8 Bq for ^{60}Co .

Analysis of ^{210}Pb was completed at the Center of Isotopic Research of VSEGEI. Extraction of Pb was executed using heat-shrinkage Teflon (Bolender)

columns filled with Sr-Spec Eichrom resin (Eichrom Europe, France). Output of Pb was about 99%. Eight milliliters of $\text{Pb}(\text{NO}_3)_2$ solution were added to 12 ml of liquid scintillator Optiphase HiSafe 3. The spectra of ^{210}Pb and daughter element decay were detected with a liquid-scintillation spectrometer, the Quantulus 1220. The content of ^{210}Pb was calculated by the beta-spectrum of ^{210}Bi . At the moment of analysis, ^{210}Pb and ^{210}Bi were in radioactive equilibrium.

RESULTS AND DISCUSSION

Ferromanganese concretions as a natural ionic trap

According to data from geological mapping at the 1:200 000 scale carried out by VSEGEI, the total calculated area of the Mn-rich spheroidal concretions within the boundaries of the concretion-rich fields (with an average abundance of about 20–30 kg/m²) situated in the Russian sector of the Gulf of Finland is about 300 km². The total weight of ore material is estimated to be about 6 million tonnes or about 1 million tonnes of manganese metal (Zhamoïda et al. 1996). The content of the main ore elements for six types of concretions and one type of crust is shown in Table 1. According to the newest data based on the large-scale investigations carried out by the mining company PetroTrans, the total weight of ore material in the Russian sector of the Gulf of Finland possibly exceeds 11 million tonnes (Rogov et al. 2005) or about 2 million tonnes of manganese metal. The volume of total annual riverine load of Mn to the Gulf of Finland varies from 728 tonnes (Kondratyev et al. 1997) to 338 tonnes (Gudelis & Emelyanov, 1976). Thus, ferromanganese concretions of the eastern Gulf of Finland accumulated Mn metal via riverine input to the gulf for 1350 to 2700 years, and the total amount of Mn accumulated in concretions is comparable with riverine input of this element to the gulf.

Average concentrations of P₂O₅ (Table 1), one of the main pollutants in the Gulf of Finland, in ferromanganese concretions are 10 times higher than for the bottom sediments (Gudelis & Emelyanov 1976).

Under natural conditions, the contents of most minor heavy metals in the shallow-water ferromanganese concretions do not, as a rule, exceed the level of regional background concentrations in the bottom sediments (Zhamoïda et al. 2004). But because of the increasing input of anthropogenically derived

toxic metals (e.g., Pb, Zn, and Cu) to the Gulf of Finland in the 20th century, the content levels of these elements in the surface micro-layers of growing flat concretions and in the smaller or younger concretions have increased by 3–5 times (Figure 4). In addition, concretions sampled at 90 sites in the northeastern part of the Gulf of Finland are characterized by high concentrations of As. The median value of As concentration in these concretions is 185 ppm, with a standard deviation of 49 ppm. This value is about 20 times higher than the background As concentration (8 ppm) in silty-clayey sediments of this area (Gudelis & Emelyanov, 1976). Consequently, it is reasonable to assume a very high capacity of the concretions to accumulate As.

The ferromanganese concretions are also enriched in some radioactive elements (Grigorïev et al. 2004). For example, the concentration of ²²⁶Ra in the concretions and crusts of the Russian part of the Gulf of Finland are much higher than in all types of bottom sediments, regardless of concretion morphology (Tables 2 and 3). The concentration of ²²⁶Ra in concretions and crusts from the relatively "deep" concretion fields situated at the edge of

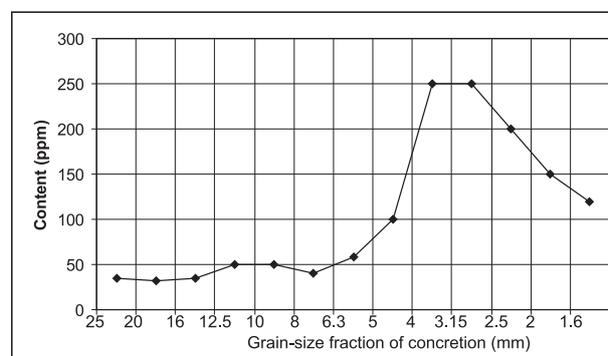


Figure 4. Dependence of Pb content and the size of the spheroidal concretions taken from one grab sample near Moshny Island in the eastern Gulf of Finland.

Table 1. Average concentrations (Av.) of major ore elements in the different types of concretions from the Gulf of Finland. All analyses in %, σ = standard deviation, N = number of samples.

Morphology of concretions	MnO + MnO ₂		Fe ₂ O ₃		P ₂ O ₅		N
	Av.	σ	Av.	σ	Av.	σ	
1. Buckshot concretions	13.1	5.9	31.2	9.3	4.4	1.5	13
2. Spheroidal concretions	24.2	9.4	23.1	7.0	2.9	0.8	109
3. Concretions of irregular forms	15.7	9.2	30.7	10.2	4.2	1.6	26
4. Discoidal concretions	8.9	4.7	45.3	12.3	4.2	1.2	58
5. Thin rings around the erratic nuclei	17.5	9.8	31.7	12.5	2.9	1.1	13
6. Large flat concretions or crusts	31.0	5.8	22.5	4.4	2.7	0.8	9
7. Crusts incorporating clastic material	8.2	9.5	25.8	10.1	2.7	1.5	18
All types	17.8	10.8	30.2	12.9	3.4	1.3	246

Table 2. Median and standard deviation of activity of gamma-emitting radioisotopes (Bq/kg) in the main types of ferromanganese concretions and crusts in the Gulf of Finland. A_b is the back-ground median value, σ is the standard deviation, N is the number of samples.

Type of concretion	N	Isotope							
		^{226}Ra		^{232}Th		^{40}K		^{137}Cs	
		A_b	σ	A_b	σ	A_b	σ	A_b	σ
Buckshot concretions	17	310	87	51	20	416	85	122	93
Spheroidal concretions	37	417	329	45	16	352	129	65	32
Concretions of irregular forms	8	275	104	38	10	437	125	36	8
Discoidal concretions	19	231	94	45	16	354	187	44	19
Concentric rings around erratic nuclei	14	265	66	76	34	719	42	47	32
Large flat concretions or crusts without erratic nuclei	7	283	96	45	27	667	71	84	63
Irregular crusts incorporating large amounts of clastic material	5	300	120	61	5	725	231	92	42

Table 3. Median and standard deviation of activity of gamma-emitting radioisotopes (Bq/kg) in bottom sediments from the Gulf of Finland. A_b is the back-ground median value, σ is the standard deviation, N is the number of samples, (I) – area of Chernobyl fall-out zone; (II) – area outside Chernobyl fall-out zone.

Type of sediments	Isotope								N
	^{226}Ra		^{232}Th		^{40}K		^{137}Cs		
	A_b	σ	A_b	σ	A_b	σ	A_b	σ	
Silty-clayey mud	52	31	75	34	805	303	560 (I) 84 (II)	458 (I) 57 (II)	221
Silty sands, sandy silts, sandy clays	49	35	30	14	678	203	61	39	34
Sands	27	15	33	14	968	210	27	17	89
Coarse-grained sands with gravel and pebbles	28	22	35	5	1005	289	21	22	19

areas of silty-clayey mud sedimentation is not much higher than in concretions of the shallow-water fields where silty clay is absent. This observation supports the idea that concretions take up most of the ^{226}Ra directly from the water column, without involvement of prior sorption on clay particles. The process of accumulation of ^{137}Cs in the concretions differs fundamentally from that of ^{226}Ra . The level of ^{137}Cs accumulation in the concretions depends mainly on the composition of the hosted sediments and the amount of clay minerals directly incorporated into the concretions. Analysis of spheroidal concretions sampled in the Finnish part of the Gulf

of Finland showed similar regularities in the distribution of radioactive elements in spheroidal concretions (Table 4, Figure 5). It is possible to note some increase in ^{226}Ra and ^{40}K activities and a decrease in ^{137}Cs .

Table 4. Activity of gamma-emitting radioisotopes (Bq/kg) in the ferromanganese concretions sampled in the Finnish part of the Gulf of Finland.

Type of concretion	Site	Isotope			
		^{226}Ra	^{232}Th	^{40}K	^{137}Cs
Spheroidal concretions	VV-04-08	826	38	623	46
Spheroidal concretions	VV-04-09	786	51	827	50

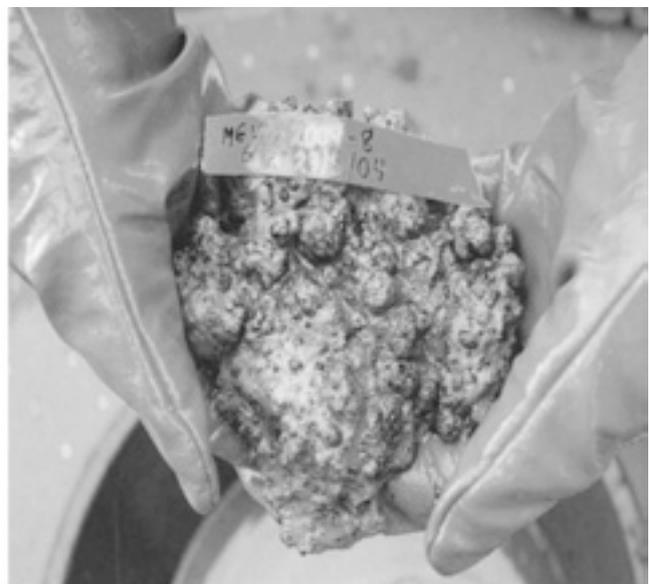


Figure 5. Spheroidal concretions sampled at SAMAGOL site MGVV-04-08 in the Finnish part of the Gulf of Finland.

Thus, we can consider the shallow-water concretions as the natural metal ionic traps "cleaning" near-bottom waters of some toxic elements. At the same time, every concretion itself is the living open system. The growth of a concretion is not a constant process; it depends on the flux of Mn, Eh, temperature, and hydrodynamics, among other factors. The stoppage of concretion growth usually triggers their gradual dissolution, sometimes allowing formation of exotic forms of concretions or their complete dissolution. Thus, the concretions could become a potential source of re-pollution of the near-bottom water.

Growth rates of concretions

Growth rates of the Baltic Sea concretions have previously been estimated by Winterhalter & Siivola (1967) based on counting microlaminae and by Suess & Djafari (1977) based on the distribution of Zn, Pb, Cu, and Cd in sediments and discoidal concretions; estimates are in the range 0.02–0.20 mm/yr. Hlawatsch et al. (2002) and Hlawatsch (2003) has determined growth rates for concretions from the western Baltic to be in the range of 0.13–0.30 mm/yr based on the increased concentrations of anthropogenic elements in the outer layers of concretions. We have observed a similar marked increase in the contents of Pb in small spheroidal concretions (Figure 4) and some heavy metals in the outer layers of recent discoidal concretions from the eastern Gulf of Finland. Using these data (Zhamoïda et al. 1996), we calculated average growth rates for the spheroidal concretions of about 0.03–0.06 mm/yr. These figures are based on the assumption that the anthropogenic input of metals into the Baltic Sea began at the end of the 19th century. However, the growth rates would be higher if the anthropogenic input is assumed to have begun in the middle of the 20th century. According to these indirect data, the maximum age of the biggest spheroidal concretions is 500 years. Estimated growth rates of concretions in the range 0.003–0.03 mm/yr were identified using the U-Th-Ra-Ba systematic approach (Liebetrau, et al. 2002). In some conditions, the growth rates of concretions achieve an extreme value, as demonstrated by findings in the sediment samples of rare artificial objects (a cap from a bottle of the Finnish beer "Karjala", or a screw made of stainless steel) within concretions rings 1–3 mm thick.

The present investigations are focused on dating concretions using ²¹⁰Pb, which is traditionally used for modern sediment dating. But sediment dating is based on determination of ²¹⁰Pb falling into the sea-water and bottom sediments from atmosphere as a result of ²²²Rn decay. In contrast with this process,

about 90% of ²¹⁰Pb detected in concretions from the Gulf of Finland are generated directly inside concretions as a result of ²²²Rn decay forming from ²²⁶Ra. Some complications of the study are connected with ²²²Rn emanation inside the concretion. As a result of this emanation, the concentration of ²²²Rn decay products, including ²¹⁰Pb, decreases in the central part of the concretion and increases in its outer layers.

For studying ²¹⁰Pb concentrations, one spheroidal concretion (10 mm in radius) sampled near the Moshny Island was selected. Four probes for ²¹⁰Pb determination were sampled: (1) from the center of the concretion (distance from the center 0–2.5 mm); (2) at 2.5–5 mm from the center; (3) at 5–8 mm; and (4) at 8–9 mm (Figure 6).

The first model does not take into account Rn emanation. Let point of time $t = 0$ (time of concretion birth), at which there will be in the central part of the concretion (named as first layer) $N_1(0)$ of ²²⁶Ra atoms (N_{1i} is the number of ²²⁶Ra atoms in i -layer of concretion, N_{2i} is the number of ²²²Rn atoms in i -layer of concretion, N_{3i} is the number of ²¹⁰Pb atoms in i -layer). It is supposed that Ra sorption to the concretion is a constant value. Then, at the point of time t_1 (age of the central part or the first layer of concretion and accordingly the age of the concretion), there will be $N_{11}(t_1) = N_{11}(0) \exp(-\lambda_1 t_1)$ of ²²⁶Ra atoms, where λ_1 is the ²²⁶Ra decay constant. Then, at point t_1 , the number of ²¹⁰Pb atoms – $N_{31}(t_1)$ will be equal:

$$N_{31}(t_1) = N_1(0) \lambda_1 \lambda_2 \left[\frac{\exp(-\lambda_1 t_1)}{(\lambda_3 - \lambda_1)(\lambda_2 - \lambda_1)} + \frac{\exp(-\lambda_2 t_1)}{(\lambda_3 - \lambda_2)(\lambda_1 - \lambda_2)} + \frac{\exp(-\lambda_3 t_1)}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)} \right]$$

$\lambda_3 = ^{210}\text{Pb}$ decay constant ($\lambda_1 = 4.3 \times 10^{-4} \text{ yr}^{-1}$, $\lambda_2 = 66.2 \text{ yr}^{-1}$, $\lambda_3 = 0.031 \text{ yr}^{-1}$).

It is possible to write similar equations for the second (2.5–5 mm), third (5–8 mm), and fourth (8–9 mm) layers (probe) of the concretion. Composing an equation set of type $\frac{N_{3i+1}(t_{i+1})}{N_{3i}(t_i)}$ and solving

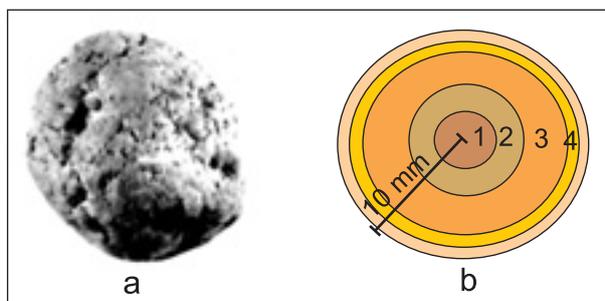


Figure 6. Photo of spheroidal concretion (a) and position of sampled layers for the study of ²¹⁰Pb concentrations (b): 1 = distance from the center of the concretion, 0–2.5 mm; 2 = 2.5–5 mm; 3 = 5–8 mm; and 4 = 8–9 mm.

it, we get the minimal volume of $t_1=670\pm 50$ yr, $t_2=150\pm 70$ yr, $t_3=140\pm 50$ yr, and $t_4=90\pm 10$ yr, respectively. Accordingly, the rate of the concretion radial growth is in the range 0.013–0.042 mm/yr.

For the second model, we tried to take into account Rn emanation. For this purpose, we applied parameter ϕ , which defines the emanation process. Let ϕ have the same dimension as decay constant λ . Then Rn decay in i -layer of concretion will be described by following equation:

$$\frac{dN_{2i}(t_i)}{dt_i} = -\lambda_2 N_{2i}(t_i) + \lambda_1 N_{1i}(t_i) - \phi N_{2i}(t_i) + \phi N_{2i-1}(t_{i-1})$$

The first item of the right part of equation describes Rn decay; the second item, Rn generating from Ra; the third item, emanation of Rn from i -layer to $i+1$ -layer; and the fourth item, emanation of Rn from $i-1$ -layer to i -layer. ^{210}Pb decay in the i -layer of concretion is described by following equation:

$$\frac{dN_{3i}(t_i)}{dt_i} = -\lambda_3 N_{3i}(t_i) + \lambda_2 N_{2i}(t_i)$$

Again, we compose an equation set of type $\frac{N_{3i+1}(t_{i+1})}{N_{3i}(t_i)}$. The solution of the equation set arises from following assumptions: according to indirect geological data, the age of the spheroidal concretion is less than 1000 yr, correspondingly $0 < t_4 < t_3 < t_2 < t_1 < 1000$ yr; $t_{i-1} - t_i \geq 30$; $t_i - t_{i+1} \approx \text{const}$; and $1 \leq \phi \leq \lambda_2$ (experimental data). After solution of the equation set, we obtained for the second model an age (t_1) of the studied spheroidal concretion in the range of 260–490 yr, or its radial growth rate in the range of 0.018–0.034 mm/yr.

Concretions as a redox buffer system

The MnO_2 contents in the concretions of the Gulf of Finland are in the range 0.6–53.4%. Mn is dominantly in the tetravalent state. For spheroidal concretions, the $\text{Mn}^{4+}/\text{Mn}^{2+}$ ratio is in the range of 3–4 and for discoidal concretions more often in the range of 1–2. Primarily, abundant concretion fields are located at the border area between areas of anoxic silty-clayey muds and badly sorted clayey sands forming in stable oxidizing conditions.

The easy transformation of Mn from 2+ to 4+ and back can smooth over the oxygen content fluctuations in water and sediments. Thus, taking into consideration the volume and concentration of concretions at the sea bottom of the investigated area, it is reasonable to assume an important role for the concretions as a buffer system partially controlling redox conditions in the near-bottom and pore waters.

The different types of characteristic profiles of the concretions layer are shown in Figure 7. The concretions in the abundant fields typically occur at a depth of 50–150 mm (up to a maximum of 400 mm) within the sediment. The upper part of the sediment column is characterized by actively growing concretions with high Mn content and is about 30–100 mm thick. At depths greater than 50–100 mm in the sediment column, the concretions actively dissolve. At the bottom of the concretion layer, further dissolution transforms them into skeletons of clastic material. More rarely, some parts of the concretions are transformed into sulfide minerals. Some of the movable Mn and Fe migrate to the upper part of concretion layer (Figure 8). Some relative equilibrium between rates of growth and dissolution of the concretions within a more or less stable concretion layer can be assumed. As a consequence, the weight of concretions in the sediment remains constant in stable conditions. The widths of the spheroidal concretion fields have also been relatively constant over a rather long period. The positions of these fields depend on the migration of Mn and Fe in the bottom waters from the mud zones to the areas of concretion deposition. We therefore predict that commercial extraction of these concretions will result in the rapid restoration of the concretion abundance (Zhamoida et al. 1996).

Concretions and organic matter

According to recent publications, Mn, Fe, and related elements are remobilized from the anoxic muds and migrate into the bottom waters (Glasby et al. 1996, Emelyanov 2004, Winterhalter 2004). The constant (or seasonal) lateral migration of these elements from the mud zones to their periphery provides the spheroidal nodules with the main source of metals. The deposition of Mn and Fe at the borders of mud zones may therefore be considered the result of chemical sorption of the metals on the active surfaces of clastic particles and Fe-Mn oxyhydroxides. However, according to the calculations of Gramm-Osipov et al. (1984), these reactions are too slow to account for the formation of these concretions.

The fine structure of ferromanganese concretions from the Gulf of Finland has been investigated in detail by energy dispersive spectrometry and transmission electron microscopy (Zhang et al. 2002). Numerous fine, almost filamental structures are observed within the concretions (Figure 9), many of which appear to be spirals several nanometers in diameter, which lie within the size range of nanobacteria. These marks of microorganism

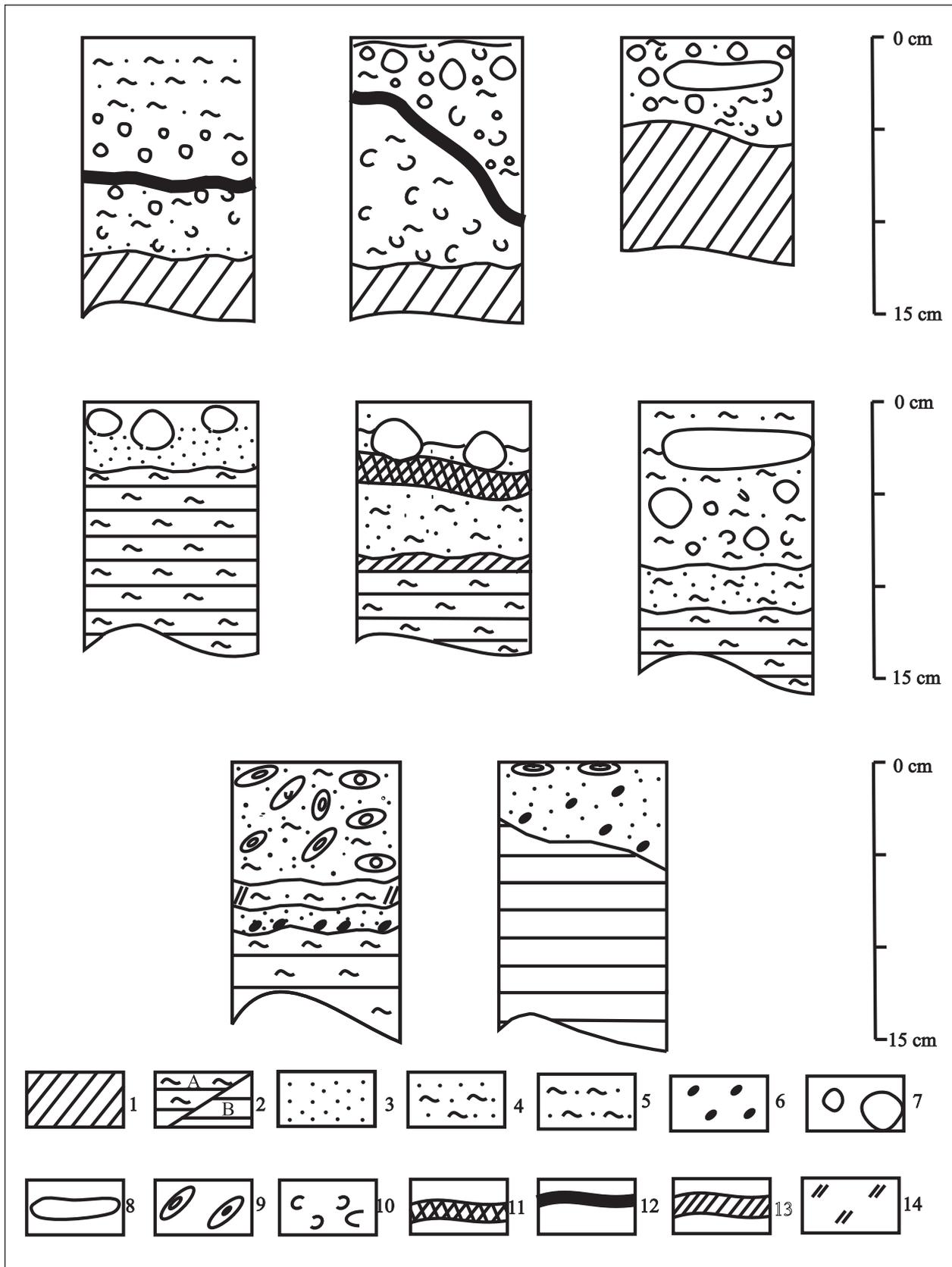


Figure 7. Examples of the occurrence of concretions in the sediment column: 1 = monotonous limno-glacial clays; 2A = thin-layered limno-glacial clays; 2B = varved clays; 3 = sand; 4 = silty sand; 5 = sandy clay; 6 = gravel; 7 = spheroidal concretions; 8 = recent discoidal concretions; 9 = relict discoidal concretions; 10 = fragments of concretions; 11 = ferromanganese crusts including concretions; 12 = iron oxyhydroxide cementation within the concretion layer; 13 = iron oxyhydroxide cementation on the surface of the clays; and 14 = dispersed organic matter.

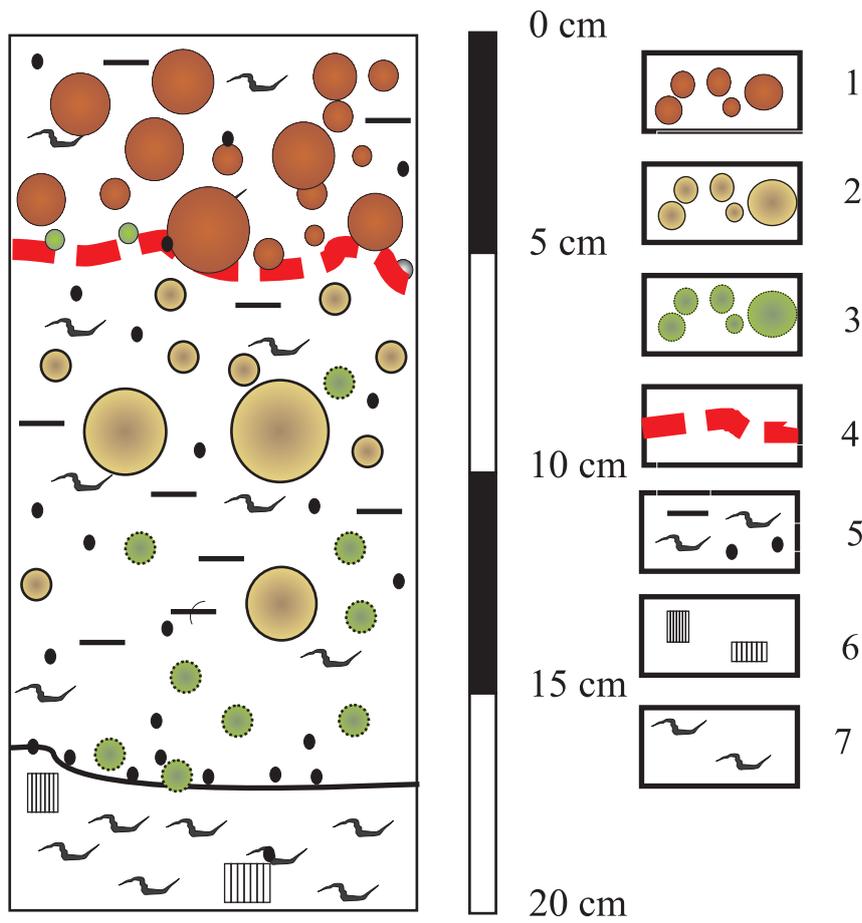


Figure 8. Idealized sediment column representing mature layer containing spheroidal concretions: 1 = growing spheroidal concretions displaying granular surface texture; 2 = dissolving or stable spheroidal concretions displaying smooth surface texture; 3 = dissolving spheroidal concretions transforming into a clot of clastic material; 4 = iron oxyhydroxide cementation; 5 = sandy-clayey silt; 6 = amorphous Fe sulfides; and 7 = lacustrine clays.



Figure 9. Transmission electron micrograph showing the filamental structures in the spheroidal ferromanganese concretion sampled near the Moshny Island, x150 000.

activity indirectly confirm the assumption that the high growth rates of Baltic Sea concretions result from the catalytic influence of microorganisms on redox processes occurring at the concretion surface.

In addition, our previous investigations identified some correlation between the processes of concretion growth and organic compounds. The content of organic matter in spheroidal concretions depends on the thickness of the concretion layer and the abundance of the concretions. If the thickness of the concretion layer within the sediment column is less than 0.1 m and the abundance of the concretions is less than 25–60% of the sediment volume, then the organic matter content is in the range of 0.15–0.19%. If the thickness of the concretions layer is 0.25–0.30 m and the abundance of the concretions is about 80% of the sediment volume, then

the organic matter content increases to 0.25–0.26%. The lowest contents of organic matter (0.08–0.09%) are characteristic of discoidal concretions. Possibly this correlation between activity of concretion growing processes and organic matter content is also connected with bacterial activity. From the other side, we find numerous remains of marine microorganisms inside concretions as a result of their mechanical entrapment during the concretion growth (Figure 10).

Underwater visual observations and calculation of the presence of macro-benthos species in the bottom sediments by S. Tchivilev during the MEP-95 cruise (Zhamoïda 1995) have shown that within the areas of actively growing concretion fields, the amount of some macro-benthos species such as *Saduria entomon* markedly increases compared with adjacent areas where concretions are absent (Table 5).

Figure 10. Scanning electron micrographs showing remains of different microorganisms in the spheroidal ferromanganese concretions sampled near the Moshny Island.

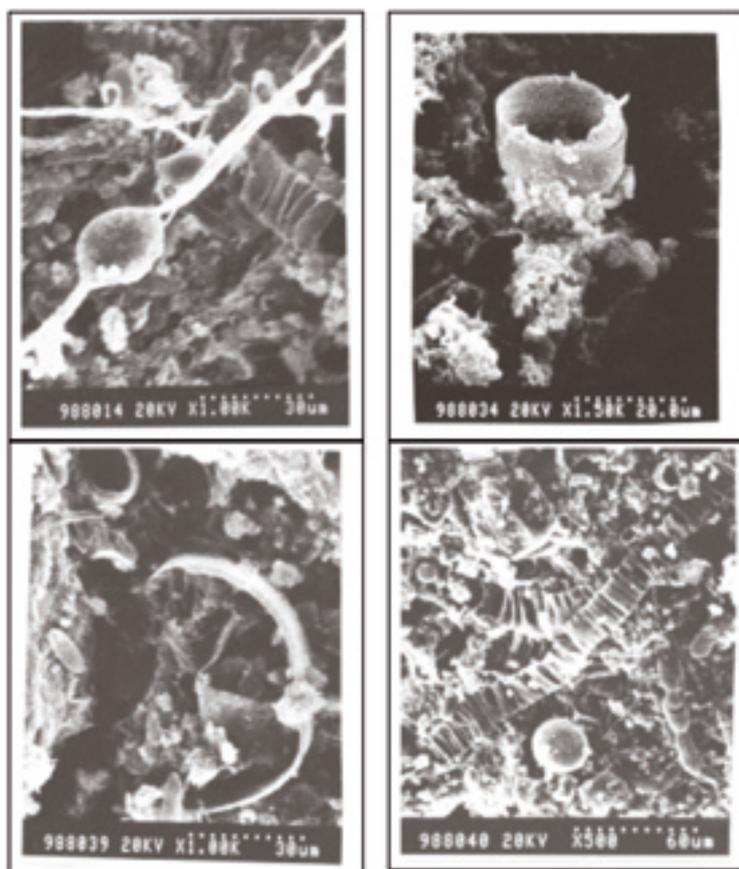


Table 5. Number of macro-zoobenthos (sp/m²) from the bottom sediments of the eastern Gulf of Finland calculated by Dr.S.Tchivilev in MEP-95 cruise. Yellow color = samples from concretion fields, white = samples where concretions are absent.

Species	95-1	95-2	95-3	95-4	95-5	95-6	95-7	95-8	95-9	95-10	95-12	95-13
<i>Saduria entomon</i>	4	0	40	4	2	4	2	26	30	18	10	4
<i>Pontoporeia affinis</i>	0	0	10	20	4	0	0	272	228	224	44	10
<i>Pontoporeia femorata</i>	0	0	0	0	0	0	0	0	128	4	4	0
<i>Ostracoda gen.sp.</i>	0	0	0	0	0	0	0	10	0	0	0	0
<i>Macoma baltica</i>	0	2	0	0	0	0	0	0	0	0	0	0
<i>Oligochaeta sp. 1</i>	1220	364	0	206	42	144	0	50	0	0	0	0
<i>Chironomus sp.</i>	2	0	0	0	0	0	0	0	0	0	0	0
<i>Chironomidae gen.sp.</i>	2	2	0	0	0	4	0	0	0	0	0	0

During the same cruise, unexplained local increases of NO_2 up to an average concentration of 0.612 ppb in the near-bottom water of the concretion fields were identified. The background con-

centrations of NO_2 in the near-bottom waters within the areas where concretions are absent were 0.166 ppb. Possibly, this increase is also connected with biological activity in the concretion layer.

CONCLUSIONS

The influence of active biogeochemical processes of ferromanganese concretion forming on the quality of near-bottom environments and character of sediment accumulation are believed to be especially significant for the water basins, such as the Baltic Sea, located in areas with moderate climate and heavy pressures from anthropogenic activity. The rates of concretions growth are extremely high. The cumulative influence of the shallow-water concretions on the quality of the marine environments is various and complex and requires detailed investigations with calculations of the balances of these processes. It is evident that actively growing concretions are the principle concentrators of some elements, including toxic ones. Concretion fields within the limited area involved millions tones of ore material during a very short period of time com-

pared with the geological time scale. Very likely, the abundant concretion fields situated in the border area between oxidized and reduced conditions in the sediments play an important role as a buffer system, partially smoothing changes of redox conditions in the near-bottom and pore waters. Some indirect evidence suggests dependence of the processes of concretion growth and biological activity.

The problem of interaction between ferromanganese concretion fields and the environment is of increasing importance as the privately owned PetroTrans begins experimental, commercial, underwater mining of these concretions in the Russian sector of the Gulf of Finland. Our previous investigations of ferromanganese concretion-forming processes allow us to propose that extraction of concretions from the sea bottom will result in the onset of rapid restoration of concretion abundance.

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Holocene sedimentary environment and sediment geochemistry
of the Eastern Gulf of Finland, Baltic Sea
Edited by Henry Vallius
Distribution of heavy metals and arsenic in soft surface sediments of
the coastal area off Kotka, North-Eastern Gulf of Finland, Baltic Sea
Geological Survey of Finland, Special Paper 45, 33–48, 2007.

DISTRIBUTION OF HEAVY METALS AND ARSENIC IN SOFT SURFACE SEDIMENTS OF THE COASTAL AREA OFF KOTKA, NORTHEASTERN GULF OF FINLAND, BALTIC SEA

by

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Vallius, H., Ryabchuk, D. & Kotilainen, A. 2007. Distribution of heavy metals and arsenic in soft surface sediments of the coastal area off Kotka, North-Eastern Gulf of Finland, Baltic Sea. *Geological Survey of Finland, Special Paper 45, 33–48, 12 figures and 5 tables.*

The modern soft surface sediments of the sea area off Kotka in the Northeastern Gulf of Finland were surveyed for heavy metal contamination. Altogether, 14 sites were sampled with a gravity corer for chemical analyses. The sea-floor sediments of this rather shallow and thus sensitive sea area have for decades been loaded with heavy metals and other harmful substances. Although a slightly improving trend can be seen, the soft sediments off Kotka and Hamina can still be classified as largely polluted, especially on the basis of cadmium and mercury contents in the surface sediments. Deeper down, at depths of 10–20 cm, the sediments are even more highly contaminated, such that concentrations occasionally reach values representing very high contamination. Mercury is the main pollutant of the near coastal areas close to the outlets of River Kymi-joki, while cadmium is the main pollutant in the remote basins in the east and southeast.

Key words (Georef Thesaurus AGI): Marine sediments, clay, mud, geochemistry, heavy metals, background level, Finland, Kotka, Baltic Sea, Gulf of Finland

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INTRODUCTION

The Gulf of Finland is an eastward extension of the Baltic Sea, an estuary-like and rather shallow sea. There is no tide and the sea is partly ice covered during the winter months. The salinity in the study area is low (2–4 salinity units) because of the rather limited water exchange with more saline waters in the west and river run-off in the north and extreme east of the Gulf. The total annual freshwater discharge to the Gulf of Finland is 112 km³ (Bergström & Carlsson 1994), of which most of it is discharged in the eastern Gulf of Finland, thus affecting the bottom in the study area. The Neva River is the largest river in the area, with a mean annual run-off of some 2460 m³ s⁻¹ (77.6 km³ a⁻¹, Bergström & Carlsson 1994). The Neva River is, according to Vallius & Leivuori (2003), the principal carrier of pollutants, but the Vyborg Bay area and River Kymijoki with its two outlets are also considerable sources of heavy metals. In addition, the cities of Hamina and Kotka, with rather large commercial harbours, add to the pollution of this sea area (Fig. 1). The hydrography in the Gulf is controlled by the Coriolis force, which forces the currents into anti-clockwise movement (Palme'n 1930, Alenius & Myrberg 1998). This is further influenced by geomorphology and meteorological factors. In the eastern Gulf of Finland this means that currents from

the River Neva and the Neva Bay are more easily forced towards the northeast, i.e. to the area of this study. Here, the waters are mixed with those from the Vyborg Bay area and from the River Kymijoki. Thus, the geochemistry of the bottom sediments in the study area is a mixture of components of local natural origin combined with transported components from the north and east.

Eutrophication is a curse of the Baltic Sea (Pitkänen 1994 and Rantajärvi 1998) and it has also strongly influenced the sea in the study area, but as several authors have already reported on this problem it will only be briefly mentioned in this paper.

This study was an outcome of the SAMAGOL project, a collaborative project between the Geological Survey of Finland (GTK) and the All-Russia Geological Research Institute (VSEGEI). The aim was to gather available marine geological data from the eastern Gulf of Finland administered by the participating institutes in order to produce a marine geological synthesis report from the study area. This paper describes the geochemistry of the recent surface sediments in the study area, including arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn). Data presented in this paper are based on samples that were collected in 2004.

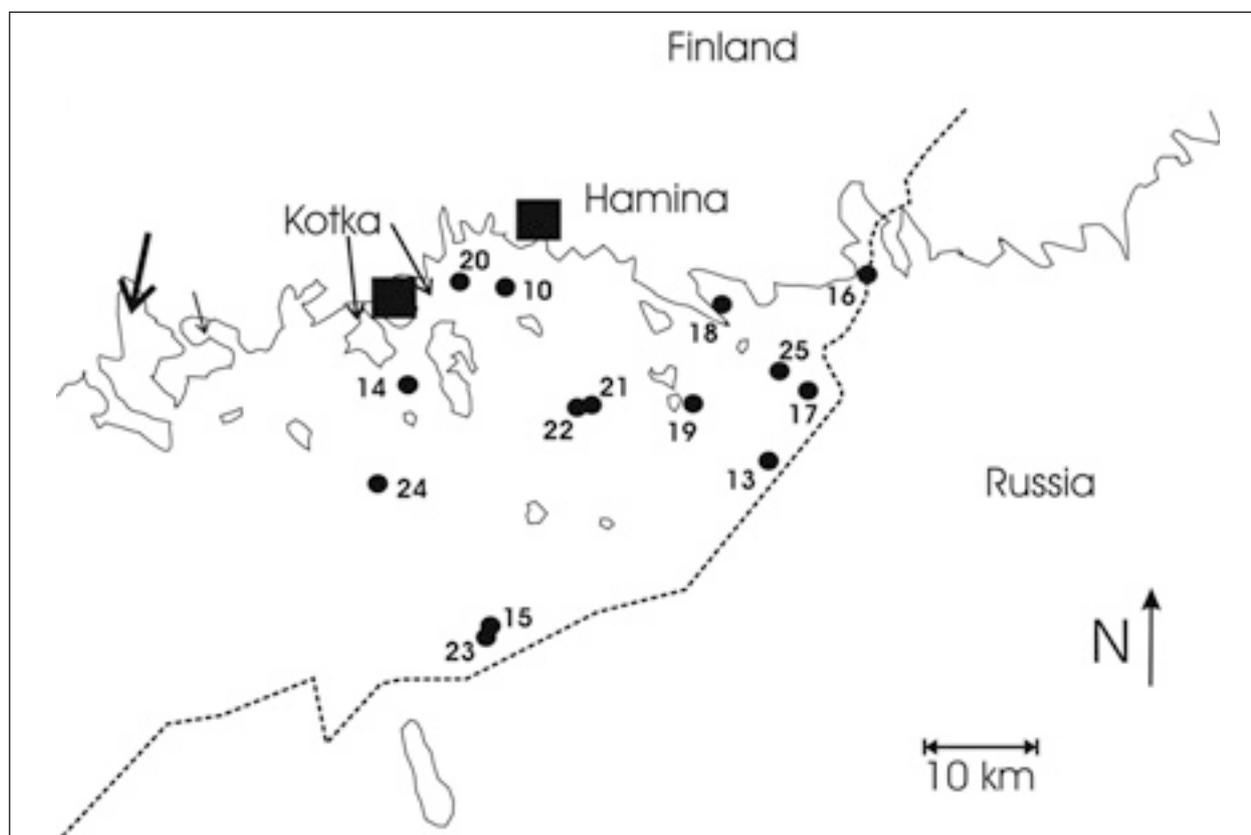


Figure 1. Study area with the cities of Kotka and Hamina indicated. Arrows indicate the approximate location of the main outlets of River Kymijoki. Thickness of arrow indicates relative water flow. The dotted line is the border between Finland and Russia.

STUDY AREA

The study area covers both sides of the national border between Finland and Russia, an area of approximately 2000 km² between the latitudes 60° 00 and 60° 30 N and the longitudes 26° 30 and 28° 00 E (Fig. 1). It is situated on the northern coast of the Gulf of Finland. The southern part of the area comprises open sea with water depths of up to some 90 metres. There are only a few bigger islands, of which the largest is the island of Gogland, a horst structure reaching up to as much as 176 metres above sea level. In the north, the study area borders land and the archipelago is typically a mosaic of a multitude of islands differing in shape and size. Similarly, the sea floor in the north is made up of a mosaic of rather small, relatively shallow and isolated accumulation basins. In the south the accumulation basins are clearly larger as the sea floor between the sparse islands is more even. The water depth increases from land in the north to the deepest parts in south. The deepest sampled site was MGVV-2004-23, with a water depth of 72,0 metres.

Earlier studies

Several earlier studies have been published from the sea area around Kotka, Hamina and the outlets of River Kymijoki. This is mainly because the River Kymijoki is known to be largely polluted by heavy metals and organic pollutants. According to Partanen (1993), the biota has largely been affected by

eutrophication in the outlets of River Kymijoki, but no chemical analyses were reported. A report by Kokko & Turunen (1988) described considerable mercury contamination in the river sediment profile caused by large discharges during the late 1950s and early 1960s. Anttila-Huhtinen & Heitto (1998), Verta et al. (1999a, b, and c) and Pallonen (2001, 2004) reported large-scale contamination of river and sea floor sediments of the River Kymijoki and sediments of the sea area outside the river outlets. Leivuori (1998), Vallius & Lehto (1998), Vallius & Leivuori (1999), Vallius (1999 a and b), Leivuori (2000) and Vallius & Leivuori (2003) have reported heavy metal distributions in the off-shore sediments of the Gulf of Finland, and in these studies the sea area outside Kotka and the River Kymijoki has also been classified as significantly, largely or very largely contaminated, depending on the element.

In several reports on the state of Finnish coastal waters (National Board of Waters 1983, Pitkänen et al. 1987, and Kauppila & Bäck 2001), the sea area off the River Kymijoki has been classified as polluted or strongly polluted, depending on the sampling site. The most polluted sites are in the river, the river mouth, or immediately outside it. In all studies mercury has been found to be the worst contaminating heavy metal in the sediments. Cadmium has also been found in high or even very high concentrations. In this study it was possible to compare the results with the data from earlier studies.

MATERIALS AND METHODS

The samples of this study were recent muddy clays or clayey muds, which were collected during the SAMAGOL cruise of R/V Geola of the Geological Survey of Finland (GTK) on 24 May to 4 June 2004. Altogether, 13 sites were sampled with a gravity corer for chemical analyses. Additionally, one sample was taken onboard R/V Aranda in August 2004 (Table 1). The sampling sites were selected based on carefully surveyed echo-sounding data. All samples were taken using a GEMAX twin barrel gravity corer with an inner diameter of 90 mm of the core liner. The core length varied between 25 cm and 65 cm, and most of the cores reached 50 cm in length. After sampling, one of the two cores obtained was split vertically for description and the other was used for sub-sampling. Thus, all cores were sliced into 10-mm-thick subsamples

Table 1. List of coring stations, coordinates in WGS-84.

Station	Latitude	Longitude	Depth (m)
MGGN-04-10	60°29.255'N	27°07.275'E	15.6
MGGN-04-13	60°20.141'N	27°35.485'E	39.0
MGGN-04-14	60°24.069'N	26°57.141'E	20.2
MGGN-04-15	60°11.298'N	27°06.029'E	63.5
MGGN-04-16	60°29.940'N	27°45.774'E	16.0
MGGN-04-17	60°23.816'N	27°39.434'E	43.5
MGGN-04-18	60°28.111'N	27°30.370'E	14.3
MGGN-04-19	60°23.043'N	27°27.252'E	30.0
MGGN-04-20	60°29.537'N	27°03.062'E	13.2
MGGN-04-21	60°23.117'N	27°17.723'E	38.3
MGGN-04-22	60°23.053'N	27°16.577'E	38.0
MGGN-04-23	60°10.751'N	27°05.432'E	72.0
MGGN-04-24	60°19.428'N	26°52.788'E	38.0
MGGN-04-25	60°24.644'N	27°36.320'E	39.7

onboard and packed into plastic bags that were immediately stored at $-18\text{ }^{\circ}\text{C}$ until they were taken ashore for freeze drying (Leivuori 1998, Vallius & Lehto 1998, Vallius & Leivuori 1999 and 2003, Vallius 1999a,b, Leivuori 2000).

Chemical analyses were performed at the analytical chemistry laboratory of GTK. The samples were completely digested with hydrofluoric – perchloric acids followed by elemental determination using inductively-coupled plasma mass spectrometry (ICP-MS) and inductively-coupled plasma atomic emission spectrometry (ICP-AES) (Vallius & Leivuori 1999, 2003). Determination of C and N was performed using a LECO analyzer and mercury was measured with an Hg analyzer through pyrolytic determination.

The analytical reliability of the laboratory was checked using commercial standard reference materials MESS-2 and NIST8704. All elements except cadmium had a recovery of $\pm 10\%$ of the reference value, most of them within $\pm 5\%$, which can be considered as satisfactory or good. The average recovery of cadmium was slightly too high for MESS-2 as it was 115%, but for NIST8704 it was exactly 100%. It seems that the matrix of NIST8704 (Buffalo River sediment) is more similar to the very low salinity marine sediment of this study. In one sample batch the recovery of lead was 112% (average of all batches for lead was 102%), while the recovery for zinc in another batch was 89% (average of all batches for zinc was 96%). Overall, the recoveries of all studied elements were good enough to be reliable.

In order to obtain a picture of the degree of contamination of the sediments in the study area the classification of Vallius and Leivuori (2003) in the offshore Gulf of Finland was used (Table 2). It is based on the Swedish marine sediment quality criteria (Naturvårdsverket 1999, WGMS 2003), where surface concentrations are compared with background values. The Swedish criteria are used because

no Finnish criteria are yet available. Quality criteria, which compare total concentrations with a reference or with background values, provide little insight into the potential ecological impacts of sediment contaminants, but they provide a base from which to evaluate Sediment Quality Guidelines (SQG, Burton 2002). In this study the surface concentrations as well as the concentrations at a depth of 14–15 cm have been classified in terms of the degree of contamination.

The classification of contamination of the surface sediment layer gives a good picture of the condition of the sediment, but in order to evaluate further threats from the sediment column it is also necessary to look at the deeper layers. If the sediment column was for some reason disturbed, older sediment from deeper layers would be exposed to the water column. Dredging and other human activities can disturb the sediment column to great depths, but so too can bottom-dwelling animals such as the spionid polychaete *Marenzelleria viridis*, which was observed to burrow into the sediment to depths of 15 cm or more. Thus, a classification of sediment contamination at the depth of 14–15 cm in the studied cores was added to the surface classification. The maximum contents of elements in different cores are dependent on the accumulation rates at different depths. Thus, the depth of 14–15 cm does not correspond to the highest concentrations in all cores, but instead represents a depth, that can easily be resuspended by human activity, bioturbation or currents.

The data are also presented as maps displaying the horizontal distribution of the elements. As there were too few samples for presentation as interpolated colour surface maps, the maps for arsenic, cadmium, cobalt, chromium, copper, mercury, nickel, lead, vanadium and zinc are presented as circular symbol maps. Golden Software Surfer 8© was used in map production.

Table 2. Classification of sediment heavy metal contamination according to the Swedish Environmental Protection Agency (mg kg⁻¹ dry weight basis, total analysis, WGMS 2003). Classification for vanadium is missing.

Metal (mg kg ⁻¹) dry weight	Class 1 Little or none	Class 2 Slight	Class 3 Significant	Class 4 Large	Class 5 Very Large
As	< 10	10–16	16–26	26–40	> 40
Cd	< 0.2	0.2–0.5	0.5–1.2	1.2–3	> 3
Co	< 14	14–20	20–28	28–40	> 40
Cr	< 80	80–110	110–160	160–220	> 220
Cu	< 15	15–30	30–60	60–120	> 120
Hg	< 0.04	0.04–0.10	0.10–0.27	0.27–0.7	> 0.7
Ni	< 33	33–43	43–56	56–80	> 80
Pb	< 31	31–46	46–68	68–100	> 100
Zn	< 85	85–125	125–195	195–300	> 300

RESULTS

On the basis of earlier studies (Anttila-Huhtinen & Heitto 1998, Verta et al. 1999a,b, and c, Leivuori 1998, Vallius & Lehto 1998, Vallius & Leivuori 1999, Vallius 1999a, b, Leivuori 2000, Vallius & Leivuori 2003, and Pallonen 2001 and 2004) it was expected that the concentrations of certain elements would be rather high in the sediments of the study area. Sedimentation rates were also expected to be high. Thus, sampling aimed towards cores that were as long as possible. Pre-industrial levels of heavy metals were reached in almost all cores. This depth varied markedly depending on the sedimentation rate, but typically it was at a depth of about 40–50 cm if cadmium is used as indicator. At some sites, however, the maximum core length of 60 cm was not enough to obtain a full sequence since pre-industrial times. At certain other sites, penetration deep into the sediment was hindered by the sediment composition, with harder silty layers resulting in clearly shorter cores. However, all cores reached a length of at least 20 cm, thus providing a good record of heavy metal accumulation at the sampled site.

Horizontal distribution of elements in the soft surface sediments

The geochemical data of all studied elements in the surface sediment (0–1 cm) are summarised in Table 3, while the maps show concentrations as circular symbols with symbol size reflecting element concentration. The location of sampling sites is indicated in Figure 1.

All arsenic values in the study area were rather low (Fig. 2), which corresponds well with earlier studies from the offshore Gulf of Finland (Vallius

& Lehto 1998, Leivuori 1998, Vallius & Leivuori 1999, Leivuori 2000, and Leivuori & Vallius 2004). Samples from deeper basins had slightly higher element concentrations than those from shallower sites.

All studied surface samples showed a high degree of cadmium contamination (Fig. 3), the lowest measured concentration being 1.05 mg kg^{-1} , which still is in the class of significant contamination (Table 2). At first it seems that cadmium concentrations increase with water depth, but at sites 15 and 23, which are situated rather close to each other, with a distance of 1.1 km between them, the concentrations differed markedly. Both sites are deep, with a water depth of 63.5 metres at site 15 (shown as a white circle on map) and a depth of 72.0 metres at site 23. However, the concentration of cadmium at site 23 (2.69 mg kg^{-1}) was twice as high as at site 15 (1.21 mg kg^{-1}) (Table 3). This difference can probably be explained by the geological setting of these two sites. Site 15 is situated in the middle of a large rather plane basin, while site 23 is situated on the slope of a scar-like hole with steep slopes. Thus, site 23 represents an exceptional environment in comparison to the other sites, which are located in rather plane basins of differing shape and size.

When looking at the average trend for cadmium (Fig. 3), concentrations were clearly higher at the eastern and southeastern sites close to the national border of Finland. It has been speculated (Vallius & Leivuori 1999) that due to geomorphological and hydrological factors, dissolved cadmium from source areas in the eastern Gulf of Finland is mostly transported westward along the northern side of the Gulf. Such transport from the east would explain the higher concentrations of cadmium in the outer regions of the study area, as the off-shore currents

Table 3. Surface sediment (0–1 cm) concentrations of studied elements. Concentrations in mg kg^{-1} . For location of sampling sites see Figure 1.

Site Nr	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	V	Zn	Station
10	7.25	1.05	14.3	71.4	47.1	0.32	30.6	37.3	77.4	161	MGGN-04-10
13	12.6	1.63	13.7	59.2	76.3	0.15	20.9	54.9	60.6	260	MGGN-04-13
14	8.14	1.12	10.6	52.0	50.9	0.20	29.8	40.2	58.1	165	MGGN-04-14
15	16.6	1.21	14.4	64.3	49.3	0.14	35.1	44.4	95.6	161	MGGN-04-15
16	8.99	1.23	12.7	72.5	57.1	0.14	40.5	58.9	66.8	178	MGGN-04-16
17	19.1	2.51	16.1	77.3	66.3	0.20	36.8	55.9	74.0	217	MGGN-04-17
18	7.58	1.35	10.1	54.3	42.1	0.11	32.5	43.7	53.7	158	MGGN-04-18
19	12.7	2.07	11.0	53.6	57.0	0.11	28.9	42.6	55.1	156	MGGN-04-19
20	10.1	0.84	14.5	82.7	49.1	0.31	39.1	44.9	83.8	198	MGGN-04-20
21	16.4	1.45	14.6	60.6	58.7	0.11	32.8	53.9	71.0	188	MGGN-04-21
22	14.0	1.45	12.4	45.8	46.7	0.09	27.2	39.6	49.4	152	MGGN-04-22
23	13.2	2.69	14.8	57.4	60.1	0.10	34.1	40.4	68.5	217	MGGN-04-23
24	13.9	1.15	11.6	55.1	49.0	0.16	29.7	40.1	65.9	153	MGGN-04-24
25	14.3	2.30	13.4	51.6	47.2	0.15	32.6	48.1	55.5	167	MGGN-04-25

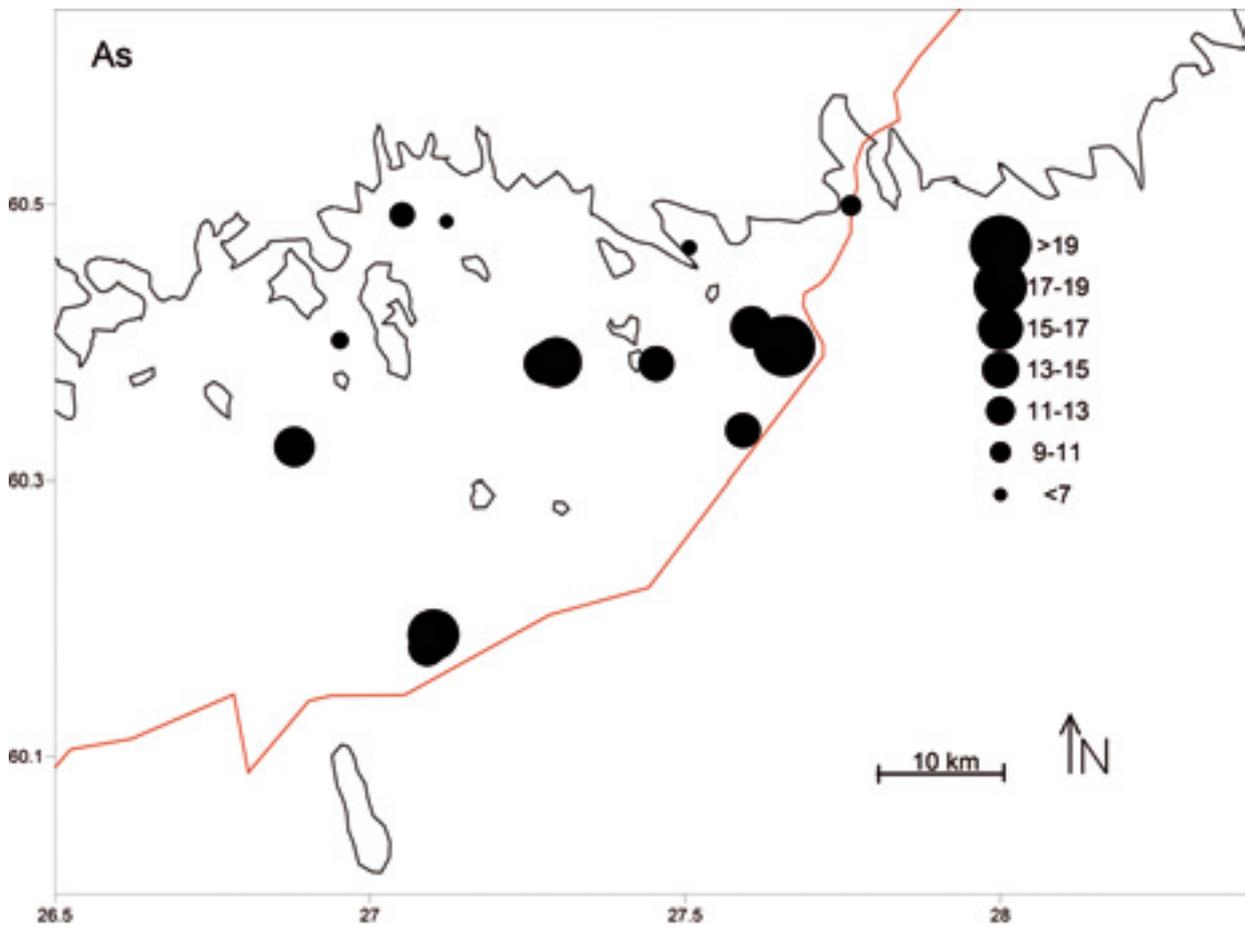


Figure 2. Distribution of arsenic in the surface sediments (0–1 cm). Concentrations in mg kg⁻¹.

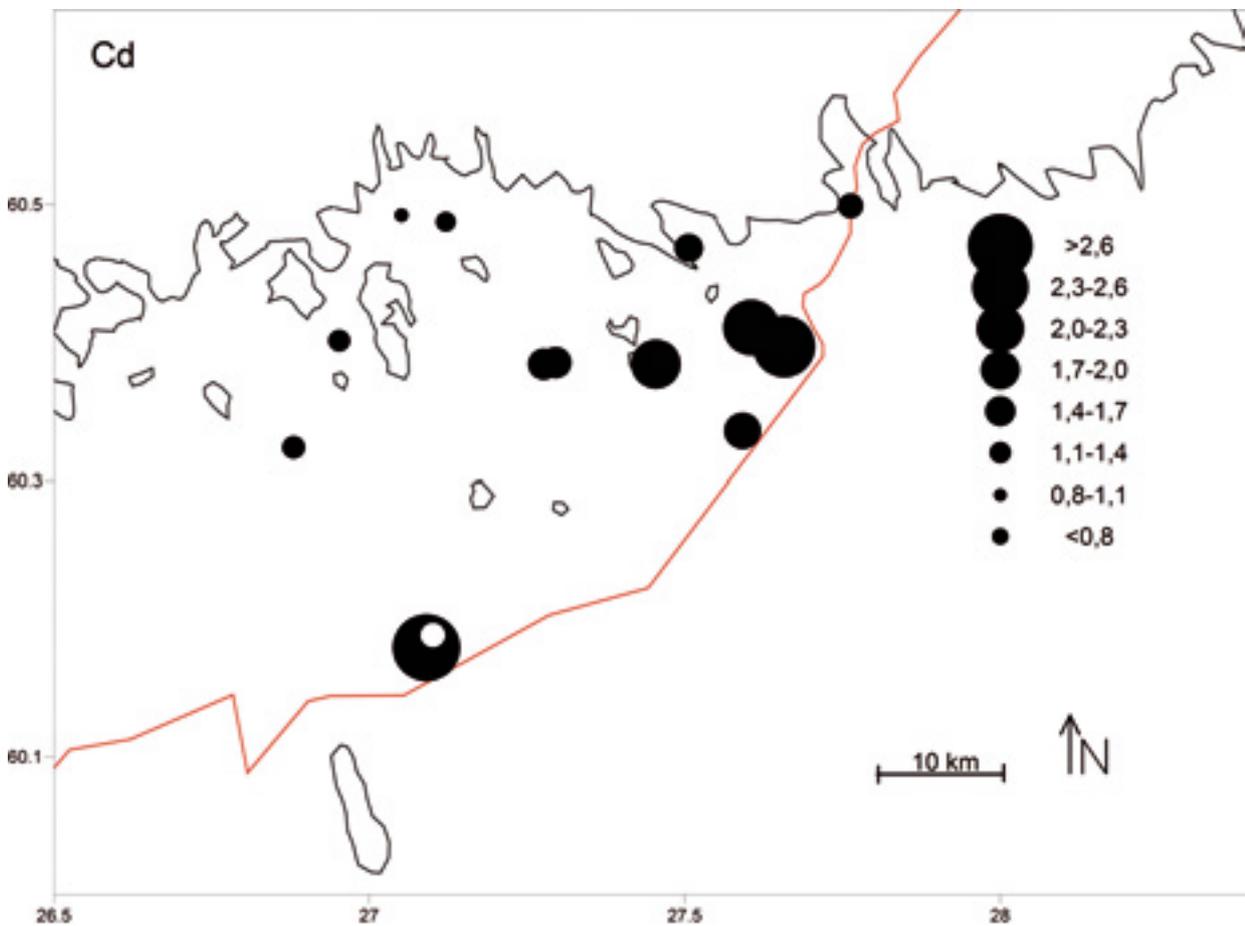


Figure 3. Distribution of cadmium in the surface sediments (0–1 cm). Concentrations in mg kg⁻¹.

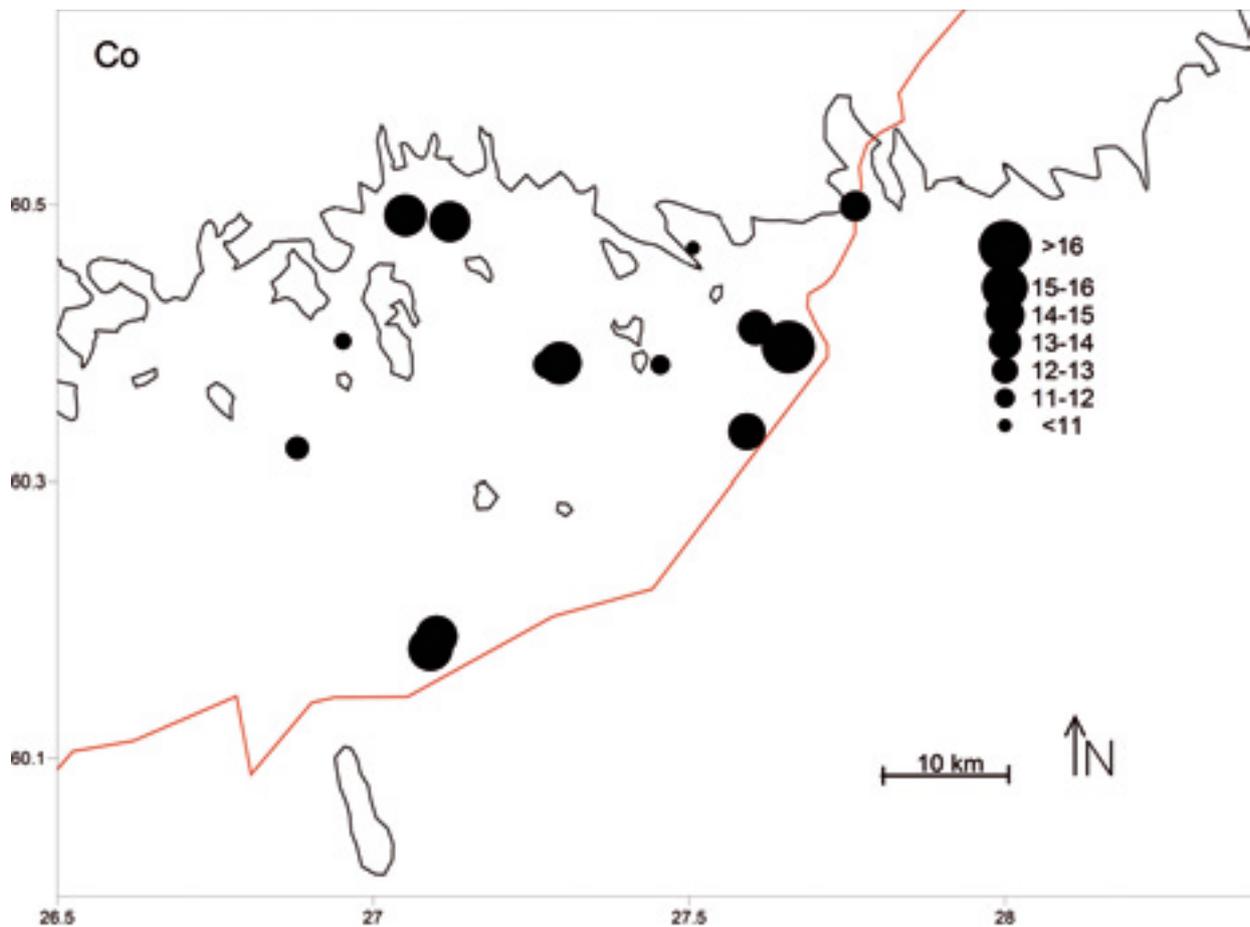


Figure 4. Distribution of cobalt in the surface sediments (0–1 cm). Concentrations in mg kg^{-1} .

do not enter the shallower near-coastal areas. According to the data presented by Anttila-Huhtinen & Heitto (1998) and Pallonen (2001, 2004), the cadmium concentrations in the outer sea area to the east and southeast of Kotka seem to have clearly decreased from 1994 to 2003. To apply this idea to the outermost sites of this study is, however, slightly speculative as no sites in the three above-mentioned studies were situated as far off-shore as the outermost samples of this study. Unfortunately, as none of the sites were from exactly the same location, comparison between these studies is less reliable.

Concentrations of both cobalt (Fig. 4) and chromium (Fig. 5) were rather low and equally distributed. Mean concentrations of chromium (61.3 mg kg^{-1} , Table 4) in this study were on a slightly lower level than the mean average concentrations of chromium in the studies of Anttila-Huhtinen & Heitto (1998) and Pallonen (2001, 2004). This might be attributed to a cleaner trend of release of these metals.

Copper concentrations were on average rather high (Fig. 6). Average surface concentrations (mean

54.1 mg kg^{-1} , Table 4) were of the same order of magnitude as the mean values recorded in earlier studies by Anttila-Huhtinen & Heitto (1998) and Pallonen (2001, 2004). At three sites (13, 17 and 23) the concentrations exceeded 60 mg kg^{-1} , with a concentration of 76.3 mg kg^{-1} measured at site 13, 66.3 mg kg^{-1} at site 17 and 60.1 mg kg^{-1} at site 23 (Table 3). All these sites are located very close to the border between Finland and Russia and a similar transport to that speculated for cadmium might be responsible for these rather high concentrations. The location of these anomalous sites and the fact that copper concentrations at these sites were higher than surface concentrations at any site during a survey in the early 1990s by Vallius & Leivuori (1999) implies an increasing trend in copper release in the easternmost part of the Gulf of Finland. Pallonen (2004) also noted an overall slight increase in copper concentrations from 1994 to 2003.

Average mercury concentrations (Fig. 7) were lower than the average recorded in earlier studies by Anttila-Huhtinen & Heitto (1998) and Pallonen (2001, 2004) in this area and by Vallius & Leivuori (1999) from the whole off-shore Gulf of Finland.

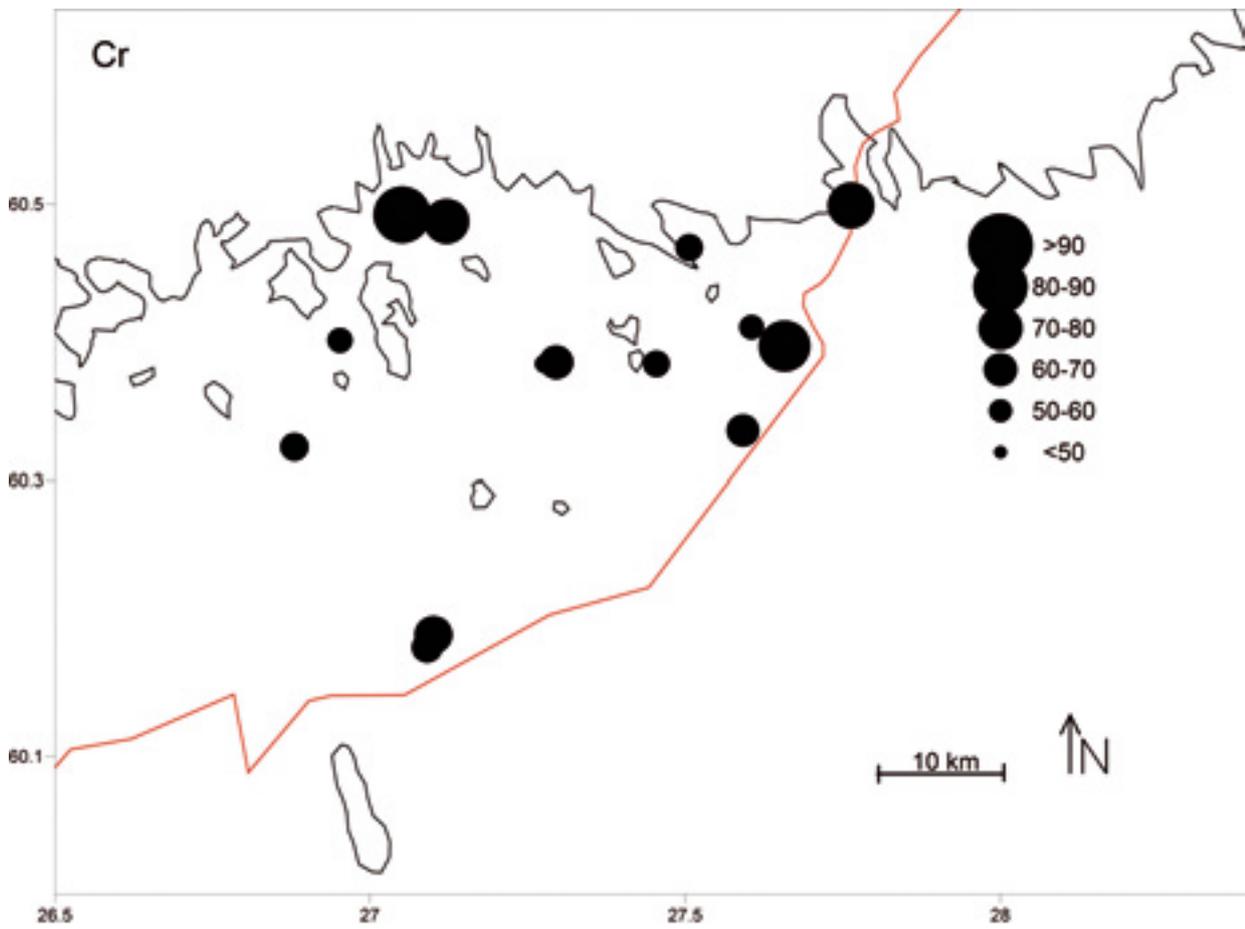


Figure 5. Distribution of chromium in the surface sediments (0–1 cm). Concentrations in mg kg⁻¹.

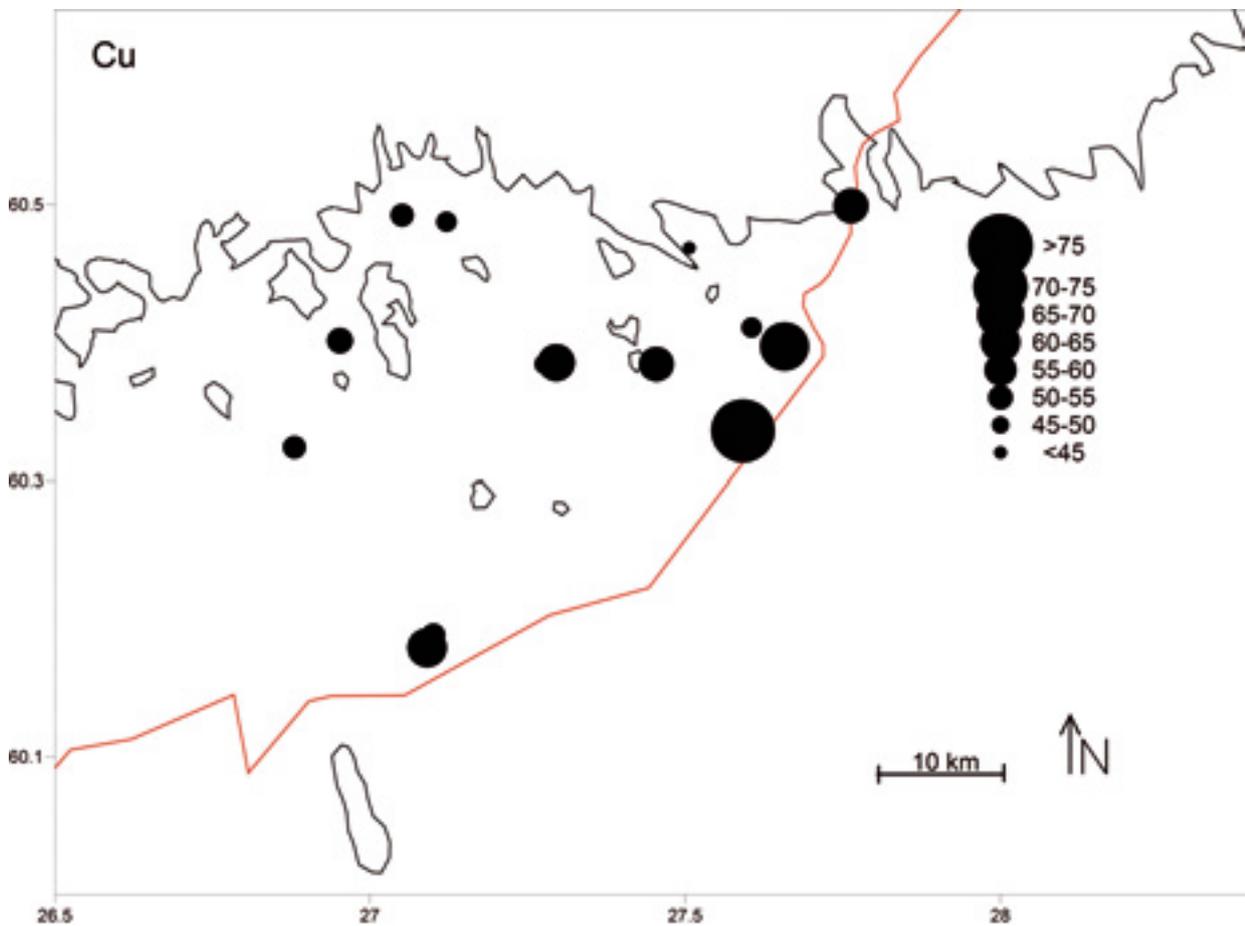


Figure 6. Distribution of copper in the surface sediments (0–1 cm). Concentrations in mg kg⁻¹.

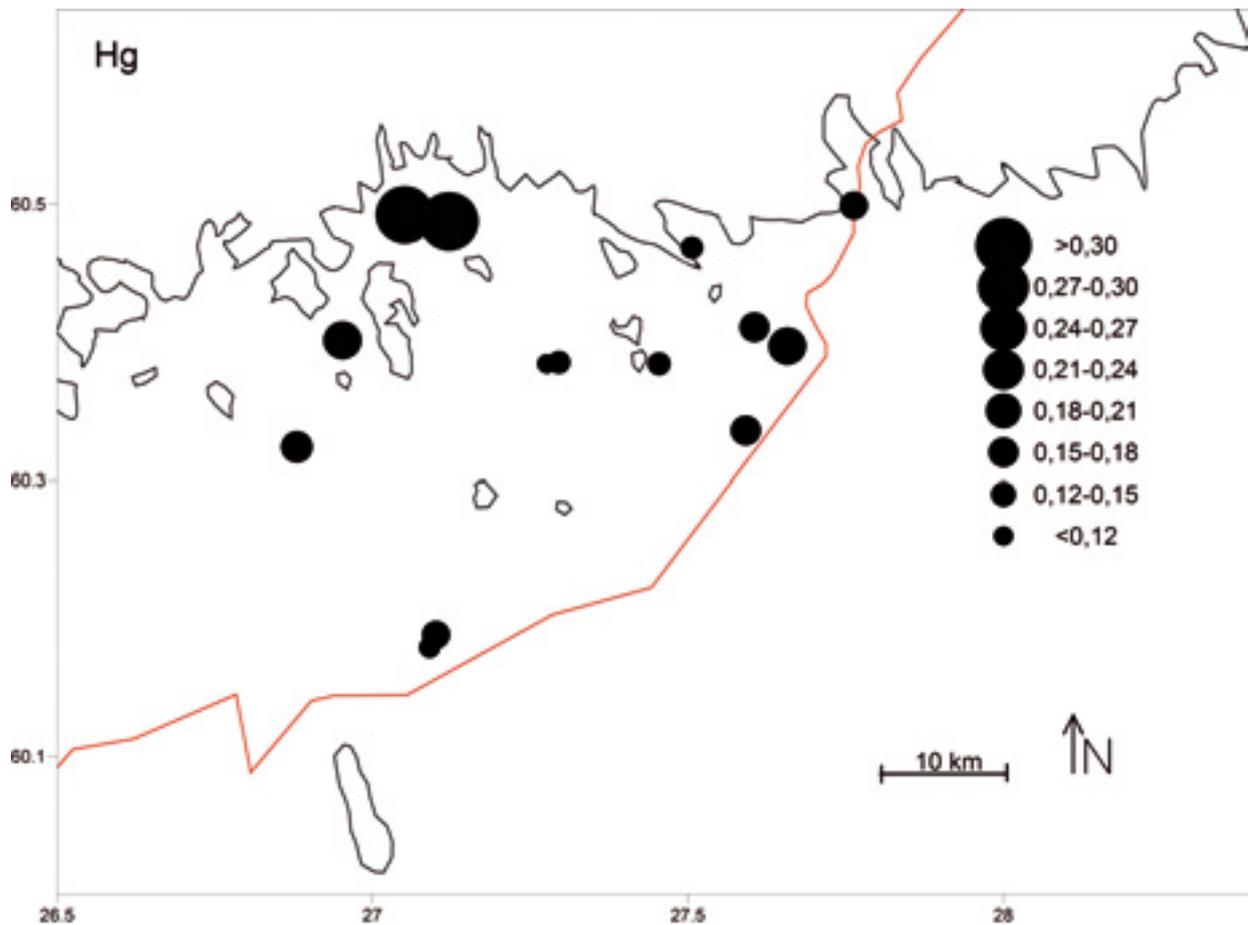


Figure 7. Distribution of mercury in the surface sediments (0–1 cm). Concentrations in mg kg^{-1} .

The samples from sites 10 and 20 with concentrations of 0.32 and 0.31 mg kg^{-1} , respectively, clearly differed from the average pattern. These sites are located rather close to the eastern outlet of the River Kymijoki (Fig. 1) and thus the much higher concentration could be attributed to the well-known mercury load of the river (Kokko & Turunen 1988, Anttila-Huhtinen & Heitto 1998, Verta et al. 1999a,b, and c, and Pallonen 2001 and 2004). As sample number 17, taken close to the border, had a clearly higher concentration (0.20 mg kg^{-1}) and its neighbouring sites 13 and 25 also had slightly higher concentrations (0.15 mg kg^{-1}), it could be speculated that some of the mercury is transported from the east, but this is rather speculative. Similarly, samples 14 and 24 had higher mercury concentrations (0.16 and 20 mg kg^{-1} , respectively), which could be attributed to their location closer to the main western outlet of the River Kymijoki (Fig. 1).

The horizontal distribution of nickel in the survey area (Fig. 8) was even, thus being similar to the distribution of cobalt and chromium. No clear trends could be found. Leivuori (2000) reported nickel values from 20 stations in the Gulf of Fin-

land that were slightly higher than those of the present study. Leivuori (2000) recorded a mean value of 42 mg kg^{-1} (32.2 mg kg^{-1} in this study, Table 4) and minimum and maximum values of 25 mg kg^{-1} and 60 mg kg^{-1} , respectively (20.9 mg kg^{-1} and 40.5 mg kg^{-1} in this study). Thus, nickel concentrations in the coastal area seem to be somewhat lower than in the open sea area of the Gulf of Finland. As the data of Leivuori's study were from the early 1990s it is also possible that there has been a decrease in nickel loading to the sediment since that time. On the other hand, Pallonen (2004) stated that in the Kotka area there were both increases and decreases in nickel concentrations from 1994 to 2003, depending on site.

Lead (Fig. 9) exhibited a similar horizontal pattern to cobalt, chromium and nickel as the distribution was even, with no clear trends in any direction. The concentrations of lead were clearly lower than in the earlier study by Vallius & Leivuori (1999) from the off-shore Gulf of Finland in the early 1990s. That earlier study reported a mean lead value of 51 mg kg^{-1} while the mean of this study was 46.1 mg kg^{-1} (Table 4). The maximum value of 58.9 mg kg^{-1} of

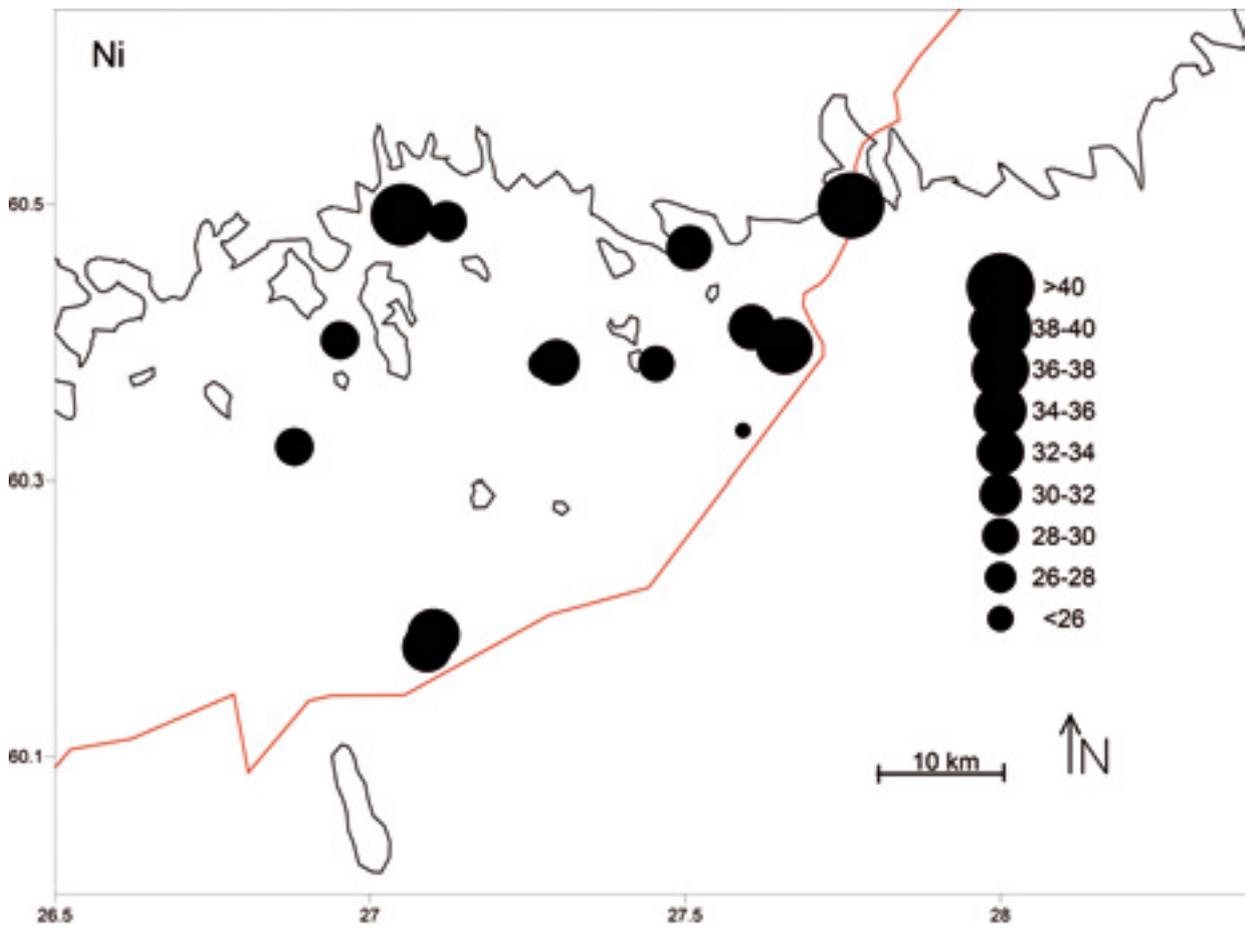


Figure 8. Distribution of nickel in the surface sediments (0–1 cm). Concentrations in mg kg⁻¹.

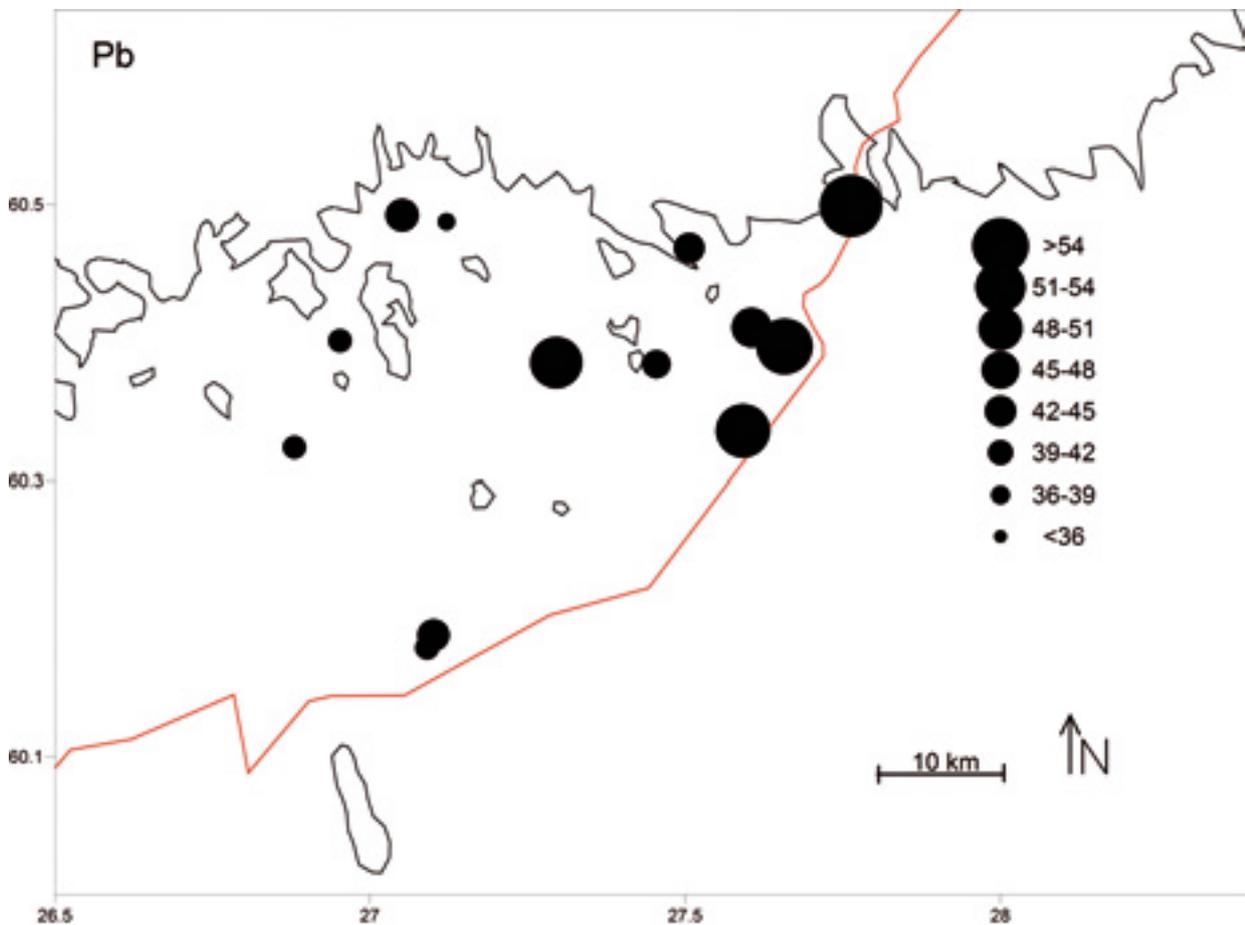


Figure 9. Distribution of lead in the surface sediments (0–1 cm). Concentrations in mg kg⁻¹.

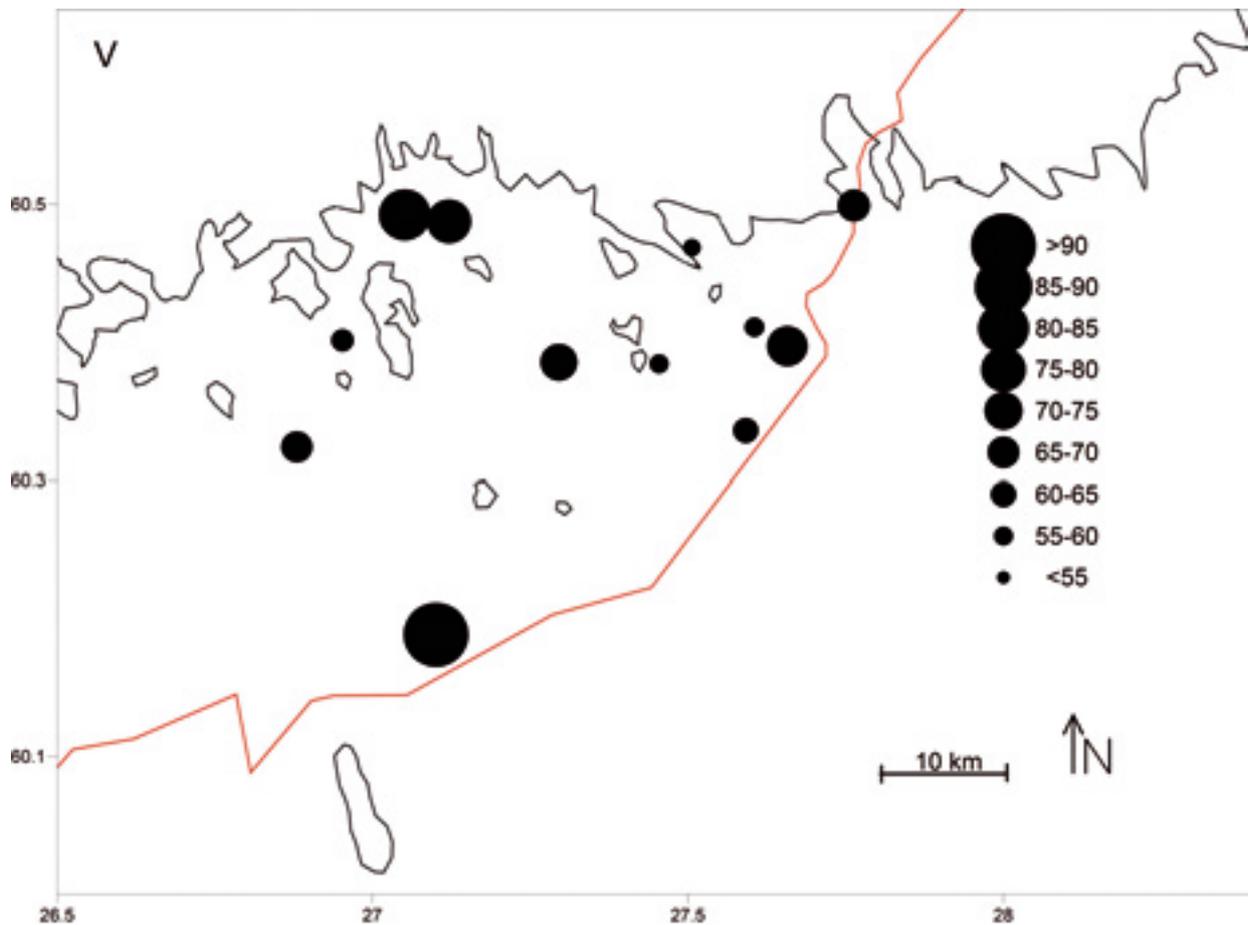


Figure 10. Distribution of vanadium in the surface sediments (0–1 cm). Concentrations in mg kg^{-1} .

this study was much lower than the maximum value of 88 mg kg^{-1} in the earlier study. Pallonen (2004) also reported a considerable decrease in lead concentrations, in some case up to 20 to 40%, from 2000 to 2003. In the case of lead it is probable that this difference can be attributed to a further reduction in the lead load that was already observed in the early 1990s (Vallius & Lehto 1998 and Vallius & Leivuori 1999).

The horizontal distribution of vanadium (Fig. 10) did not exhibit any clear trends, as slightly higher concentrations were found in various locations around the study area. Vanadium concentrations from 20 stations in the off-shore Gulf of Finland have earlier been reported by Leivuori (2000). The average values of the present study were slightly lower than those of that earlier study, but the maximum values of the two studies were on same level. Leivuori (2000) reported a mean value of 76 mg kg^{-1} (66.8 mg kg^{-1} in this study, Table 4) and minimum and maximum values of 57 mg kg^{-1} and 96 mg kg^{-1} , respectively (49.4 mg kg^{-1} and 95.6 mg kg^{-1} in this study, Table 4). The difference in

mean concentrations could be attributed to differences in sample site location or to a real decrease in the vanadium load.

The distribution of zinc showed only a very slight elevation of zinc concentrations in the vicinity of the Finnish-Russian border (Fig. 11). Otherwise, the distribution was quite even throughout the study area. When comparing the data from this study with the earlier study of Vallius & Leivuori (1999), the mean concentrations in the samples of this study (181 mg kg^{-1} , Table 4) were slightly lower than those of the earlier study (199 mg kg^{-1}). The maximum concentration of 260 mg kg^{-1} zinc in this study was also clearly lower than the maximum of 391 mg kg^{-1} zinc recorded earlier. This difference is probably due to differences in the location of sampling sites, with slightly different environments sampled, as Pallonen (2004) noted that in the Kotka area the concentrations of zinc remained rather constant from 1994 to 2003. According to Pallonen (2004), there have been both increases and decreases in zinc concentrations in the coastal area, depending on the sample site.

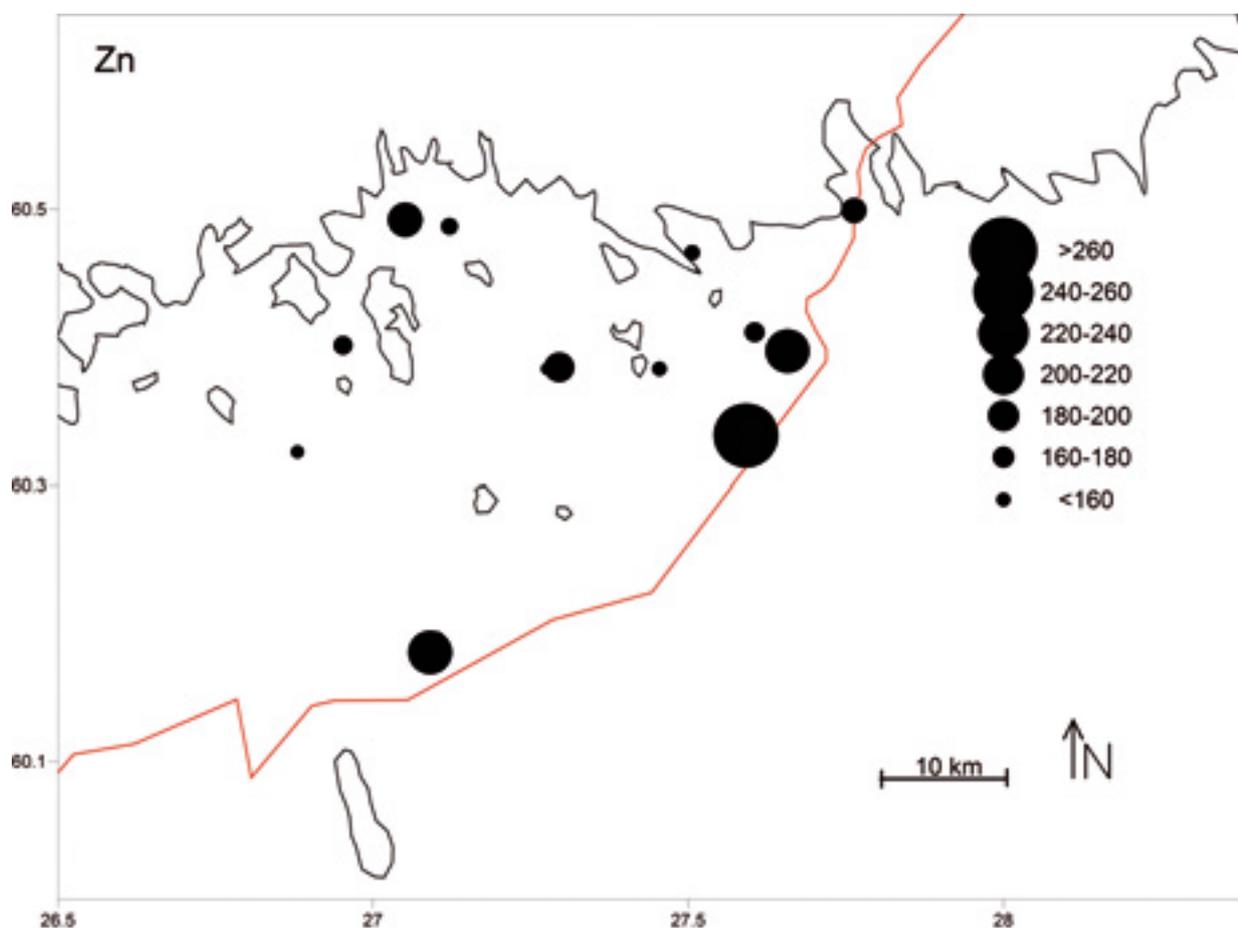


Figure 11. Distribution of zinc in the surface sediments (0–1 cm). Concentrations in mg kg^{-1} .

Classification of contamination

Surface sediments (0–1 cm)

As shown in Table 4, most classified metals were in the contamination classes of little or none (class 1) or slight (class 2) when examining the surface concentrations. Only cadmium, copper, zinc and mercury were clearly strong contaminants of the seafloor sediments in the study area (Naturvårdsverket 1999). All these metals were in the classes of significant or large contamination, but they were still below the values representing very large contamination (class 5).

Deeper sediments (14–15 cm)

Table 5 presents the concentrations of studied metals in the depth layer of 14–15 cm at the studied sites. As expected, the concentrations were higher in the deeper layers and thus the sediment was in many cases classified as more strongly contaminated than in the surface sediments. The worst case

was mercury, whose maximum content of 0.83 mg kg^{-1} reached the class of very large contamination (class 5). This sample (MGGN-2004-20) was not surprisingly from a bay situated immediately outside the eastern outlet of the River Kymijoki. The maximum cadmium concentration of 4.45 mg kg^{-1} was also recorded at a site close to the River Kymijoki outlet (MGGN-2004-10), but in another accumulation basin closer to the port of Hamina; thus, the source of this anomalous peak probably originated in the port instead of the river. This is also supported by the fact that the site closest to the river mouth (MGGN-2004-20) showed clearly lower cadmium values. When looking at the mean values for the elements it is clear that in addition to mercury and cadmium, copper, lead and zinc are also strong contaminants of the sediments in the study area.

Vertical distribution

As can be seen in the classification of the degree of contamination of the cores, there was a clear trend of decreasing concentrations towards the

Table 4. Concentrations and descriptive statistics for studied elements in the surface sediments (0–1 cm). Concentrations in mg kg⁻¹. See the explanations of classes in Table 1. Classification for vanadium is missing in the Swedish EPA

	As	class	Cd	class	Co	class	Cr	class	Cu	class	Ni	class	Pb	class	V	class	Zn	class	Hg	class
Mean	12,5	2	1,56	4	13,2	1	61,3	1	54,1	3	32,2	1	46,1	2	66,8		181	3	0,16	3
Median	13,0	2	1,45	4	13,6	1	58,3	1	50,1	3	32,6	1	44,1	2	66,4		166	3	0,15	3
SD	3,64		0,58		1,80		10,9		9,18		5,02		7,06		12,9		31,8		0,07	
Minimum	7,25	1	0,84	3	10,1	1	45,8	1	42,1	3	20,9	1	37,3	2	49,4		152	3	0,09	2
Maximum	19,1	3	2,69	4	16,1	2	82,7	2	76,3	4	40,5	2	58,9	3	95,6		260	4	0,32	4
Count	14		14		14		14		14		14		14		14		14		14	

Table 5. Concentrations and descriptive statistics for studied elements in the sediments at a depth of 14–15 cm. Concentrations in mg kg⁻¹. See the explanations of classes in Table 1.

	As	class	Cd	class	Co	class	Cr	class	Cu	class	Ni	class	Pb	class	V	class	Zn	class	Hg	class
Mean	13,3	2	2,30	4	18,6	2	91,9	2	62,9	4	41,9	2	69,1	4	90,8		237	4	0,33	4
Median	13,1	2	2,47	4	17,8	2	90,7	2	64,2	4	40,4	2	68,4	4	89,2		238	4	0,31	4
SD	4,24		1,23		4,79		12,4		14,2		3,97		17,8		12,4		44,7		0,19	
Minimum	9,24	1	1,00	3	12,5	1	66,6	1	28,1	2	36,8	2	21,1	1	70,4		112	2	0,17	3
Maximum	25,4	3	4,45	5	30,3	4	111	3	82,8	4	49,3	3	87,8	4	114		297	4	0,83	5
Count	14		14		14		14		14		14		14		14		14		14	

surface of the sediment for all elements except arsenic. Such a trend was also observed in the early 1990s by Vallius & Lehto (1998), Vallius (1999), Vallius & Leivuori (1999) and Leivuori (2000). As an example, Figure 12 illustrates mercury, cadmium and zinc concentrations in cores 20 and 17, these sites representing the extremes in terms of the concentrations of these contaminants. Site 20 is located close to the river mouth while site 17 is the most distantly situated site in the east (Fig. 1), very close

to the border of Finland and Russia. These curves show the typical trend of metal concentrations in cores from the study area. The depths of the anomalies depend on the sampling site, mostly due to differences in the sedimentation rate, but the cores display a common pattern of concentration changes. First, there is an increase from the bottom of the core from pre-industrial values to maximum values, then an anomaly with rather high concentrations, and usually a slow decrease in concentrations near

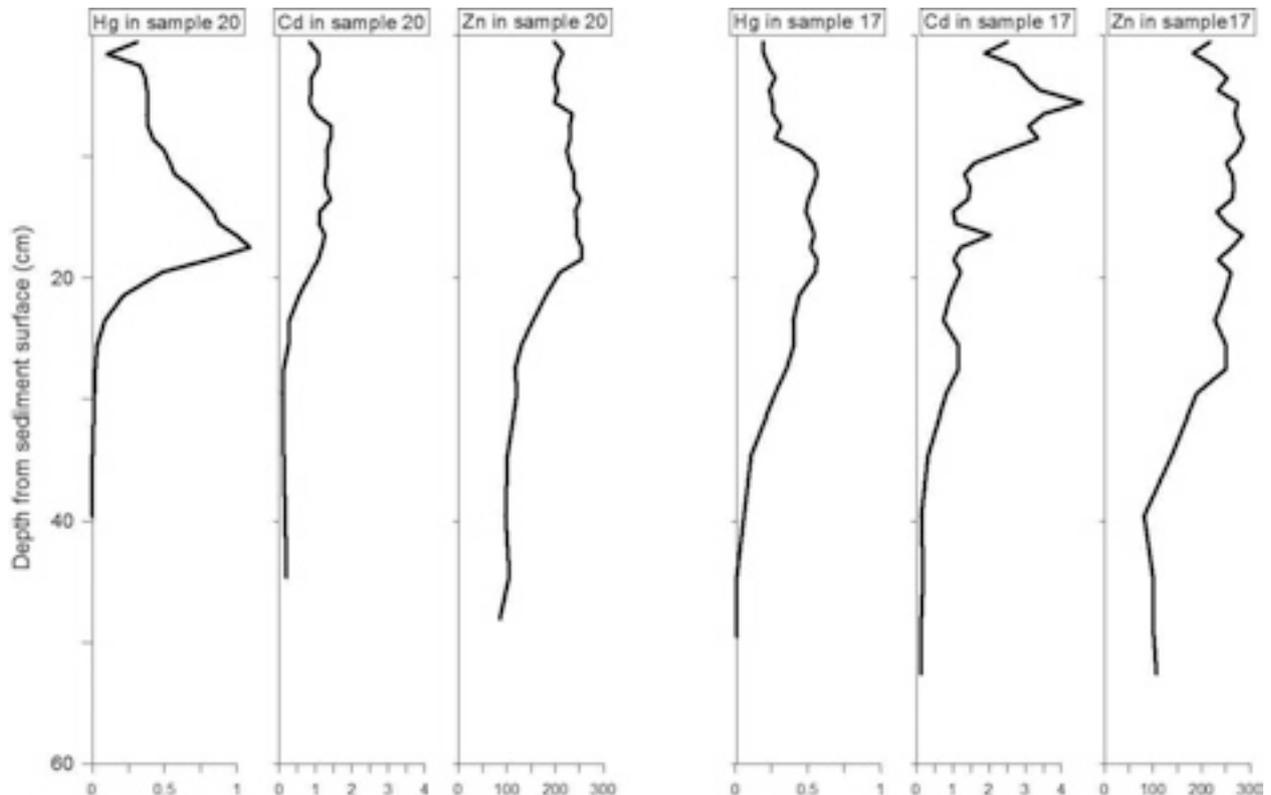


Figure 12. Vertical profiles of mercury (Hg), cadmium (Cd), and zinc (Zn) at stations 20 and 17. Concentrations in mg kg⁻¹.

the surface. In core 20 the decrease in the mercury load from maximum values in the late 1960s is clearly visible. In the same core, cadmium concentrations are rather low in comparison to other sites in the study area. Like mercury, zinc also shows rather high concentrations in the upper half of the core, with only a slight decrease during the last decades. In core 17, mercury concentrations are clearly lower than at site 20 and the concentrations have been steadily decreasing. Cadmium, on the other hand, shows high concentrations in the upper half of the core, with a clear decrease during the last decade or two. The overall concentrations of cadmium are clearly higher in core 17 than core 20. It is notable that at the depth of 3–9 cm in core 17 the concentrations exceed 3 mg kg^{-1} , which is the threshold

for classification as having very large contamination (Table 2), reaching a maximum value of 4.57 mg kg^{-1} at the depth of only 5–6 cm. Thus, sediments very close to the sediment surface at site 17 are very strongly contaminated with cadmium. Zinc in core 17 shows a similar pattern to that in core 20, with an almost negligible decrease during the last decades. Copper has followed a similar trend to zinc, but particularly at site 17 near the border it seems that copper concentrations have not decreased during the last decades. This is consistent with the finding of Pallonen (2004), who also noted an overall slight increase in copper concentrations from 1994 to 2003. The findings at this site can probably be attributed to transport from source areas in the eastern part of the Gulf of Finland.

DISCUSSION

According to the findings in this study, the Kotka–Hamina sea area is in a broad sense a badly polluted area, perhaps one of the worst polluted in the whole Baltic Sea. This is not a surprising result, as similar findings have earlier been published from this area (Kokko & Turunen 1988, Anttila-Huhtinen & Heitto 1998, Verta et al. 1999a,b, and c, and Pallonen 2001 and 2004). Studies from the offshore Gulf of Finland have also indicated that not only the eastern part of the Gulf but also the northeastern part between the cities of Vyborg in Russia and Kotka are largely polluted (Vallius & Leivuori 1999, Vallius 1999b, Leivuori 2000, and Vallius & Leivuori 2003).

The horizontal distribution of most metals does not follow any clear pattern, as there are slight anomalies in different parts of the study area, while on the other hand mercury and cadmium display rather distinct anomalies. Mercury is the main pollutant of the near-coastal areas close to the outlets of the River Kymijoki, while cadmium is the main pollutant in the remote basins in the east and southeast.

The vertical profiles indicate that concentrations of most of the studied metals have decreased during the last decade or two, but the concentrations of especially mercury, cadmium, copper and zinc are still much too high in the sediment surface. As there are even higher concentrations deeper in the sediment, which could easily be exposed by human activity or bottom-dwelling animals and erosion, the situation cannot be considered satisfactory. Copper concentrations seem to decline rather slowly, and at site 17 its concentration has not decreased at all during the last decades.

This study has shown that the distribution of cadmium in the sea area off Kotka is zoned, such that cadmium concentrations in the sediment surface increase towards the east and southeast. This is better seen in the maps of this study than in earlier studies (Kokko & Turunen 1988, Anttila-Huhtinen & Heitto 1998, and Pallonen 2001 and 2004), as the study area here has been extended all the way to the Finnish–Russian border. The higher concentrations close to the border can probably be attributed to cadmium transport to the west from sources in the easternmost Gulf of Finland. This might also be the case for some of the other heavy metals, such as copper and zinc.

The pollution load in the study area is generally decreasing, which can also be seen in the sea-floor sediments. Unfortunately, the process is slow and the concentrations have been so high that a long time will be needed for the area to be normalized. When the surface sediments are classified as largely polluted, in many cases due to high concentrations of especially cadmium and mercury, the situation cannot be considered satisfactory. As there are even more highly polluted sediments close to the sediment surface, at depths of only 10–20 cm where the sediment can easily be exposed due to human activity or burrowing by bottom-dwelling animals, the situation is still very chronic. If dredging is carried out in any parts of the area, which is of course necessary at least along the shipping channels, more metals will be released from the deeper sediments. This will also be the case if dredging is allowed in the river itself.

CONCLUSIONS

The classification used in this paper is taken from Sweden, as no similar classifications are available in Finland. The problem with the Swedish classification is that the intervals within each class seem to be too narrow. In addition, small differences in element concentrations between separate studies from different years might not be of relevance, as the small differences almost fall within the range of analytical accuracy. Thus, such findings should be looked upon as only suggestive.

Geology also plays a role in the interpretation of the level of contamination. As the surveyed area is located within the large Vyborg rapakivi massif, the natural concentrations of many of the studied metals in this area are lower than in areas of supracrustal rocks. Thus, the actual degree of contamination in this area is probably even higher than the measured level, as the classification does not take into account cases where natural levels of metals are clearly lower than average.

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SEAFLOOR ANOXIA AND MODERN LAMINATED SEDIMENTS IN COASTAL BASINS OF THE EASTERN GULF OF FINLAND, BALTIC SEA

by

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Kotilainen, A., Vallius, H. & Ryabchuk, D. 2007. Seafloor anoxia and modern laminated sediments in coastal basins of the Eastern Gulf of Finland, Baltic Sea. *Geological Survey of Finland, Special Paper 45, 49–62, 12 figures and one table.*

Examination of surface sediment cores from the northern coastal basins of the eastern Gulf of Finland, the Baltic Sea, revealed that almost all of the studied basins have been continuously or seasonally anoxic for at least the last 10 years. This can be seen as rather similar laminated sequences in the topmost parts of the sediment cores. Moreover the results indicate an overall shallowing of anoxia since 1950's in the coastal area of the eastern Gulf of Finland. Towards the present, laminated sediments were developed also in the shallower basins.

Extended and prolonged seafloor anoxia could enhance the environmental problems by releasing metals and nutrients, like P, from the seafloor sediments. Anoxic periods at the seafloor of the Baltic Sea have occurred in the past too, but together with increased anthropogenic loading, its effects to the Baltic Sea ecosystem are harmful.

Key words (Georef Thesaurus AGI): Environmental geology, marine pollution, marine sediments, heavy metals, cadmium, mercury, arsenic, classification, Finland, Kotka, Baltic Sea, Gulf of Finland

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INTRODUCTION

The Gulf of Finland is a relatively shallow eastward extension of the main Baltic Sea. It is a rather heavily polluted and strongly nutrient-loaded sea area (HELCOM 2001, 2003, 2004), which is a result of several factors. First of all, the sea is very shallow, the average depth is only 38 m (Vallius 1999). Secondly, the drainage basin includes the capital cities of all the neighbouring countries, Finland, Estonia, and Russia, including large industrial and agricultural areas.

The structure of the archipelago in the eastern part of the Finnish coast is not very complicated. Thus it would be expected rather well ventilated seafloor by oxic surface waters, at least during storms. However, the accumulation basins of modern soft sediment, muddy clays, have been almost entirely anoxic during the last 10 years (Anttila-Huhtinen 2005). This is surprising as these accumulation basins are relatively open towards the open sea, suggesting that there must thus be a process that hinders ventilation or consumes all oxygen that is introduced to the near bottom water. According to the results of Jaala & Mankki (2005) ventilation between surface and bottom waters are poor in winter as well as in the summer. Lack of ventilation of the seafloor, especially in the presence of strong eutrophication, causes local seafloor anoxia, which can persist for long periods. In a study from western Gulf of Finland Vallius (2006) observed seafloor anoxia in coastal accumulation basins, which has persisted for decades.

In 2003 the Geological Survey of Finland (GTK) launched together with the All-Russia Geological Research Institute (VSEGEI) a project in order to acquire new information about the geology of the coastal zone around the national border between Finland and Russia and to describe the zone's environmental condition. The aim of this paper is to report and describe the anoxic bottoms and laminated sediments found in the eastern archipelago of the Gulf of Finland.

Laminated sediments provide an excellent archive for detailed reconstructions of past environmental changes. The development of a laminated sediment sequence requires variation in input/chemical conditions/biological activity that will result in compositional changes in the sediment (Kemp 1996). In the boreal environment, characterized e.g. by strong seasonal contrast of ice cover, spring floods, water column stratification and algae blooms, the annual cycle is the main cause of rhythmic sedimentation. Thus laminated sediments could provide information on annual cycles of sedimentation (Saarnisto 1986). The laminated structure is preserved in sediments only if the environmental conditions are favourable (e.g. no bioturbation, no water turbulence in sediment-water interface) (Renberg 1982, Saarnisto 1986). In the marine environment the dominant control on lamina preservation is reduced sea bottom oxygen conditions (Kemp 1996).

STUDY AREA

The study area of this paper covers the eastern archipelago of the Finnish side of the Gulf of Finland (Fig. 1). Thus it covers the area between latitude 60° 10' N and 60° 30' N and between longitude 26° 50' E and 27° 45' E, a sea-area of approximately 1100 km². It is situated on the north-eastern coast of the Gulf of Finland. The southern and south-eastern parts of it comprise open sea with water depths up to some 90 meters. There are some bigger islands and in the north the study area borders mainland. The inner archipelago is typically a mosaic of islands of different shape and size. Similarly the seafloor in north consists of a mosaic of

rather small, relatively shallow and isolated accumulation basins. In the south and east the accumulation basins are clearly larger as the seafloor between the sparse islands is more even. The water depth increases from land in the north to the deepest parts in south. The deepest sampled site is MGGN-2004-23 (04-23) with a water depth of 72 metres.

On the northern coast there are two cities, Kotka and Hamina, with rather large industrial and harbour activities, which affect the surrounding marine environment. Several rivers, like Kymi River and Virojoki River, drain into the area.

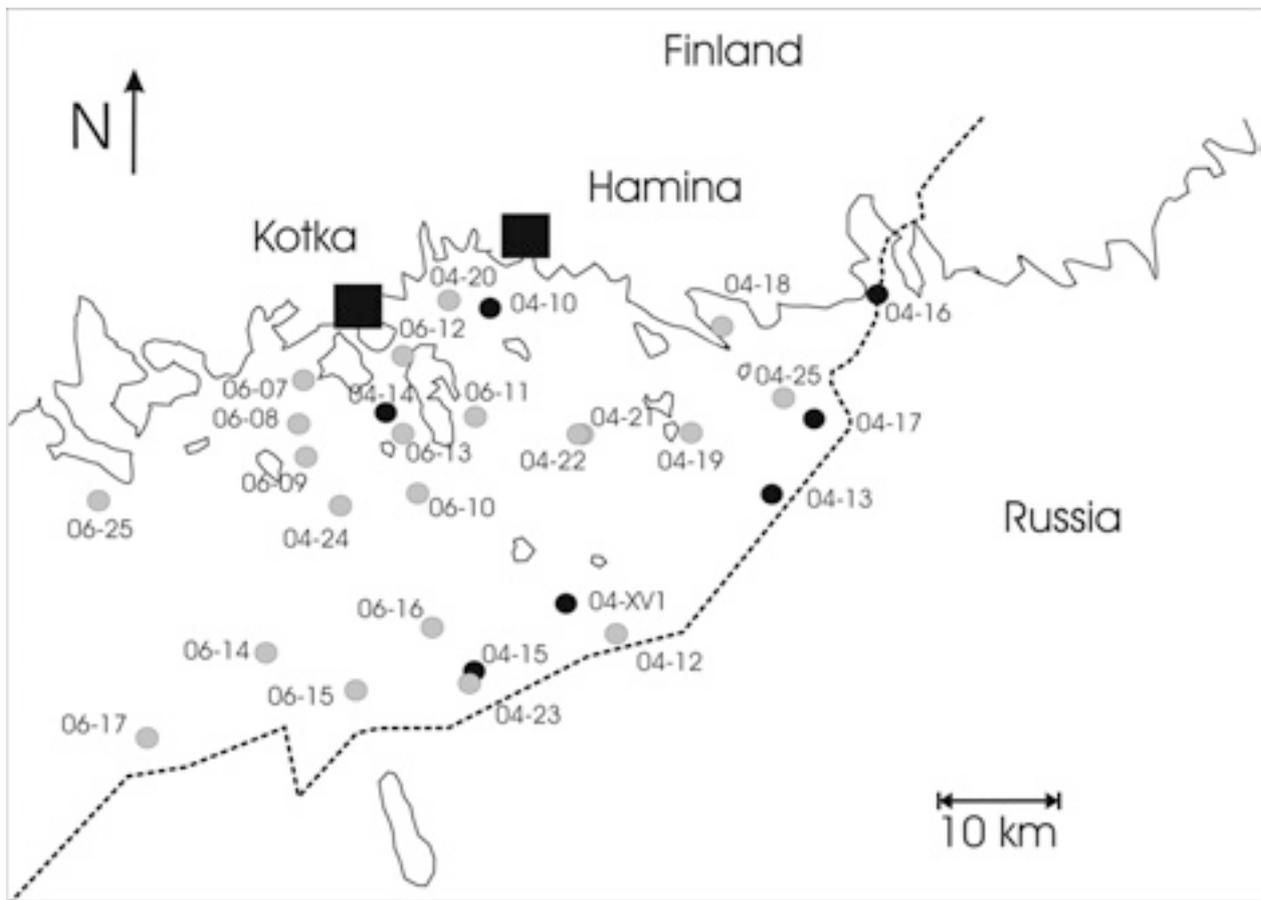


Figure 1. The study area in the eastern archipelago of the Finnish side of the Gulf of Finland, the Baltic Sea. Seafloor sediment sampling locations have been indicated by black and grey dots. Site 06-26 is located outside of the map area.

EARLIER STUDIES

Several authors have reported studies on nutrient and dry matter distributions and/or accumulations in the Gulf of Finland (Pitkänen et al. 1987, 2001, Tervo & Niemistö 1989, Grönlund & Leppänen 1990, Emelyanov 1995, Perttilä et al. 1995, Leivuori 1996, 1998, 2000, Kankaanpää et al. 1997a, 1997b, Leivuori & Vallius 1998, Vallius 1999, Vallius & Leivuori 2003, Lehtoranta 2003, Weckström 2006). Some of these studies (Vallius 1999, Leivuori 1998, Vallius & Leivuori 2003) imply that the situation in the Gulf of Finland is not good, but that at least in some aspects (e.g. decreased heavy metal concentrations in the surface sediments) it might be improving. Eutrophication is considered as the worst problem of this brackish sea. A clear sign of eutrophication are the massive algal blooms that during hot summers have occurred in the Baltic Sea and especially the Gulf of Finland (Rantajärvi 1998). Internal loading from bottom sediments is regarded as one of the main reasons, together with the ongoing, although clearly decreased, release of nutrients through human activities (HELCOM

2001, 2002, Pitkänen et al. 2001). Internal loading is closely linked to seafloor oxygen deficiency. In the anoxic conditions nutrients (e.g. phosphorus) are released from the seafloor sediments. The latest observations, which show that seafloor anoxia in the Gulf of Finland was extended larger than in 44 years (FIMR 2006), do not unfortunately forecast improving trend of internal loading, and thus of eutrophication.

A few studies have examined the environmental situation in the coastal region of the Gulf of Finland (National Board of Waters 1983, Pitkänen 1994, Puomio et al. 1999, Kauppila & Bäck 2001, Lehtoranta & Heiskanen 2003). In a study of all Finnish coastal waters Kauppila & Bäck (2001) provide a good summary of all related coastal studies; most areas were classified as satisfactory, passable, or even poor.

There are also several earlier studies published from the sea area around Kotka, Hamina and the outlets of Kymi River. This is mainly because the Kymi River is known to be largely polluted by

heavy metals and organic pollutants. One of the first reports was the report by Kokko & Turunen (1988), who describe large mercury contamination in the river sediment-profile caused by discharges during late 1950's and early 1960's. Later biota was according to Partanen (1993) largely affected by eutrofication in the outlets of Kymi River, but no chemical analyses were reported. Anttila-Huhtinen & Heitto (1998) and Verta et al. (1999a, 1999b, 1999c) have reported large scaled contamination of river and sea floor sediments of the Kymi River and

in the sediments of the sea area outside the river outlets. Pallonen (2001, 2004) reports accumulation of nutrients and harmful substances in this area and finds out that accumulation of nutrients from the Kymi River is still high. Anttila-Huhtinen (2005) and Jaala & Mankki (2005) also report the status of the sea-area and find it eutrophied, and its seafloor partly "dead".

Detailed sedimentological studies of surface sediment cores of this coastal area are relatively scarce.

MATERIAL AND METHODS

The samples for this study were collected during the SAMAGOL cruises of R/V Geola of the Geological Survey of Finland (GTK) on May 24th to June 4th 2004, and R/V Geomari of the GTK in May-October 2006. Altogether 27 sites were sampled with a twin-barrel gravity corer. Additionally 2 samples were taken on board R/V Aranda on August 28th 2004. Sampling sites were chosen carefully according to surveyed echo sounding data. The gravity corer used is a GEMAX twin barrel gravity corer with an inner diameter of 90 mm of the core liner. The core length varied between 22 cm and 72 cm, most of the cores reached 50 cm in length. After sampling one of the two cores obtained was usually split vertically for description and the other one was used for sub-sampling. The description core was vertically split, photographed, and described. Standard GTK description forms were used. The 10-mm thick sliced sub-samples of the other core were stored on board at 4–6 °C. The samples originally labelled MGGN-year-number will be abbreviated thereafter 04-number and 06-number for year 2004 and 2006 samples, respectively.

In the laboratory, the samples were weighed for wet weight, freeze-dried and weighed for dry

weight. All samples were sieved <2 mm in order to remove objects larger than 2 mm (plant and animal remains, FeMn-concretions). The grain size of the investigated modern mud is so fine that no finer sieving was considered necessary. Finally, the samples from different depths from all sampled cores were analyzed for carbon and nitrogen using a Leco CHN-600 instrument. Phosphorus and heavy metal (not reported here) concentrations were obtained from the inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) analyses (Vallius & Leivuori 1999, 2003). It has been reported (Carman & Cederwall, 2001) that in the sediments of the Gulf of Finland total carbon is mainly composed of organic carbon. Thus, total organic carbon (TOC) analyses were not made in the present study.

Seven cores were dated for ¹³⁷Cs by gamma spectrometry using an EG&E Ortec ACE™-2K spectrometer with a 4" NaI/Tl detector. The ¹³⁷Cs curves of these analyses mark the depths of the sediment accumulated from the trajectory of the Chernobyl nuclear power plant accident of April 24th 1986.

RESULTS

Surface sediment cores

A total of 29 sites were sampled in the eastern archipelago of the Finnish side of the Gulf of Finland, the Baltic Sea (Table 1). The sampling locations, from water depths between 13.2–72 m, were selected carefully using acoustic (echo-sounding) profiles. Sites 04-12, 04-15, 04-23, 04-XV1, 06-14,

06-15, 06-16 and 06-17 are located in the outer archipelago/open sea area and the rest of the sites in the inner archipelago. On acoustic profiles, a weak, transparent light layer was recognizable above the substrate at all locations, indicating (relative recent) accumulation at the sea bottom. The length of recovered sediment cores varied from 22 up to 72 cm (Table 1).

Table 1. Characteristics of surface sediment cores; core, site location (Lat, Lon), water depth (m), length of sediment core (cm), thickness of laminated sediment sequence (cm) in the uppermost sediment column, number of counted lamina, and bottom class for the surface sediments. Thickness (cm) of the oxic surface sediment layer is indicated in parenthesis.

Core	Latitude (N, WGS84)	Longitude (E, WGS84)	Water depth(m)	Length of the sediment core (cm)	Thickness of non-disturbed laminated sequence (cm)	Number of counted lamina couplets (triplets)	*Bottom class and thickness of brown layer (cm)
04-10	60.29257	27.07289	16.8	38	15	?	oxic (2)
04-12	60.13150	27.19139	61	41	10	?	anoxic/bm
04-13	60.20141	27.35485	39	58	27.5	34	oxic (0.2)
04-14	60.24069	26.57141	20.2	50.5	11	13	oxic (0.4)
04-15	60.11298	27.06029	63.5	60	5.0	>3	anoxic/bm
04-16	60.29940	27.45774	16	32	1.4	3	oxic (0.3)
04-17	60.23809	27.39399	43.5	50	19.7	51	oxic (1.2)
04-18	60.28111	27.30370	14.3	30	9.1	12–13	oxic (0.3)
04-19	60.23043	27.27252	30	53	25.7	29	oxic (0.2)
04-20	60.29537	27.03062	13.2	50	9.5	10	oxic (0.6)
04-21	60.23117	27.17723	38.3	56	12	19	oxic (0.3)
04-22	60.23053	27.16577	38	42	6.0	6–7	oxic (0.6)
04-23	60.10751	27.05432	72	47	9.2	12	anoxic/bm
04-24	60.19428	26.52788	38	61	7.5	4	oxic (0.3)
04-25	60.24629	27.36313	39.7	72	24.5	53	oxic (0.2)
04-XV1	60.14942	27.15898	60	50	7.9	11	anoxic/bm
06-07	60.26070	26.49640	20	58	12	12	oxic (1.0)
06-08	60.24250	26.48790	36	61	19.5	>13	anoxic/bm
06-09	60.22127	26.49484	31	45	7.8	8	oxic (0.5)
06-10	60.19800	27.00910	38	45	?	?	oxic (1.0)
06-11	60.23620	27.05370	29	58	37	30	oxic (1.0)
06-12	60.26670	26.59150	15	49	0	0	oxic (1.5)
06-13	60.22980	26.57900	26	45	22	17	oxic (1.0)
06-14	60.11860	26.45500	52	42	10	9	oxic (0.3)
06-15	60.10100	26.53980	51	22	4.0	6	anoxic/bm
06-16	60.12960	27.00820	58	60	8.5	?	anoxic/bm
06-17	60.05470	26.27230	60	66	4.0	?	anoxic/bm
06-25	60.19529	26.29047	25	58	20.7	34	anoxic/bm
06-26	60.14864	26.07645	41	56	18.5	57	anoxic/bm

*Bottom class at the time of sampling, bm indicates occurrence of white bacterial mat at the surface of the sediment.

Sediments and sediment structures

The sediments were mainly gyttja clay or clayey gyttja. Plant material were found at the surface of cores 04-13, 04-14 and 06-15, and in the subsurface depths of cores 04-19, 04-20, 04-21 and 04-22. Coarser material were found in the lowermost part of some cores; 04-10 (33–38 cm) sandy clay, 04–13 (43 cm) sandy silt (Fig. 2), 06-11 (54 cm) sand, 06-13 (22–26 cm) sand and stones, 06-14 (19 cm) silt. FeMn -concretions were found in the subsurface depths of two sediment cores. Spherical FeMn -concretions was found in the core 04-10 below the depth of 33 cm. In the core 04-22 discoidal FeMn -concretions, with diameter greater than 10 mm, and some small spherical -concretions were found between depths of 6 and 9 cm (Fig. 3).

Surface sediments were categorized onboard roughly into 2 classes (oxic and anoxic) according to their visual characteristics (Table 1). In the oxic (or suboxic) sediments surface layer was fluffy with high water content, and brown (or greyish brown)

in colour (Fig. 4). These brown surface sediments were observed in 19 sediment cores. Thickness of the brown sediment surface layer varied between studied sites from 2 up to 20 mm (Table 1). It has been suggested that the brown colour is indicative of the presence of solid Fe(III) (oxy)hydroxides, which precipitated under oxidizing conditions (Mortimer 1941, 1942). Thus it was interpreted that brown colour of sediment indicates oxic conditions at the sediments surface. These oxic bottom sediments occurred in the basins with water depths between 13 and 52 meters (Fig. 5), however mainly in the water depths shallower than 40 meters. The black surface sediments were observed in 10 sediment cores, and all of them included white bacterial mats at the sediment surface. The black colour of sediment is typical for reduced Fe(II) monosulphides (Mortimer, 1941, 1942). Thus the black surface sediments were interpreted to indicate reducing conditions at the sediment surface, anoxic conditions at the seafloor. The black coloured sediments occurred in all outer archipelago/open sea

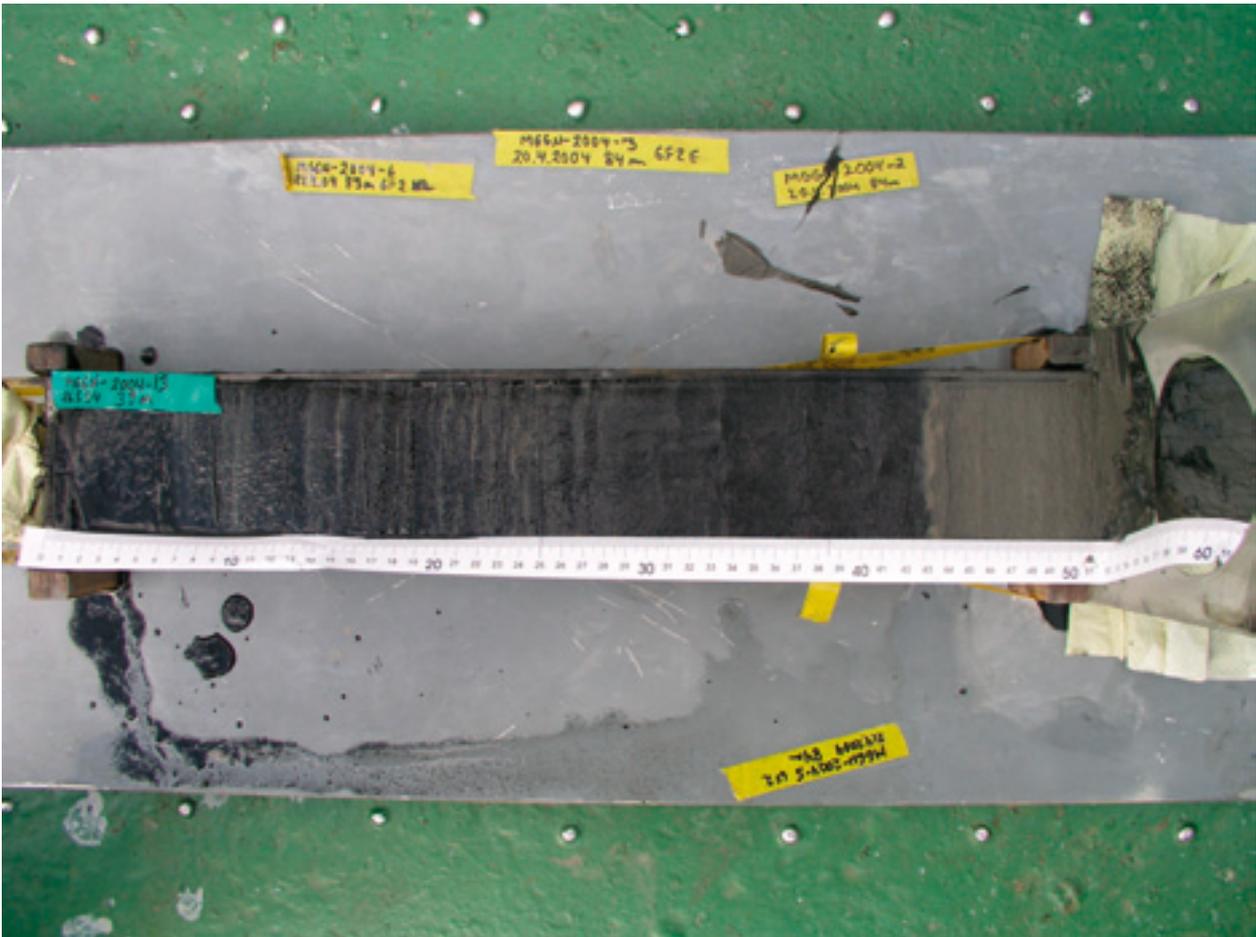


Figure 2. Photograph of the sediment of core MGGN-2004-13.

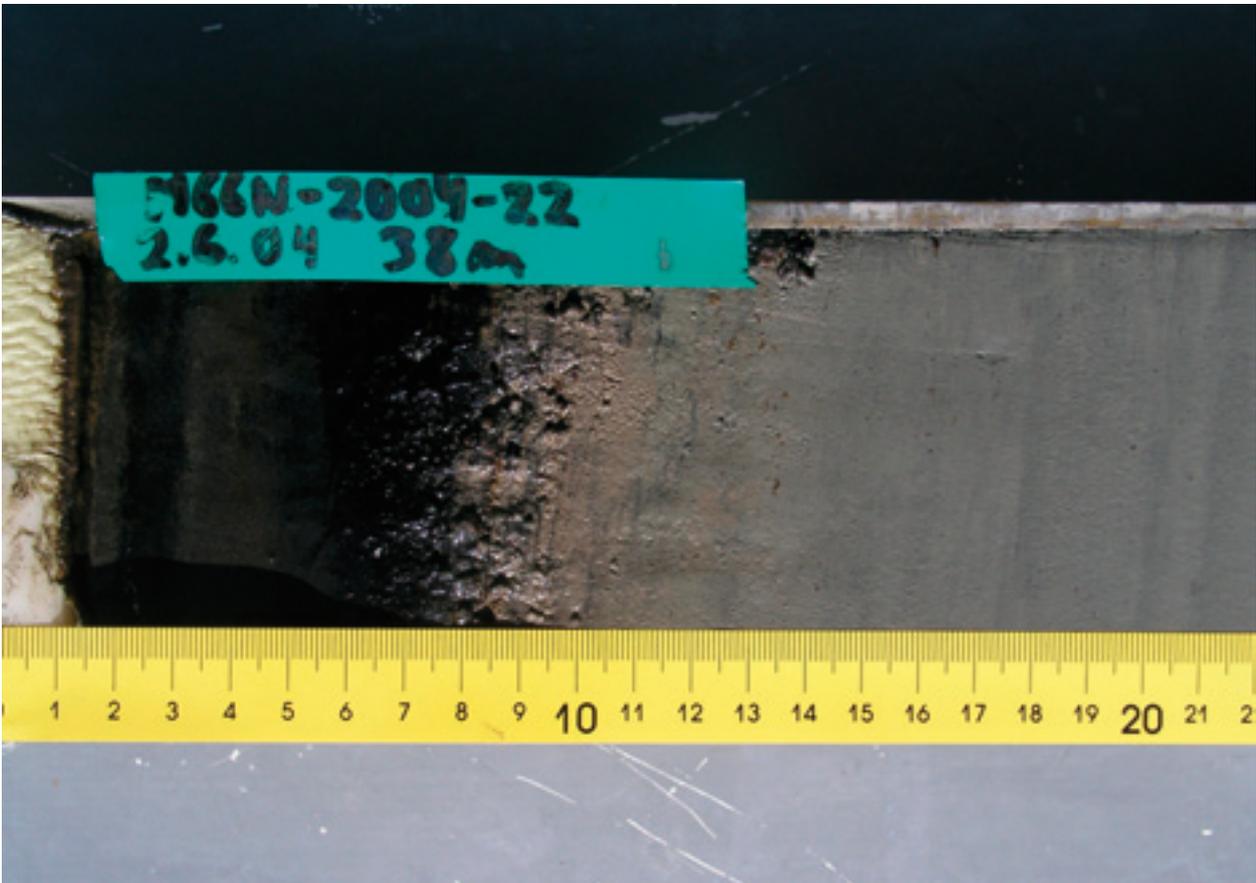


Figure 3. Photograph of the splitted sediment of core MGGN-2004-22.



Figure 4. The surface layer in the sediment of core MGGN-2004-22.

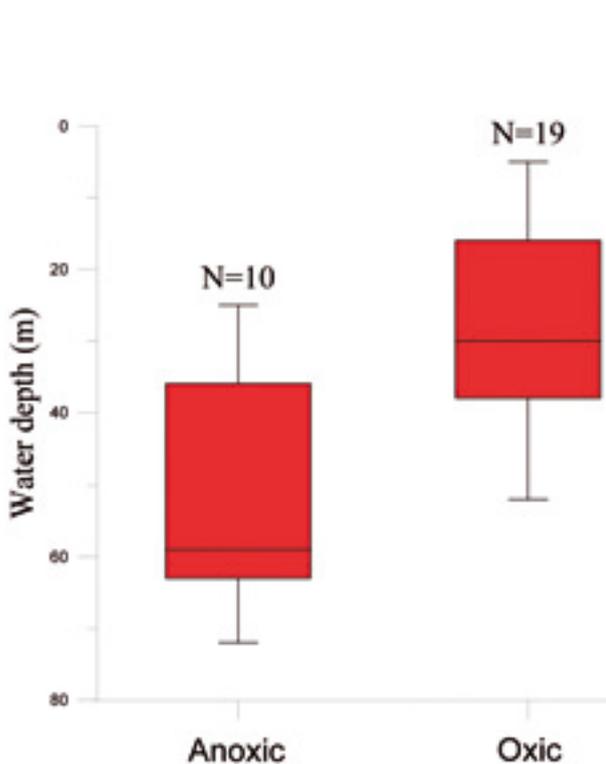


Figure 5. Box-and-whiskers plot of the distribution of anoxic and (sub)oxic bottoms with the water depth (in meters).

sites (except at site 2006-14). The anoxic bottoms were found in the basins with water depths between 25 and 72 meters (Fig. 5), however mainly in the water depths greater than 40 meters.

Living bottom fauna were observed at the surface of several cores (04-10, 04-14, 04-17, 04-20, 04-21, 04-22, 04-23, 04-24, and 04-25). In the sediment cores recovered during 2006 expeditions no living bottom fauna were observed. However traces (ichnofossils) like burrows can be seen in some intervals of several sediment cores.

Vertical variation in the sediment structure, between homogenous (massive), partly laminated and laminated (and back), was observed in several studied cores. In all cores, except the core 06-12, laminated sediments occurred at the topmost part of the core. Thickness of laminated sediment unit varied from 1.4 to 37 cm (Table 1). Lamina structure composed mainly of brownish – light olive grey, olive grey, dark grey – black and white layers (laminae), or different combinations of them (couplets, triplets and quadruplets). The white laminae were relatively scarce and usually very thin ($\ll 1$ mm). These structures are similar to clastic-organic varve structures

(Renberg 1982). Mifrofabric studies of laminated sediments were not done in the present work. Lamina counts show that thickness of a single couplet (or triplet/quadruplet) varies from <1mm up to 20 mm. The total number of lamina couplets (or triplets/quadruplets) in the uppermost laminated sediment unit varies between sites from 3 to 57 (Table 1). Thickness of laminated sediment unit

correlate relatively well with the total number of lamina couplets in the unit (Fig. 6), which is obvious. Results suggest also that at the deeper sites (greater water depth), in the inner archipelago, the total number of lamina couplets in the uppermost laminated sediment unit is generally larger than in the shallower locations (Fig. 7). However, this is not the case for the open sea sites.

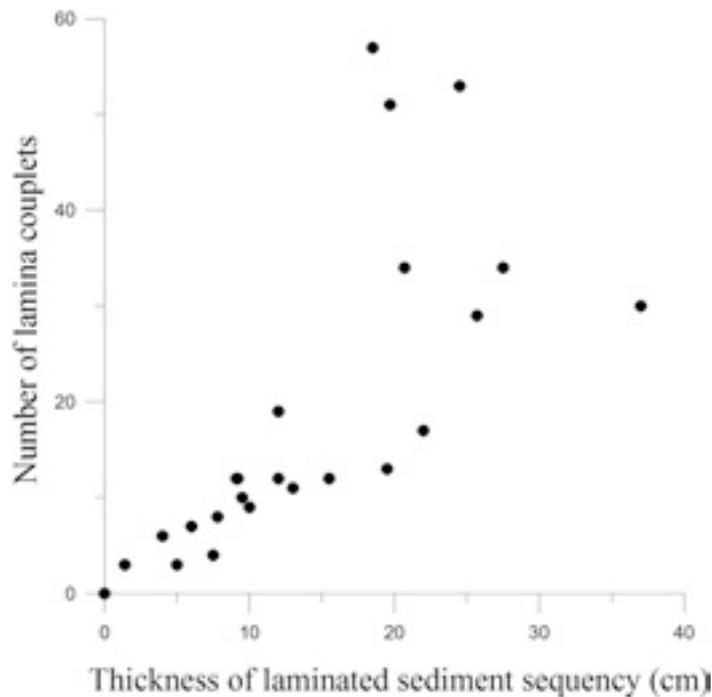


Figure 6. Thickness of the laminated sediment unit (in centimetres) vs. the total number of lamina couplets.

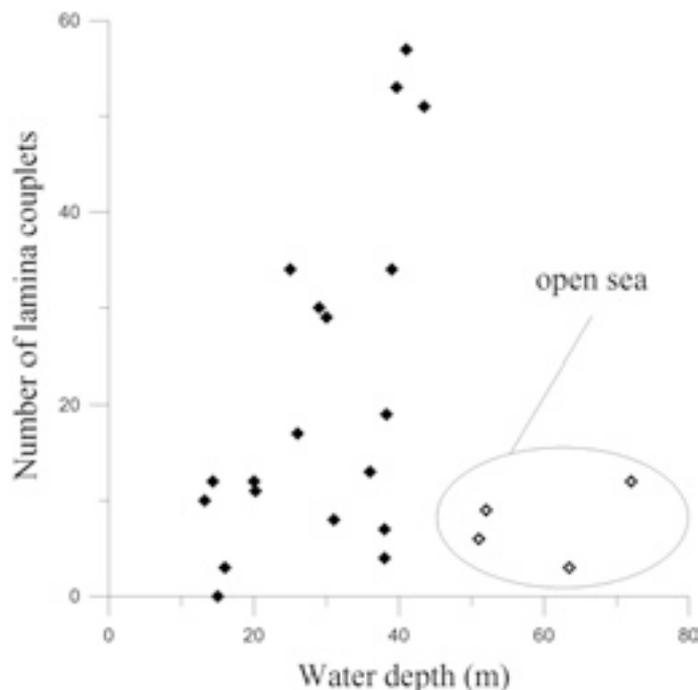


Figure 7. Water depth (in meters) vs. the total number of lamina couplets in the uppermost laminated sediment unit.

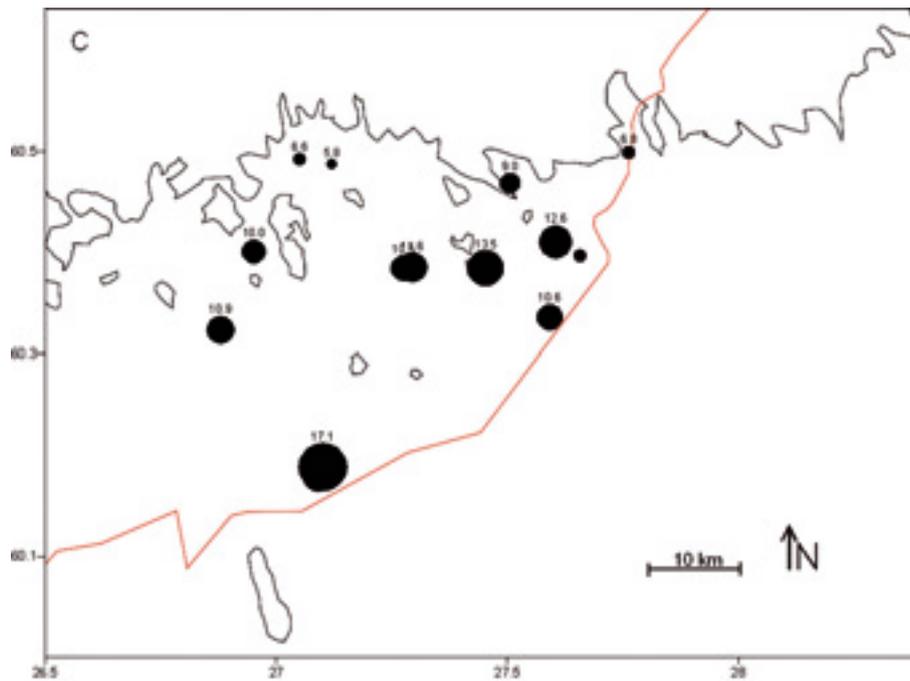


Figure 8. Total carbon content (% dry weight) in the surface (0–1 cm) sediments.

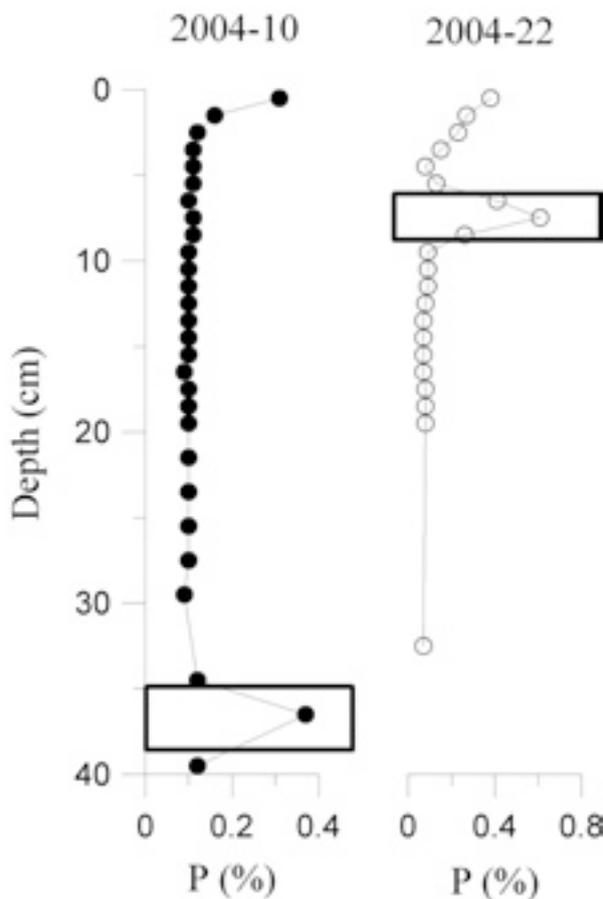


Figure 9. The vertical distribution (% dry weight) of phosphorus (P) in the sediment cores MGGN-2004-10 and MGGN-2004-22. The rectangles indicate the subsurface depths where FeMn –concretions were observed.

Total carbon (TC) concentrations in the surface sediments (0–1 cm) varied between 5.8–17.1 % (dry weight) (mean 10.5 %) (Fig. 8). The highest concentration was in the core 04-15. Generally the TC concentrations decrease downwards in the sediment core. In the lowermost subsamples (usually 40 cm or deeper) the total carbon content varied between 1.1–4.1 % (mean 3.2 %). Figure 8 shows that the TC concentrations in the surface sediments are greater in the open sea area than in the archipelago.

Total phosphorus (P) concentrations in the surface sediments (0–1 cm) varied between 0.18–0.43 % (dry weight) (mean 0.31 %). The total P concentrations mainly decrease downwards in the sediment core. However, in the cores 04-10 and 04-22 the highest P concentrations (0.37 and 0.61 % dry weight) occurred at the depths of 35–38 and 7–8 cm, respectively (Fig. 9). These values occurred at the depths where FeMn –concretions were found in the sediment cores. Note, concretions of size larger than 2 mm were sieved away, micro-concretions are probably included in analysed samples.

Datings

Recent sedimentation rates were determined using ^{137}Cs distribution in the sediment cores. It was estimated that the strong increase of the ^{137}Cs activity in the sediment cores corresponds to the fall-out of the Chernobyl nuclear power plant accident of the year 1986. In the cores 04-10, 04-13-17 and 04-25 this increase of the ^{137}Cs activity was found at the depths of 15.5, 12, 16, 14.5, 18 (?), 9 and 8.5 cm, respectively (Fig. 10). These results suggest that the linear net accumulation rates at these sites (since 1986) have been 8.6, 6.7, 8.9, 8.1, 10 (?), 5 and 4.7 mm a^{-1} , respectively. Figure 11 indicates that the increase of the ^{137}Cs activity in the core MGGN-2004-25, found at the depth of ~ 8.5 cm, corresponds relatively well with the lamina counts. This suggests that the lamina couplet (triplet and quadruplet) could represent a single annual unit. Using data from both, the ^{137}Cs determinations and

the lamina counts, we estimated timing of the onset of the accumulation of the latest laminated sediment unit in the eastern archipelago of the Gulf of Finland. In the early 1950's laminated sediments were developed (and preserved) only in the deepest basins of the inner archipelago (Fig. 12). Towards the present, laminated sediments were developed also in the shallower basins. Results indicate an overall shallowing of the anoxia (OSA) in the area since 1950's (Fig. 12).

In some of the studied sites coarser material were found below the soft surface sediments. Thus it was also possible to estimate the onset of the accumulation of these gyttja clays using data from both, the ^{137}Cs determinations and the lamina counts. We suggest that this drastic change in sedimentation occurred between ~ 1950 –1997 at different sites. In the sediment cores 04-10, 04-13, 04-22, 06-11, 06-13 and 06-19 this onset was estimated at ~ 1966 , 1951, 1997, 1962, 1989 and 1989, respectively.

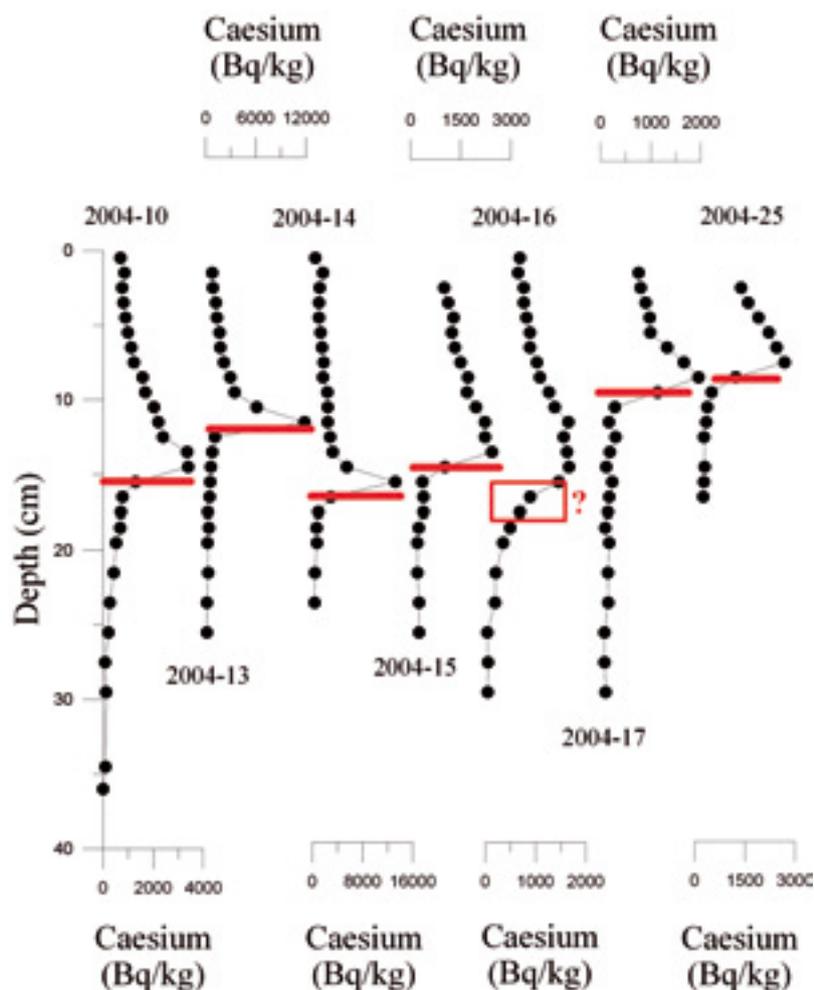


Figure 10. The ^{137}Cs activity in the sediment cores MGGN-2004-10 and MGGN-2004-13-17. The red lines correspond to year 1986.

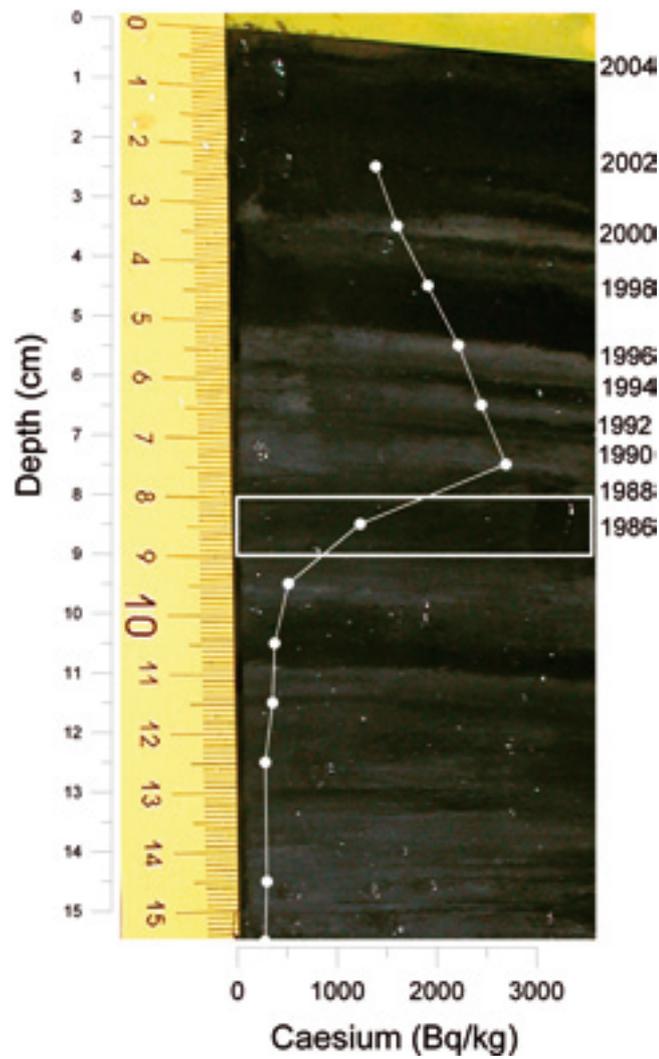


Figure 11. The ^{137}Cs activity (white dots) in the sediment core MGGN-2004-25. The rectangle indicates the subsurface depth where caesium concentration increases, probably due to Chernobyl fallout in year 1986. The dashed lines show the lamina counts.

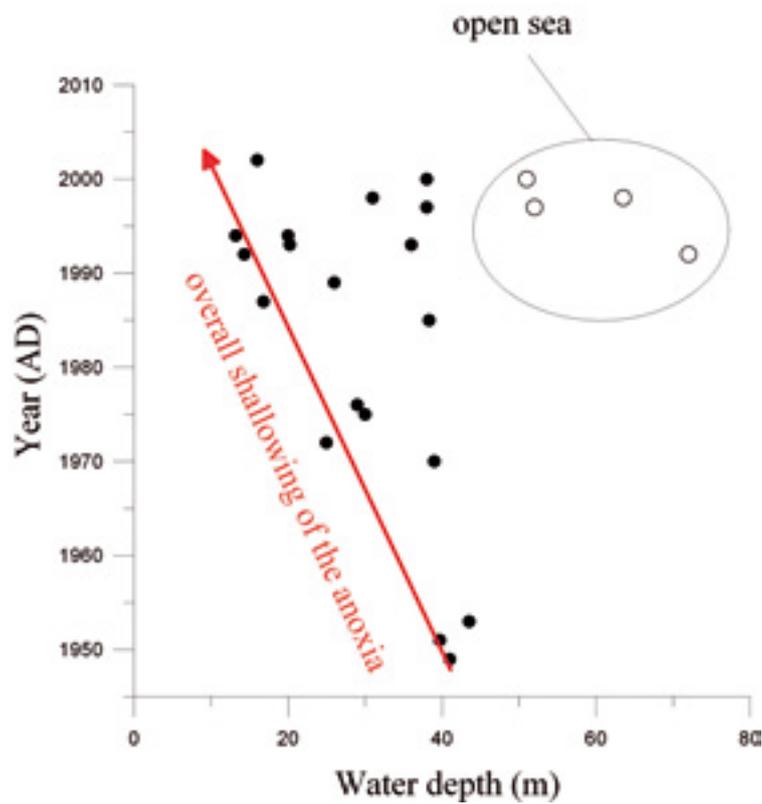


Figure 12. The onset (year AD) of the accumulation of the uppermost laminated sediment unit in the eastern archipelago of the Gulf of Finland vs. water depth (m). The open circles indicate the open sea sites.

DISCUSSION AND CONCLUSIONS

Sediment recovered from the coastal basins of the eastern Gulf of Finland reveal several drastic changes in the area during the last decades. Generally the soft sediments (gyttja clay or clayey gyttja) have been accumulated in the studied basins over the past centuries or even millennia. This is verified also by the acoustic surveys (echo-sounding). However at some sites the accumulation of gyttja clays has started just during the end of the last millennia (~1950–1997). Temporal and spatial distribution of this onset does not show any significant correlation. It rather suggests the patchy nature of sedimentation in the area. However the studied sites are still scarce and new sites are needed to make more reliable conclusions of this change in sedimentation.

Observations of FeMn -concretions in the subsurface depths of two sediment cores also indicate the changes in the environment. During the formations of these FeMn -concretions the seafloor conditions at these locations were oxic, and accumulation did not occur at these sites.

To estimate the trends and state of oxygen conditions at the seafloor we used sediment data. In some earlier successful studies the surface sediments have been divided into three classes (oxic, suboxic and anoxic) according to their visual characters (Virtasalo et al. 2005). In the present work, however, we categorized the surface sediments just into two classes (oxic and anoxic), including possible suboxic sediments into oxic category. According to this surface sediment classification, our results show that the oxic bottoms occurred mainly in the basins with water depths shallower than 40 meters. The anoxic bottoms, with white bacterial mat (probable *Beggiatoa* sp.) were found mainly in the basins with water depths greater than 40 meters (Fig. 5). It should be noticed that these results show the state of oxygen conditions at the seafloor only during the time of coring. Moreover, the used cores were recovered during two field seasons, 2004 and 2006. Occurrence of laminated sediments at the topmost part of the sediment core at almost every site suggests that conditions between oxidizing and reducing have been shifted several times at the seafloor. The laminated structure is preserved in these sediments probably due to the depleted oxygen conditions of the sea floor (bottom water), and thus decreased bottom fauna activity. We used data from both, the ^{137}Cs determinations and the lamina counts, for dating the onset of the accumulation of this latest laminated sediment unit. We suggest that the observed lamina couplet (triplet and quadruplet) represent a single annual unit. The annual nature of the laminae couplets, e.g. the annual diatom

succession (Simola 1977, 1979), was not studied and confirmed here. However the ^{137}Cs determinations used for dating of sediment cores are relatively reliable. Using this information from laminated sediments we suggest that the studied coastal basins of the eastern Gulf of Finland have been, at least seasonally, anoxic for at least the last 10 years. In the early 1950's laminated sediments were developed (and preserved) only in the deepest basins of the inner archipelago (Fig. 12). Towards the present, laminated sediments were developed also in the shallower basins. These results indicate an overall shallowing of the anoxia (OSA) in the area since 1950's. Our results are in line with the latest monitoring results, which show that the oxygen situation near the bottom of the Gulf of Finland is worse than it has ever been during 44 years of surveys by research vessel Aranda (FIMR 2006). Results from macrozoobenthic monitoring, which indicate degradation of macrofaunal communities in the coastal basins and open sea areas of the Finland (Haahti & Kangas 2006), support our results too. Increased P concentrations of near-bottom water in the eastern Gulf of Finland off Haapasaari during the early 1990's (Pitkänen et al. 2001) could also be related to these changes in oxygen conditions. Results from the deeper areas of the Baltic Sea suggest also that the area of laminated sediments started to expand in the late 1950's (Jonsson et al. 1990).

Our observations, that anoxic surface sediments (anoxic bottoms) were not found shallower than 25 meters, do not explain the preservation of laminated sediment structures in the shallow water depths. It requires decrease in bottom fauna activity during some periods of time. We suggest that the lamina preservation in these depths is controlled by seasonally depleted oxygen conditions of the seafloor. Even though there are not so many islands in the archipelago of the area; the complex topography of the seafloor might control the oxygen conditions at the seafloor, together with strong thermal stratification in summer and accumulation of the organic material into the seafloor. The observations, that oxic surface sediments (oxic bottoms) were not found in the water depths greater than 52 m, could be explained by the halocline depth that is in the summer at a depth of 60 m in the Gulf of Finland (Haahti & Kangas 2006).

Extended and prolonged seafloor anoxia could enhance the environmental problems by releasing metals and nutrients, like P, from the seafloor sediments. In the Gulf of Finland large areas of the seafloor are covered by FeMn -concretions, thus degraded oxygen conditions at the seafloor could cause se-

vere changes in nutrient balance. Anoxic periods at the seafloor of the Baltic Sea have occurred in the past too, but together with increased anthropogenic loading, its effects to marine environment are harmful.

The results shown here are suggestive and more fieldwork, and especially long sediment cores, is required to confirm and complete these preliminary results.

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Holocene sedimentary environment and sediment geochemistry
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Background concentrations of trace metals in modern muddy clays
of Eastern Gulf of Finland, Baltic Sea
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BACKGROUND CONCENTRATIONS OF TRACE METALS IN MODERN MUDDY CLAYS OF THE EASTERN GULF OF FINLAND, BALTIC SEA

by
Henry Vallius

Vallius, H. 2007. Background concentrations of trace metals in modern muddy clays of Eastern Gulf of Finland, Baltic Sea. *Geological Survey of Finland, Special Paper 45, 63–70, 2 figures and 3 tables.*

The modern soft surface sediments in the sea area off Kotka in the Northeastern Gulf of Finland was surveyed for heavy metal concentrations. Altogether 10 sites were sampled with a gravity corer for chemical analyses. Data gathered during a three years period from the Northeastern Gulf of Finland with background concentrations of 12 trace metals is presented as a baseline for future studies and for sediment guidelines.

Key words (Georef Thesaurus AGI): Marine environment, coastal environment, marine sediments, cores, laminations, anaerobic environment, sedimentation rates, Cs-137, Finland, Baltic Sea, Gulf of Finland

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INTRODUCTION

The clays of recent decades and centuries have collected the best possible mixture of land and sea-derived material, reflecting the geological, and biological background as well as the amount of matter, which has been released by human activity. In the marine environment this material is the best possible matrix for evaluation of environmental change through time. Data on background concentrations of metals in muddy clays are valuable when dealing with estimates on the human impact of the marine environment. Sediment quality issues have become an important focus in the environmental assessment, protection, and management of marine ecosystems. In spite of this, in very few countries around the Baltic Sea detailed presentation on approaches, levels and status of sediment quality criteria have been made (WGMS 2003). Sediments have a profound influence on the health of aquatic organisms, which may be exposed to chemicals through their immediate interactions with seabed sediments. There are no sediment guidelines or environmental quality criteria for marine sediments in Finland. There is, however, one paper published (Vallius & Leivuori 2003), which classifies the sediment quality in the Gulf of Finland based on Swedish marine sediment quality criteria (Naturvårdsverket 1999). Such quality criteria, which compare total concentrations with a reference or with background provides little insight into the potential ecological impact of sediment contaminants, however, they provide a base from which to evaluate sediment quality guidelines (Burton 2002).

The Baltic Sea, and the Gulf of Finland, has become an area of increasing economic interest. This can be seen for example in the planning of the Nord Stream gas pipeline, which according to recent plans, will be constructed on the bottom of the Baltic Sea. The construction of such mega-structures will inevitably expose the marine ecosystem to different threats, such as resuspension of enormous

masses of fine-grained sediments. As sediment quality issues thus have become of increasing importance in the environmental assessment, protection, and management of marine ecosystems, the need for accurate data is growing. In spite of this, there are still very few data published on the background concentrations of elements in the Gulf of Finland, and there are still no sediment guidelines or environmental quality criteria for marine sediments in Finland.

Quite a few studies have dealt with the concentrations of surface sediments (Anttila-Huhtinen & Heitto 1998, Leivuori 1998, Vallius & Lehto 1998, Vallius & Leivuori 1999, Vallius 1999a and b, Leivuori 2000, Pallonen 2001 and 2004, and Vallius & Leivuori 2003), but there are virtually no data on background concentrations of trace metals. Leivuori (2000) presented background concentrations for cadmium, lead, copper, zinc and mercury for the Gulf of Finland and Leivuori & Vallius (2004) presented background arsenic concentrations for the Gulf of Finland. Those data are from the off shore Gulf of Finland. During the SAMAGOL project, which was organized by the All-Russia Geological Research Institute (VSEGEI) and the Geological Survey of Finland (GTK) a multitude of cores were taken from the soft sea floor sediments in the sea area off Kotka, eastern Gulf of Finland. The geochemical data of this dataset was combined with data from two earlier studies, and thus a dataset covering 10 cores was achieved. This data is here presented as background concentrations and summary statistics of arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V), zinc (Zn), and mercury (Hg) for the whole study area. These data can in the future be used as a basis for national sediment quality criteria and sediment guidelines.

STUDY AREA

The study area is situated on the Northeastern coast of the Gulf of Finland (Figure 1). The southern part of it comprises open sea with water depths up to some 90 meters, while in north the study area borders land and the archipelago is typically a mosaic of a multitude of islands of different shape and size. Similarly the sea floor in north is made up of a

mosaic of rather small, relatively shallow and isolated accumulation basins. In the South and South East the accumulation basins are clearly larger as the sea floor between the sparse islands is more even. The water depth increases from land in the north to the deepest parts in south.

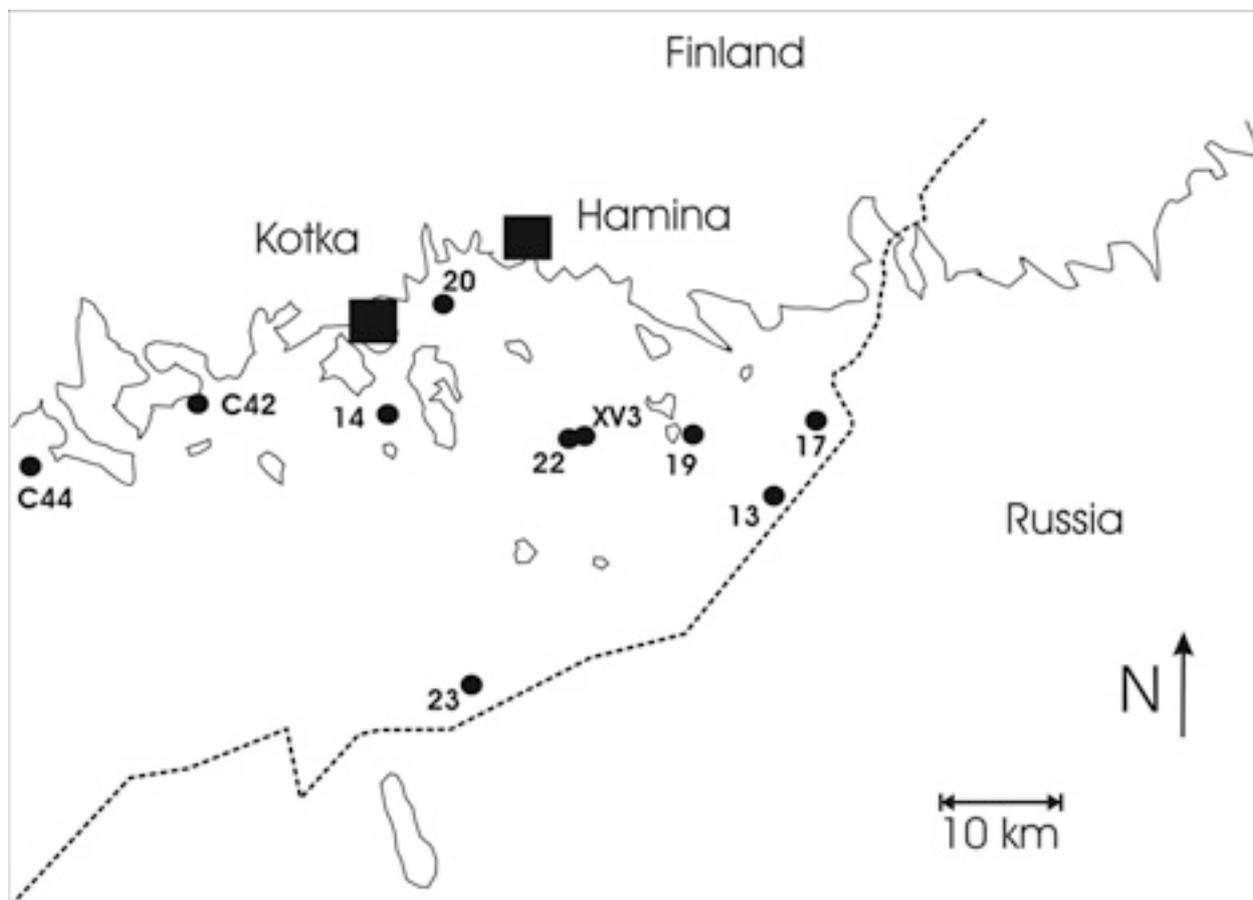


Figure 1. Study area with sampling sites.

MATERIALS AND METHODS

The samples of this study are modern muddy clays or clayey muds, which were collected during the SAMAGOL cruise of R/V *Geola* of the Geological Survey of Finland (GTK) on May 24th to June 4th 2004. Additionally two samples from a R/V *Kaita* cruise in October 2001 and 1 sample taken on board R/V *Aranda* in December 2002 were added to the data set, Table 1. During these cruises also other cores were taken but they were not long enough in order to provide background concentrations in the lowermost parts of the core.

All sampling sites were chosen according to carefully surveyed echo sounding data. The samples were taken using a GEMAX twin barrel gravity corer with an inner diameter of 90 mm of the core liner. The core length varied between 35 cm and 65 cm, but most of the cores reached 50 cm in length. After sampling one of the two cores obtained was split vertically for description and the other one was used for sub-sampling. All cores were sliced into 10 mm thick sub samples on board and packed in plastic bags that immediately were

stored in $-18\text{ }^{\circ}\text{C}$ until they were taken ashore for freeze drying. Only the lowermost samples in each core were used in this study.

All chemical analyses were performed at the chemistry laboratory of the GTK. The samples were totally digested with hydrofluoric – perchloric acids followed by elemental determination by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) (Vallius & Leivuori 1999, 2003). Mercury was measured with an Hg-analyzer through pyrolytic determination.

The analytical reliability of the laboratory was checked using standard reference materials MESS-2 and NIST8704. All elements except cadmium had a recovery of $\pm 10\%$ of the reference value, most of them within $\pm 5\%$, which can be considered as satisfactory or good. The average recovery of cadmium was slightly too high for MESS-2 as it was 115%, but for NIST8704 it was exactly 100%. In one sample batch the recovery of lead for MESS-2 was 112% (average of all batches for MESS-2 lead

Table 1. List of stations, coordinates in WGS-84

WGS84	Lat	Lon	Depth	Date	Vessel
MGGN-04-13	60°20,141'N	27°35,485'E	39,0 m	26.5.2004	Geola
MGGN-04-14	60°24,069'N	26°57,141'E	20,2 m	27.5.2004	Geola
MGGN-04-17	60°23,816'N	27°39,434'E	43,5 m	31.5.2004	Geola
MGGN-04-19	60°23,043'N	27°27,252'E	30,0 m	1.6.2004	Geola
MGGN-04-20	60°29,537'N	27°03,062'E	13,2 m	2.6.2004	Geola
MGGN-04-22	60°23,053'N	27°16,577'E	38,0 m	2.6.2004	Geola
MGGN-04-23	60°10,751'N	27°05,432'E	72,0 m	3.6.2004	Geola
XV3	60°23,08'N	27°17,66'E	39,0 m	11.12.2002	Aranda
C42	60°22,61'N	26°38,95'E	14,0 m	2.10.2001	Kaita
C44	60°24,61'N	26°21,94'E	11,0 m	3.10.2001	Kaita

is 102%). For NIST8704 the recovery of lead is very close to 100% with an average of 101%. It seems that the matrix of NIST8704 (Buffalo River sediment) is more similar to the very low saline marine sediment of this study. Altogether the recoveries of all studied elements are good enough to be reliable.

Three cores (MGGN-2004-13, 14 and 17) were dated for ^{137}Cs by gamma spectrometry using an EG&E Ortec ACETM-2K spectrometer with a 4"

NaI/Tl detector. The ^{137}Cs curve of these analyses mark the depth of the sediment accumulated from the trajectory of the Chernobyl nuclear power plant accident of April 1986. The obtained net accumulation rate was extrapolated to indicate approximate minimum ages for the bottom of the cores. For the rest of the cores counts of couplets/triplets of laminae with annual/seasonal character (Kotilainen et al., 2007) were used for the same purpose.

RESULTS AND DISCUSSIONS

From all data obtained during the last cruises to the study area, only those cores that were long enough to provide background data of elements were chosen for this study. Altogether 10 rather evenly distributed cores from different environments were chosen for this study. Some samples are from rather shallow locations (11–14 meters) while others represent intermediate or even deep bottoms, the deepest being from a basin with a depth of 72 meters. The sites represent thus different environments of deposition, but a common denominator is that these bottom samples of the cores represent pre-industrial values in this area. All samples represent the deepest layer possible to penetrate with the GEMAX-corer. Minimum ages of 80–100 years for the bottom samples were estimated by extrapolation from present net sedimentation rates measured with gamma spectrometry of ^{137}Cs of the Chernobyl power plant accident of April 1986, or by counts of lamina couplets (triplets) of the laminated upper parts of the cores, where the laminae have been described as annual/seasonal (Kotilainen et al. 2007).

Borg and Jonsson (1996) present a general pattern of the overall pollution history of the Baltic Proper. According to that no significant changes in the trace metal concentrations can be distinguished

before year 1930. Thus the samples of this study can be classified as pre-industrial in age, which does not necessarily mean pre-anthropogenic, as at least the samples from near-coastal sites have been affected by agriculture and other earlier human activities. Figure 2 shows as example vertical profiles of cadmium, mercury, lead and zinc concentrations at site MGGN-2004-17 in the easternmost part of the study area. It can easily be seen from the figure that background concentrations are reached in the bottom of the profiles.

All background data is presented in Table 2 (for sample locations see Figure 1), while Table 3 shows how the data of this study fit into the classes of the Swedish sediment quality classification. It is interesting to see, that many of the values from this study area fall into the Swedish class 2, which classifies contamination as slight. Many of the values are, however, according to the Swedish classification significantly contaminated, which applies especially to copper. For zinc and cobalt it applies for some of the maximum values. Arsenic shows one value (26.7 mg kg^{-1}) that falls hardly into class 4, which is classified in Sweden as largely contaminated (limit 26 mg kg^{-1}), while two more values are in the class of significant contamination. Cadmium,

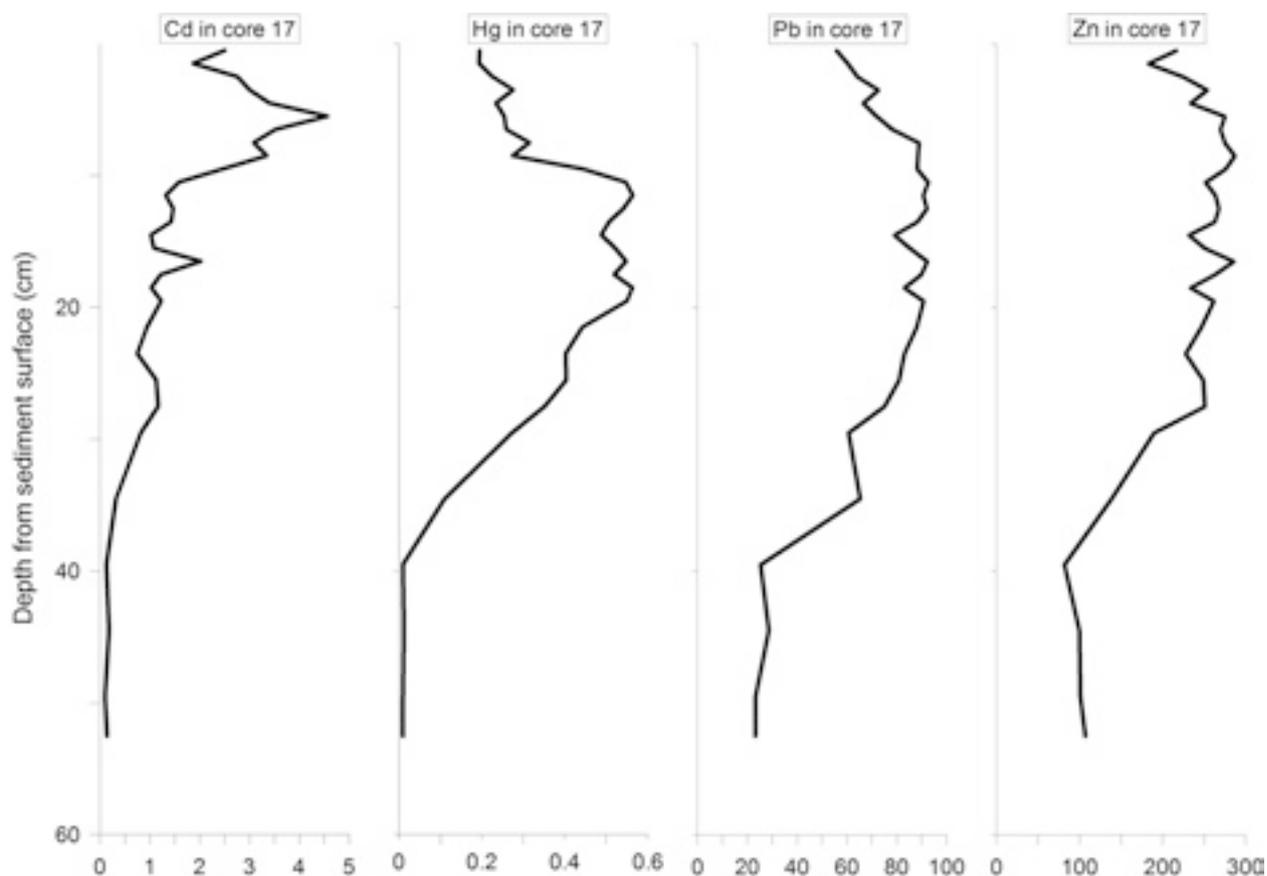


Figure 2. Vertical distributions of cadmium, mercury, lead and zinc in core MGGN-2004-17, concentrations in mg kg⁻¹.

chromium, and lead stay on the other hand rather well within the class of none or little contamination or they are at the most slightly contaminated. Mercury shows actually no values above the Swedish class of little or none contamination (class 1). As a matter of fact also cadmium, chromium and lead are only very slightly exceeding the lower limit of class 2 of the Swedish classification, and are thus almost within the Swedish classification of non-contaminated sediments. Similarly there are only two values of nickel, which clearly exceed the lower

level of class two of the Swedish classification. On the bottom of Table 3 are reference data from three depths of a vibro hammer core from the central Gulf of Finland (latitude 59° 51'N, longitude 24° 50'E). Two of them represent Litorina sediments of at least hundreds of years of age, which definitely represent background concentrations. The lowermost sample is from Ancyclus clays, which represents an age of some 8 000–9 000 years, and sweet water conditions.

Table 2. Background concentrations of selected heavy metals. Depth indicates depth interval of the sample from sediment surface, in centimeters. One value of cadmium and four values of mercury are missing due to the concentrations being below detection limit (BDL). Two samples lack determination of mercury = no data (ND).

Sample ID	Depth cm	As mg/kg	Cd mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Mo mg/kg	Ni mg/kg	Pb mg/kg	Sb mg/kg	V mg/kg	Zn mg/kg	Hg mg/kg
MGGN-2004-13	50–53	18,6	0,160	14,2	68,5	29,3	7,08	34,8	20,0	0,42	86,0	120	0,012
MGGN-2004-14	55–62	12,1	0,190	13,5	66,7	33,3	5,47	22,4	31,4	0,40	91,0	124	0,021
MGGN-2004-17	50–55	17,2	0,140	14,6	67,3	25,4	7,16	34,2	23,1	0,57	87,5	107	BDL
MGGN-2004-19	50–57	26,7	0,240	23,7	38,6	16,8	21,5	24,7	24,7	0,38	52,0	81,1	BDL
MGGN-2004-20	45–51	14,5	BDL	11,9	45,1	17,3	6,57	22,1	20,5	0,20	58,9	85,8	BDL
MGGN-2004-22	30–35	11,8	0,110	20,3	70,2	31,0	8,08	35,0	23,3	0,33	86,9	120	BDL
MGGN-2004-23	40–47	25,8	0,160	19,5	83,7	34,4	9,64	40,7	28,4	0,46	113	138	0,014
XV3	48–55	13,1	0,250	15,0	72,7	30,9	6,91	35,4	32,9	0,53	91,2	100	0,020
C42	39–40	15,6	0,140	16,1	81,9	33,1	3,86	35,7	31,1	0,26	97,1	129	ND
C44	44–45	23,8	0,180	23,2	76,0	29,5	16,4	39,3	19,2	0,37	88,4	133	ND

Table 3. Comparison between the data of this study and the Swedish Sediment Quality Criteria (SQC). Swedish classification on the top. In the middle of the table the data of this study is expressed as summary statistics with classification according to the Swedish SQC and on the bottom the individual values of this study classified similarly. White cells fall into the Swedish class 1, while light grey into Swedish class 2 and darker grey into Swedish class 3. Only one arsenic value is within the Swedish class 4 and none in class 5. The lowermost three samples are reference samples from central Gulf of Finland, representing Litorina and Ancylus sediments of older age.

Swedish SQC	Degree of Contamination	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Hg
Class 1	Little or none	< 10	< 0.2	< 14	< 80	< 15	< 33	< 31	< 85	< 0.04
Class 2	Slight	10–16	0.2–0.5	14–20	80–110	15–30	33–43	31–46	85–125	0.04–0.10
Class 3	Significant	16–26	0.5–1.2	20–28	110–160	30–60	43–56	46–68	125–195	0.10–0.27
Class 4	Large	26–40	1.2–3	28–40	160–220	60–120	56–80	68–100	195–300	0.27–0.7
Class 5	Very large	> 40	> 3	> 40	> 220	> 120	> 80	> 100	> 300	> 0.7

Data of this study	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Hg
<i>Mean</i>	17,9	0,174	17,2	67,1	28,1	32,43	25,5	114	0,017
<i>Median</i>	16,4	0,160	15,6	69,4	30,2	34,9	24,0	120	0,017
<i>Standard Deviation</i>	5,64	0,046	4,17	14,6	6,35	6,81	5,12	19,6	0,004
<i>Minimum</i>	11,8	0,110	11,9	38,6	16,8	22,1	19,2	81,1	0,012
<i>Maximum</i>	26,7	0,250	23,7	83,7	34,4	40,7	32,9	138	0,021
<i>Count</i>	10	9	10	10	10	10	10	10	4

Individual values	Depth	As	Cd	Co	Cr	Cu	Ni	Pb	Zn	Hg
MGGN-2004-13	51,5	18,6	0,160	14,2	68,5	29,3	34,8	20,0	120	0,012
MGGN-2004-14	58,5	12,1	0,190	13,5	66,7	33,3	22,4	31,4	124	0,021
MGGN-2004-17	52,5	17,2	0,140	14,6	67,3	25,4	34,2	23,1	107	
MGGN-2004-19	53,5	26,7	0,240	23,7	38,6	16,8	24,7	24,7	81,1	
MGGN-2004-20	48,0	14,5		11,9	45,1	17,3	22,1	20,5	85,8	
MGGN-2004-22	32,5	11,8	0,110	20,3	70,2	31,0	35,0	23,3	120	
MGGN-2004-23	42,5	25,8	0,160	19,5	83,7	34,4	40,7	28,4	138	0,014
XV3	51,5	13,1	0,250	15,0	72,7	30,9	35,4	32,9	100	0,020
C42	39,5	15,6	0,140	16,1	81,9	33,1	35,7	31,1	129	
C44	44,5	23,8	0,18	23,2	76,0	29,5	39,3	19,2	133	
1/2001	140–150	8,18	0,180	20,8	103	35,9	47,1	25,2	136	0,010
1/2001	270–290	5,86	0,250	19,8	103	36,1	46,7	24,1	127	0,012
1/2001	420–440	5,29	0,270	20,8	113	40,5	50,1	26,3	139	0,009

When comparing the background concentrations of this study with the backgrounds presented by Leivuori (2000) for the Gulf of Finland (cadmium 0.1 mg kg⁻¹, lead 21 mg kg⁻¹, copper 25 mg kg⁻¹, zinc 100 mg kg⁻¹, and mercury 0,02 mg kg⁻¹), it can be seen, that most values in the present study are slightly higher than those of Leivuori, while mercury is on the same level in both studies. When comparing the arsenic values of this study with the average for the Gulf of Finland, presented by Leivuori & Vallius (2004), 14–16 mg kg⁻¹, it can be seen that the results of both studies are on the same level of magnitude. When comparing the data of this study with the reference samples from deeper sediments in the central Gulf of Finland (reference, Table 3), which represent sediments of clearly older age, it can be seen that most of the concentrations of the present study are on similar or even lower level than the concentrations of the reference samples. Thus the samples of this study can be considered representing local background values. Only arsenic of this study shows clearly higher concentrations than

the reference samples, which is probably attributed to sulphide forming processes, as presence of solid arsenic is strongly controlled by the presence of pyrite (Belzile & Lebel 1986, Belzile 1988). Arsenic is thus enriched in the near surface zone of the sediments, where sulphides are formed.

It seems that it is the local geology, which mainly controls the chemical composition of the soft sediments. As the background concentrations of this study differs from the Swedish background values, it seems that the geology of this study area probably differs clearly from the geology of the areas that has been used for the Swedish background data for the classification of contamination. Without knowledge on the criteria used for making the Swedish classification, neither than knowledge on sampling sites of the Swedish samples used for the classification, it is impossible to estimate the real reason for the clear difference in these two datasets. On the other hand it is possible, as the samples of this study represent minimum ages of 80–100 years, that some earlier human activity (agriculture etc.)

has affected the sea areas and the chemical composition of the sea floor sediments slightly. That is, however, not very plausible, as it would have needed really a lot of activity of a much smaller community of those days to significantly increase average sediment concentrations of trace metals.

Although many of the samples in this study clearly exceed the limits of contamination according to the Swedish classification, the very low concentrations of mercury clearly indicate pre-industrial age of the samples as increased concentrations of mercury in general can be considered a pollution indicator (Aston et al. 1973). In this case there are known releases of mercury from paper mills and chemical

industry along the River Kymijoki, which easily is reflected in the coastal and off shore sediments (Vallius et al, 2007). The first chlor-alkali factory was established in Kuusaansaari, more than 50 kilometers upstream in the river, in the year 1927. The factory was upgraded in 1936 with new mercury electrolysis cells, which can be seen as the definite beginning of human pollution of the river and off shore waters and sediments (Kokko & Turunen 1988).

Also the fact that all data of the present study, except for arsenic, are on similar level as the reference samples of clearly pre-anthropogenic age indicates that the samples of this study represent true background values in the study area.

CONCLUSIONS

In this report a data set of ten cores are presented as background data on heavy metal distribution in modern soft sediments of the Northeastern Gulf of Finland. As minimum ages of 80–100 years for the bottom samples were estimated, the samples of this study can be classified as pre-industrial in age, which does not necessarily mean pre-anthropogen-

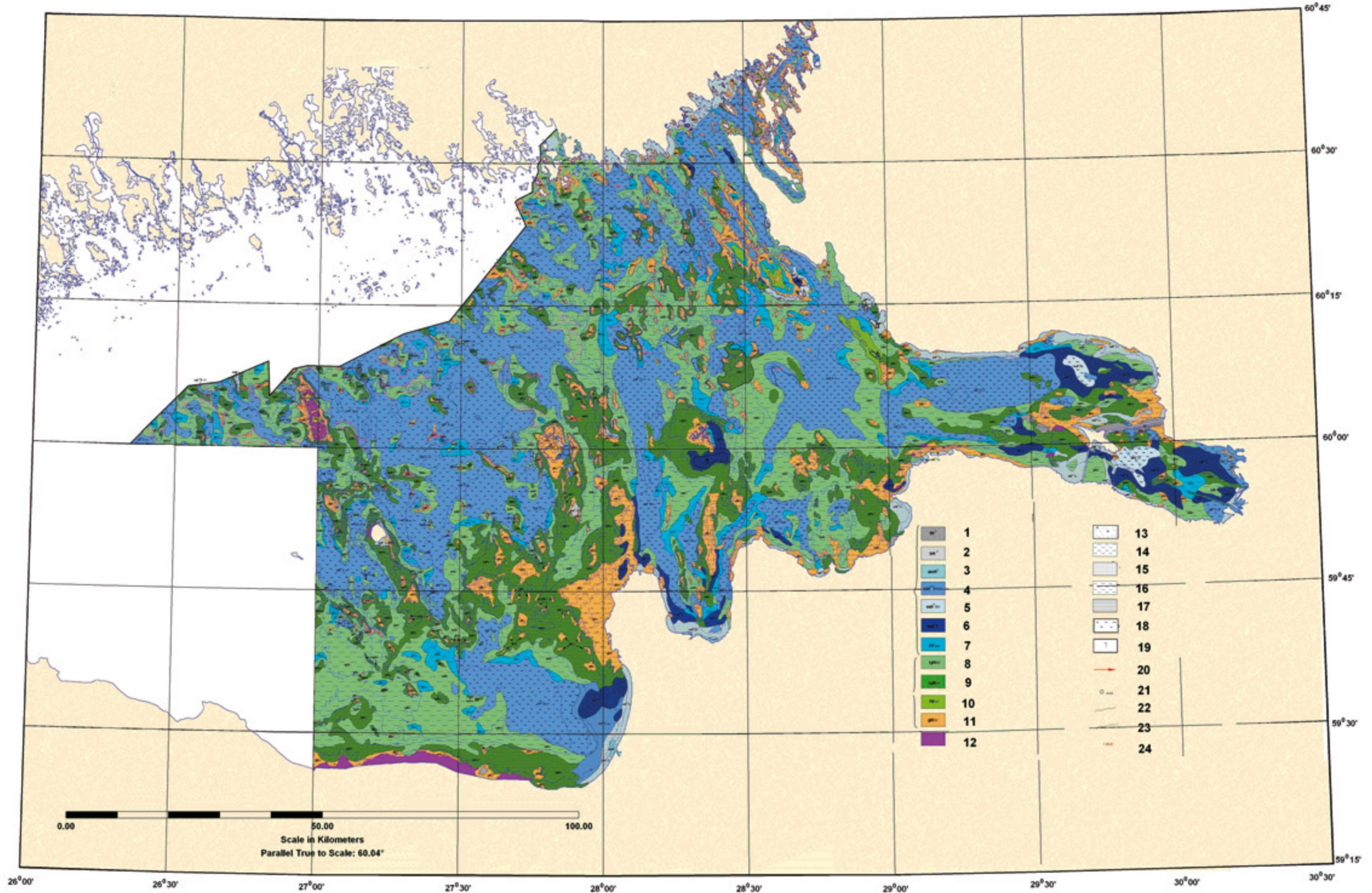
ic, as at least the samples from near-coastal sites have been affected by agriculture and other earlier human activities. Nevertheless, the metal concentrations are low and thus these data can in the future be used as a basis for national sediment quality criteria and sediment guidelines.

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Appendix 1. Map of the Quaternary deposits of the eastern the Gulf of Finland. Holocene: (1) anthropogenic sediments; (2) biogenic deposits: peat; (3) marine-alluvial deposits: sand; (4) marine Litorina and Limnea deposits: sand, clay; (5) marine Limnea deposits: sand, clay; (6) marine Litorina deposits: sand, clay; (7) Ancylus Lake deposits: clay, Pleistocene: (8) Baltic Ice Lake deposits: clays, thin-varved clays; (9) glaciolacustrine deposits of the marginal ice laces: varved clay; (10) glaciofluvial deposits; (11) glacial deposits (till); (12) bedrocks: lithological types; (13) boulders; (14) pebbles, gravel; (15) sands; (16) clay; (17) varved clay; (18) silty-clay mud; and (19) peat.



The joint Finnish-Russian project “*Sediment geochemistry and natural and anthropogenic hazards in the marine environment of the Gulf of Finland (SAMAGOL)*” is filling a gap in knowledge of the geology and the environmental state of the seafloor in the Eastern Gulf of Finland. This publication contains five separate papers based partly on old existing data combined with new data collected during the time-frame of the SAMAGOL project. The Quaternary deposits of the seafloor are described and correlations with Quaternary deposits on land are discussed. The Gulf of Finland is known to be strongly affected by anthropogenic impact, thus different aspects of the environmental conditions in the area are discussed in several papers. High levels of heavy-metals in the soft surface sediments together with increased seafloor anoxia are examples of problems which have to be dealt with in coastal zone management and in planning large-scaled infrastructures in the Gulf of Finland.

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