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the coastal area off Kotka, North-Eastern Gulf of Finland, Baltic Sea
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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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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 Kymijoki, 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 km^3 (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 runoff of some 2460 $m^3 s^{-1}$ (77.6 $km^3 a^{-1}$, 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 anticlockwise 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.

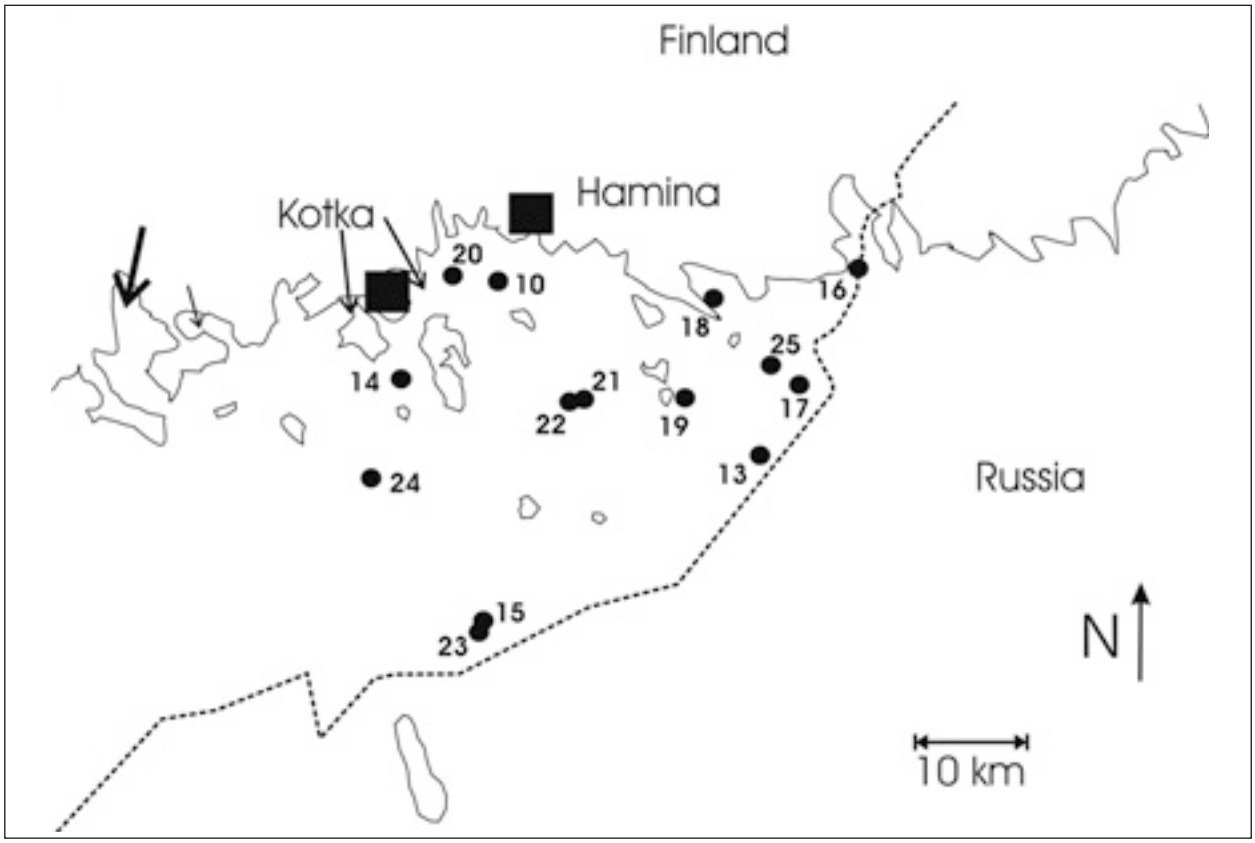

Figure 1. Study area with the cities of Kotka and Hamina indicated. Arrows indicate the approximate location of the main outlets of River Kymijoki. Thickness of arrow indicates relative water flow. The dotted line is the border between Finland and Russia.

STUDY AREA

The study area covers both sides of the national border between Finland and Russia, an area of approximately 2000 km^2 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	60º29.255'N	27°07.275'E	15.6
MGGN-04-13	60º20.141'N	27º35.485'E	39.0
MGGN-04-14	60º24.069'N	26º57.141'E	20.2
MGGN-04-15	60º11.298'N	27º06.029'E	63.5
MGGN-04-16	60º29.940'N	27º45.774'E	16.0
MGGN-04-17	60º23.816'N	27º39.434'E	43.5
MGGN-04-18	60º28.111'N	27º30.370'E	14.3
MGGN-04-19	60º23.043'N	27º27.252'E	30.0
MGGN-04-20	60º29.537'N	27º03.062'E	13.2
MGGN-04-21	60º23.117'N	27º17.723'E	38.3
MGGN-04-22	60º23.053'N	27º16.577'E	38.0
MGGN-04-23	60º10.751'N	27º05.432'E	72.0
MGGN-04-24	60º19.428'N	26º52.788'E	38.0
MGGN-04-25	60º24.644'N	27º36.320'E	39.7

onboard and packed into plastic bags that were immediately stored at –18 °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 ± 10% of the reference value, most of them within ± 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

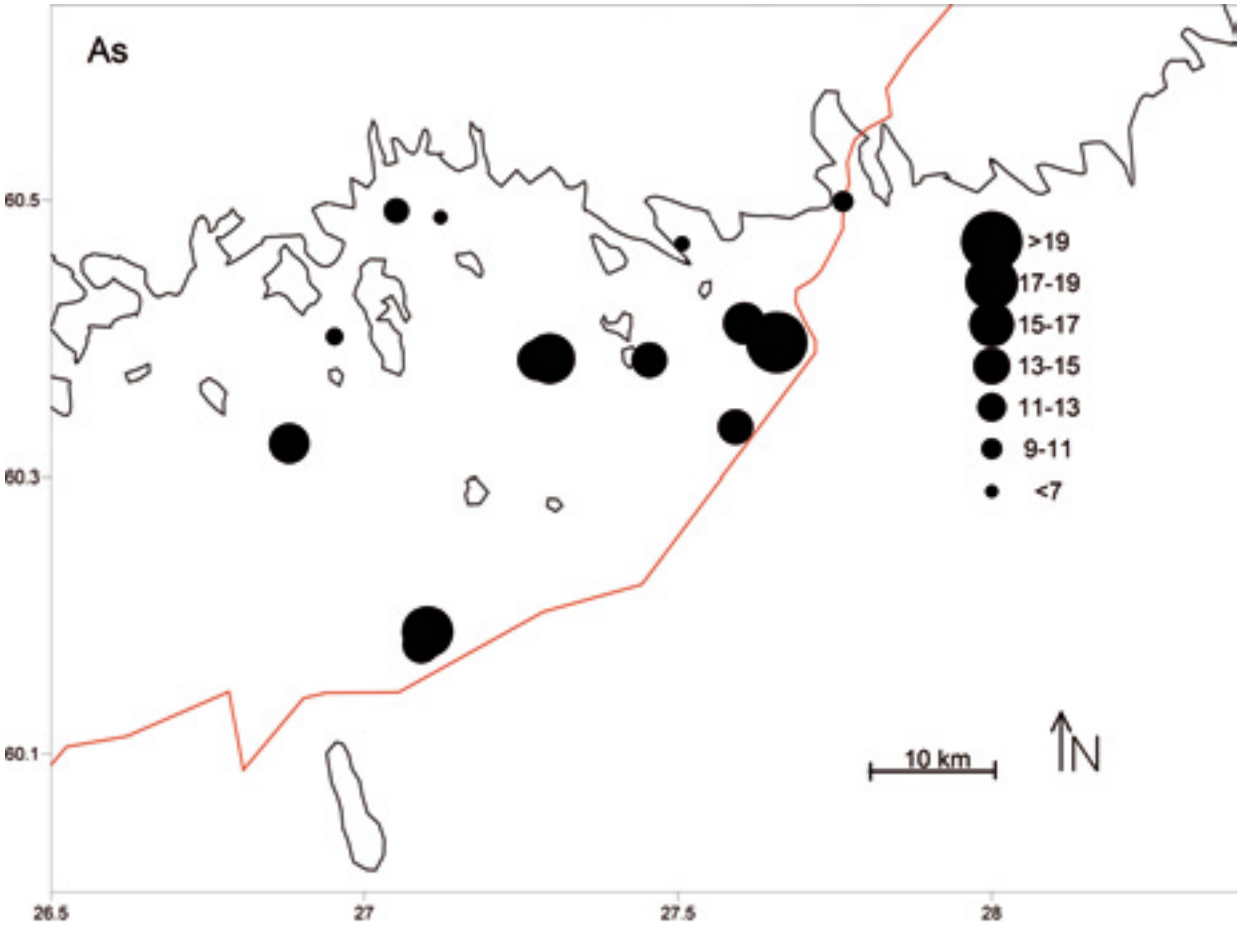

Figure 2. Distribution of arsenic in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

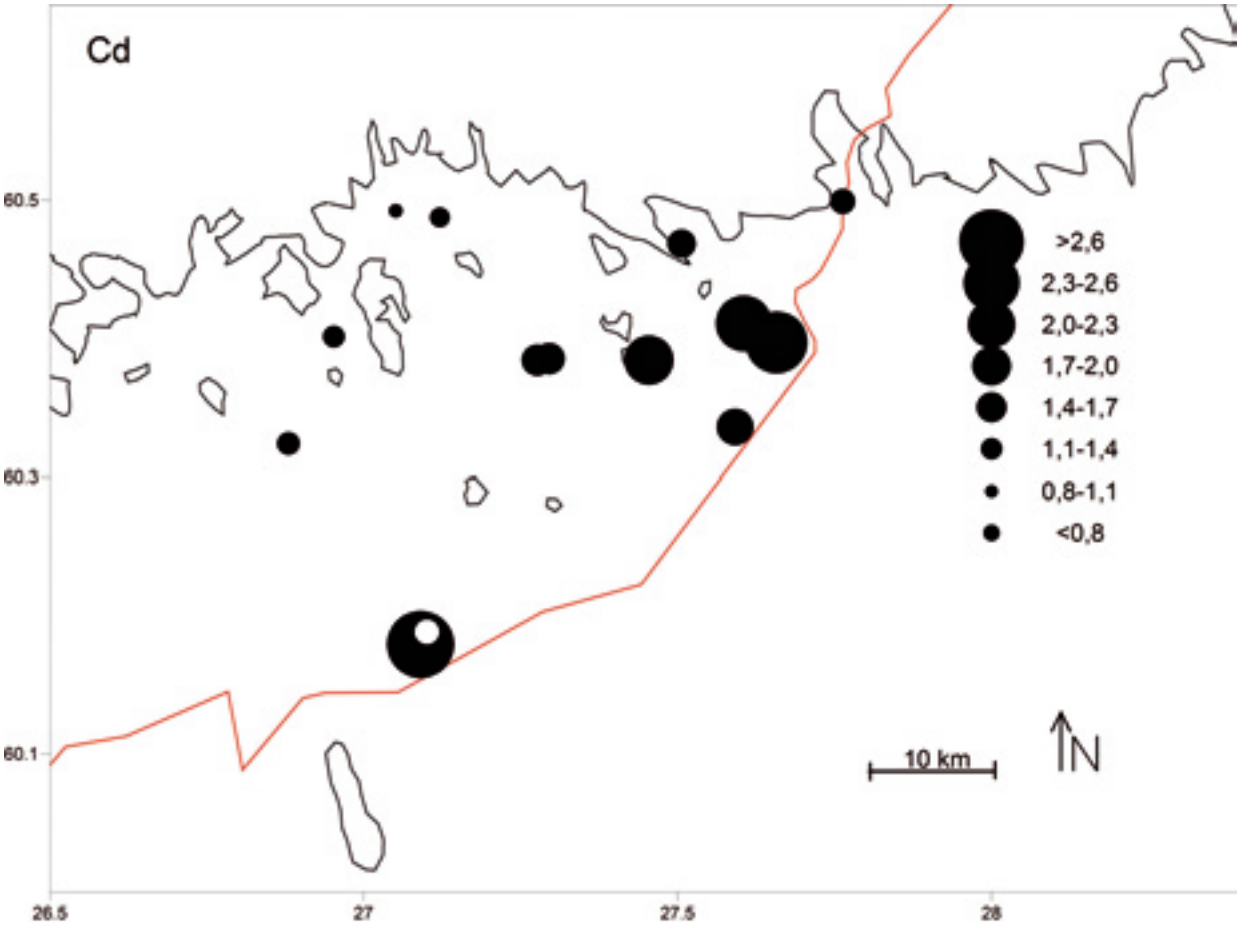

Figure 3. Distribution of cadmium in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

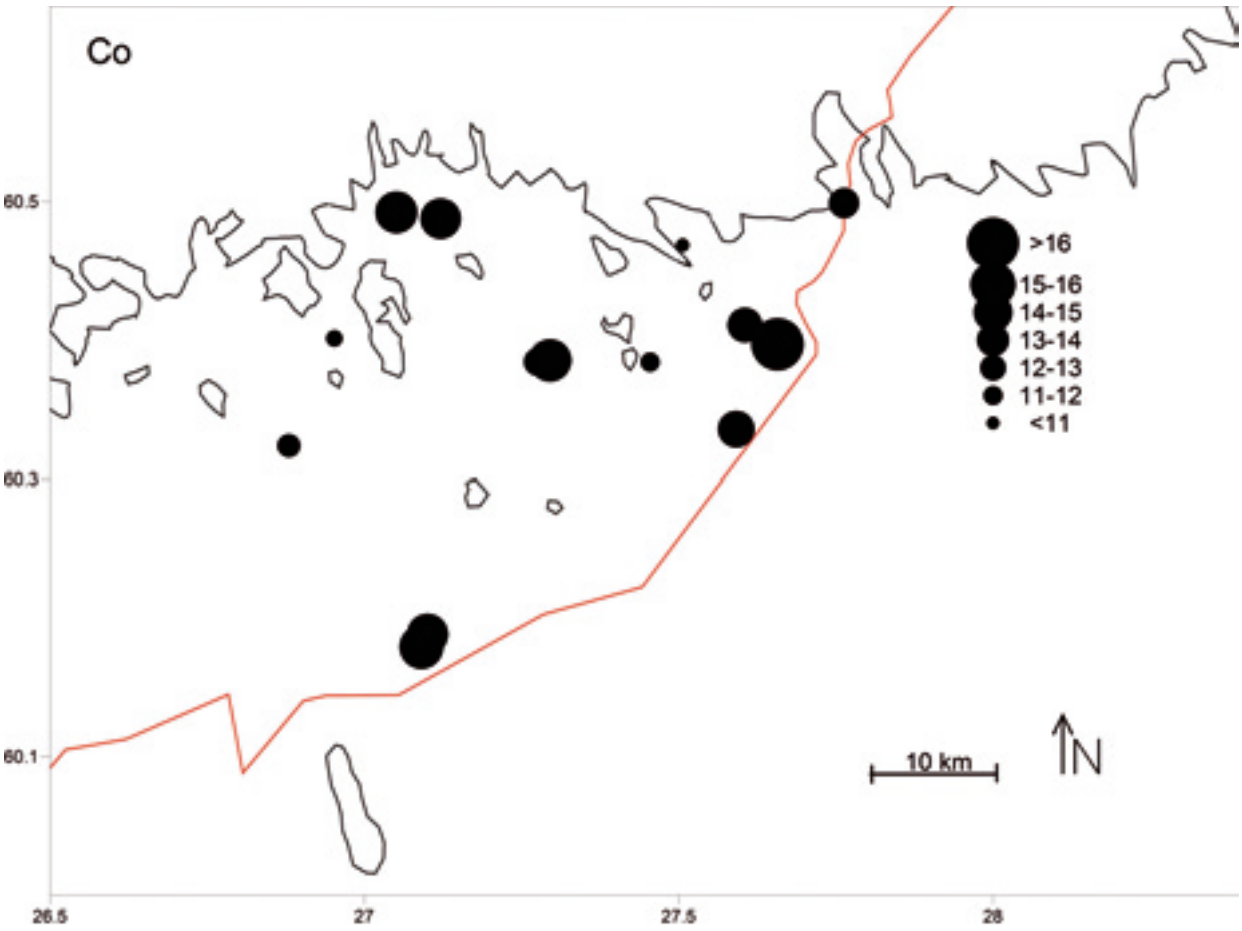

Figure 4. Distribution of cobalt in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

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 exeeded 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.

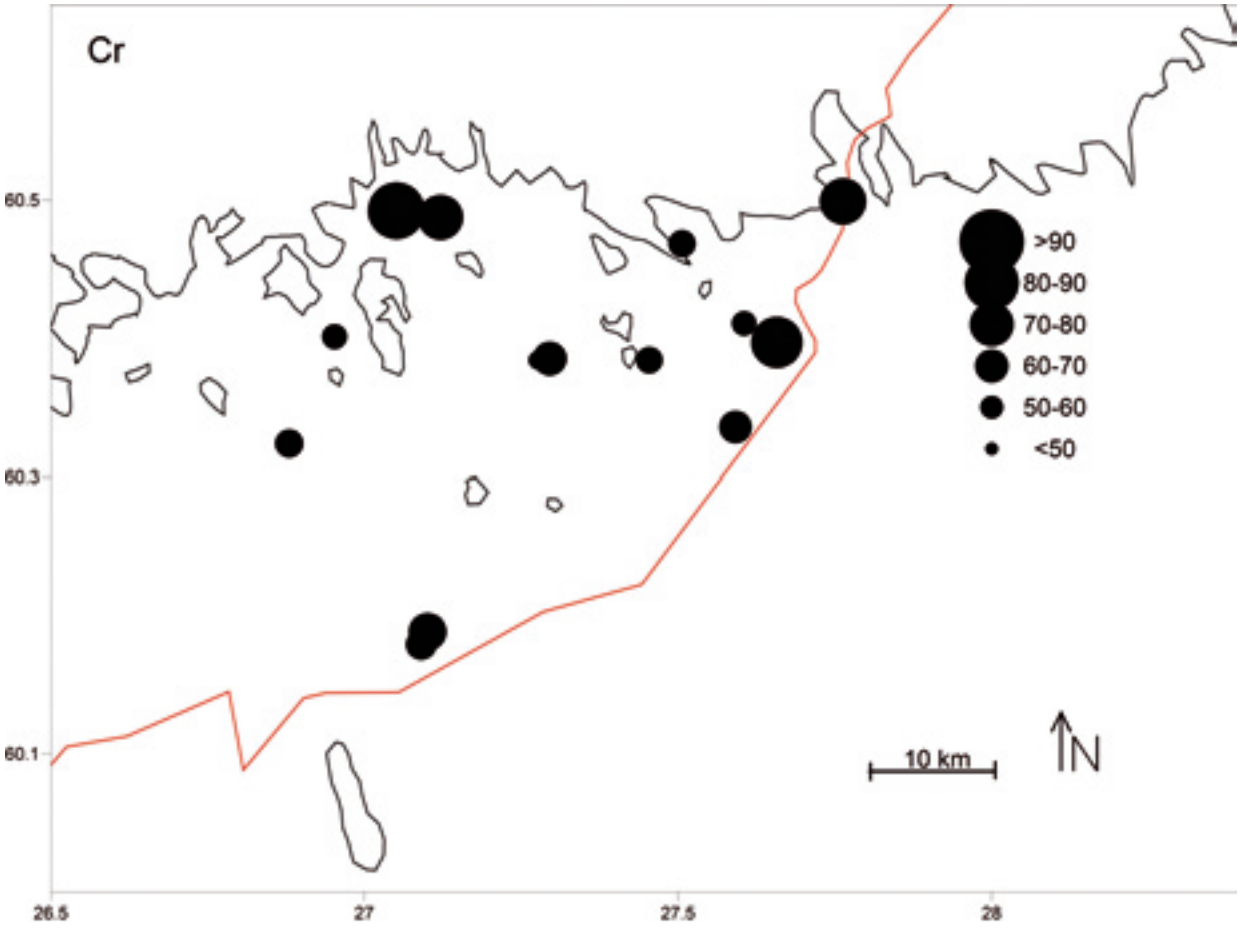

Figure 5. Distribution of chromium in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

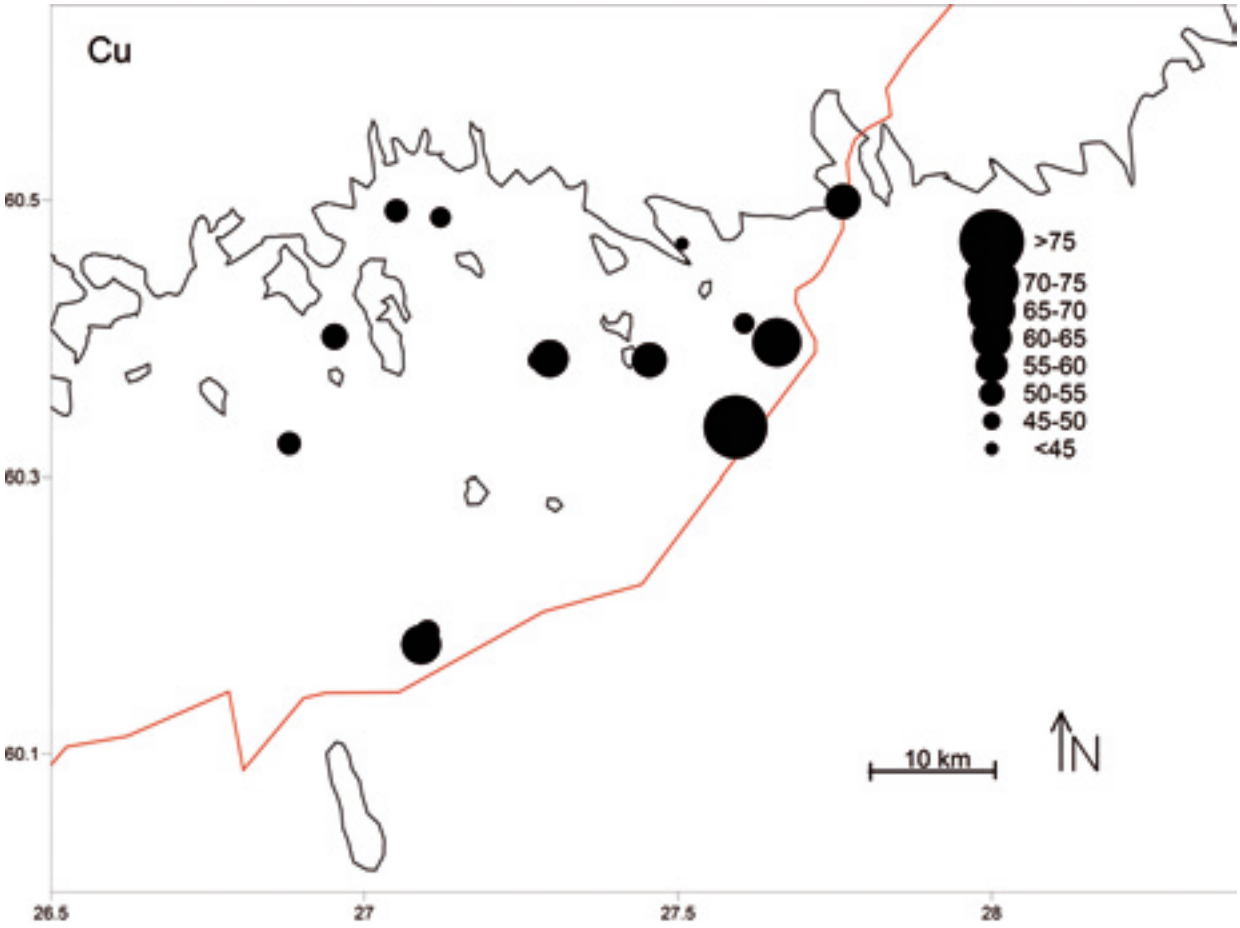

Figure 6. Distribution of copper in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

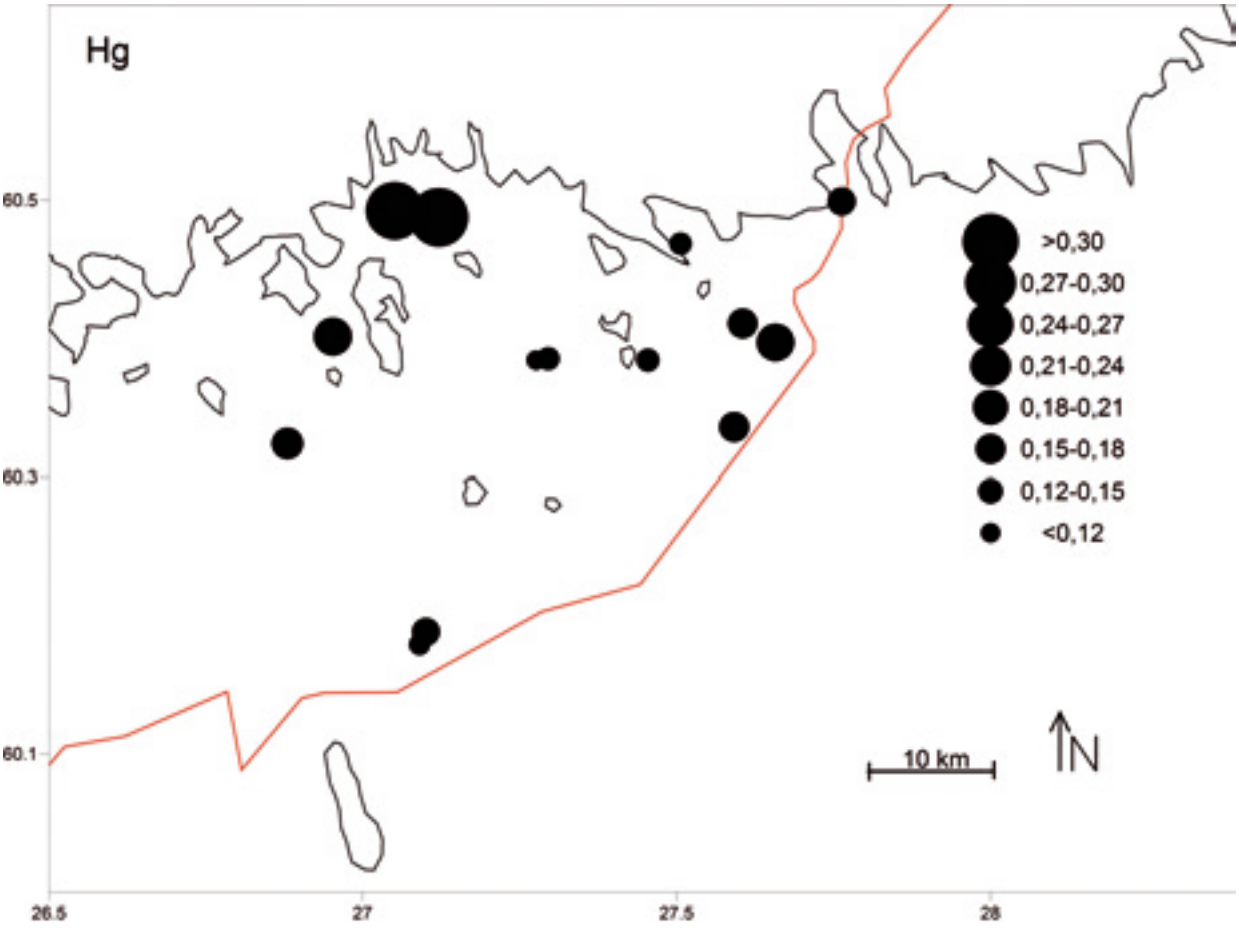

Figure 7. Distribution of mercury in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

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 Finland 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-sore 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

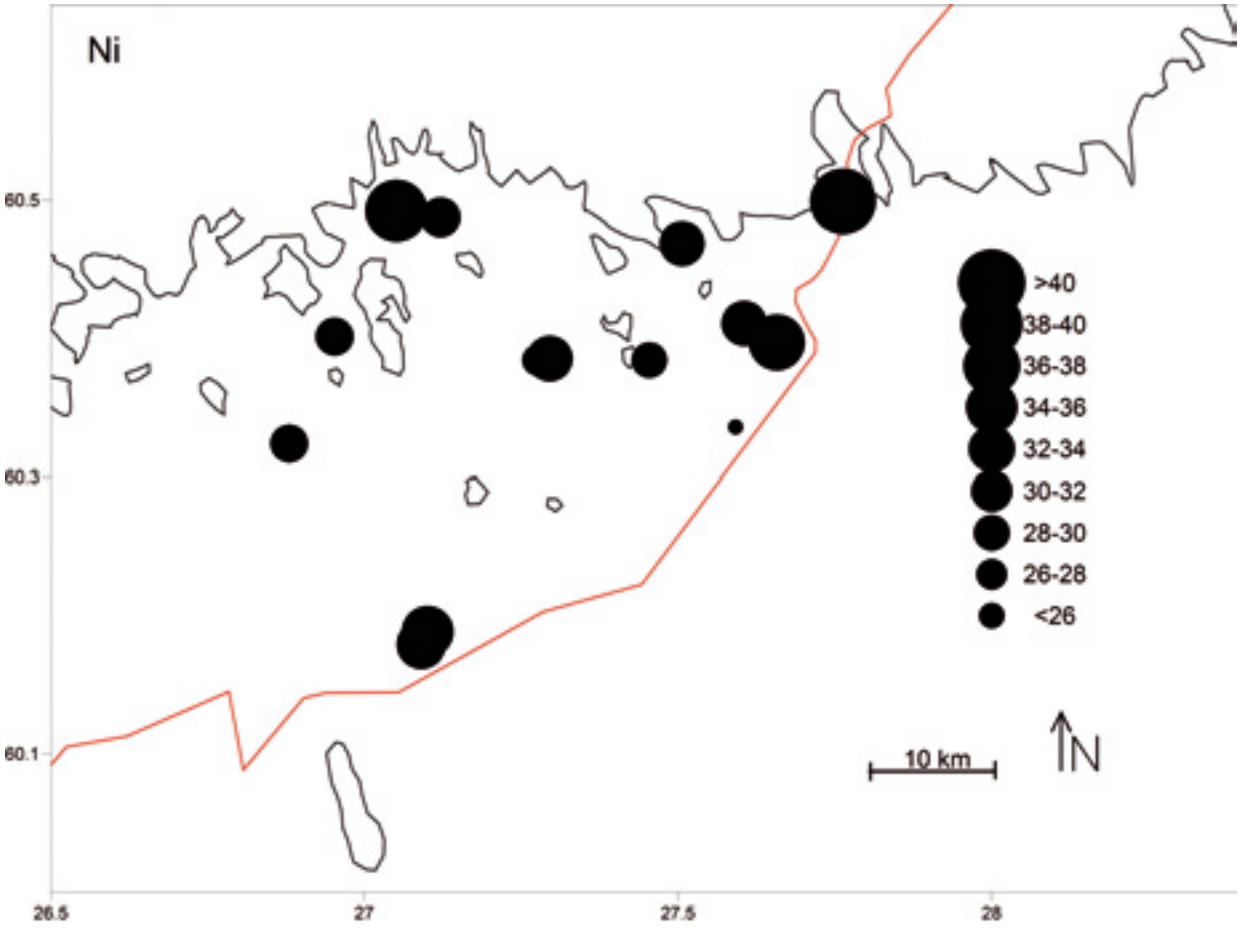

Figure 8. Distribution of nickel in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

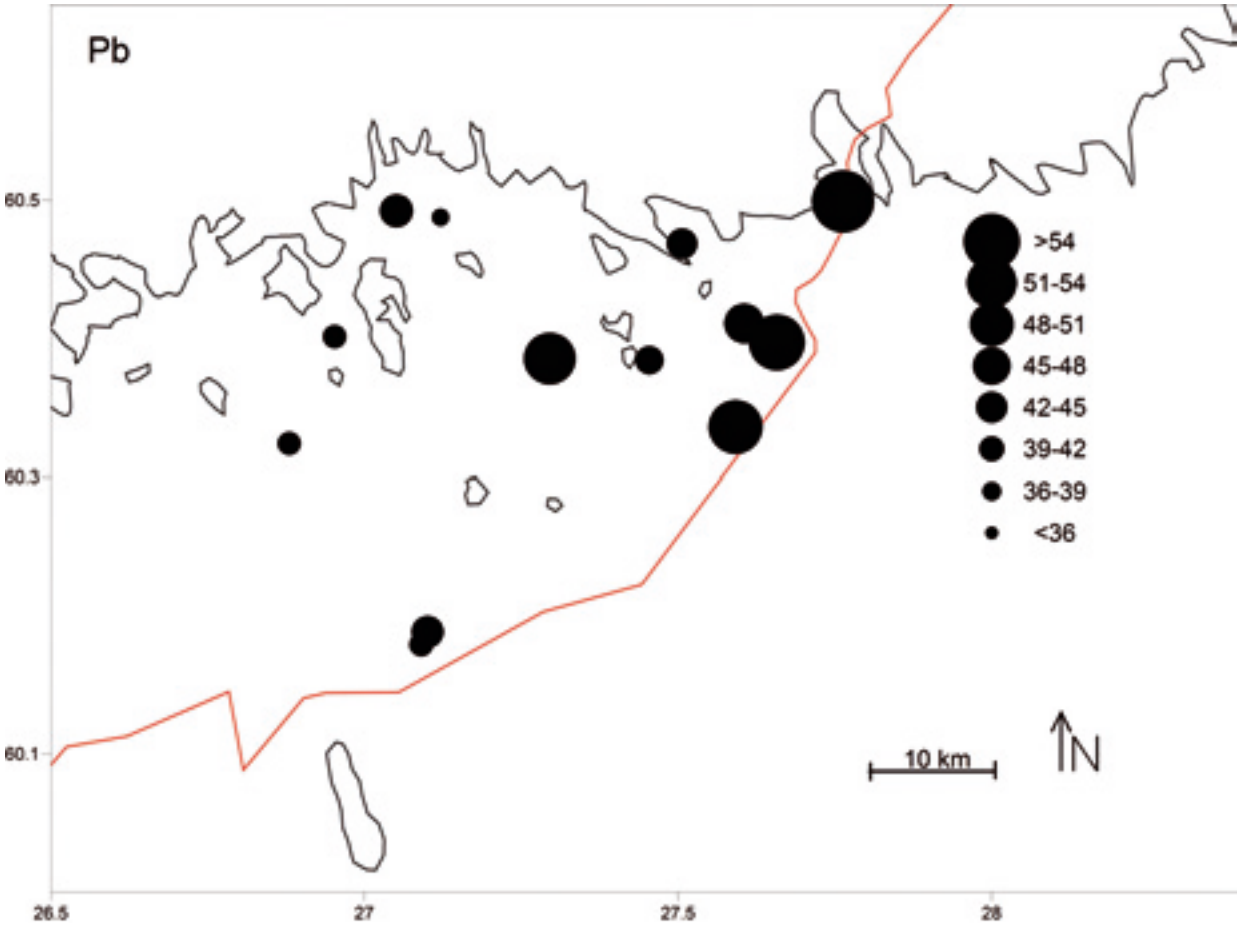

Figure 9. Distribution of lead in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

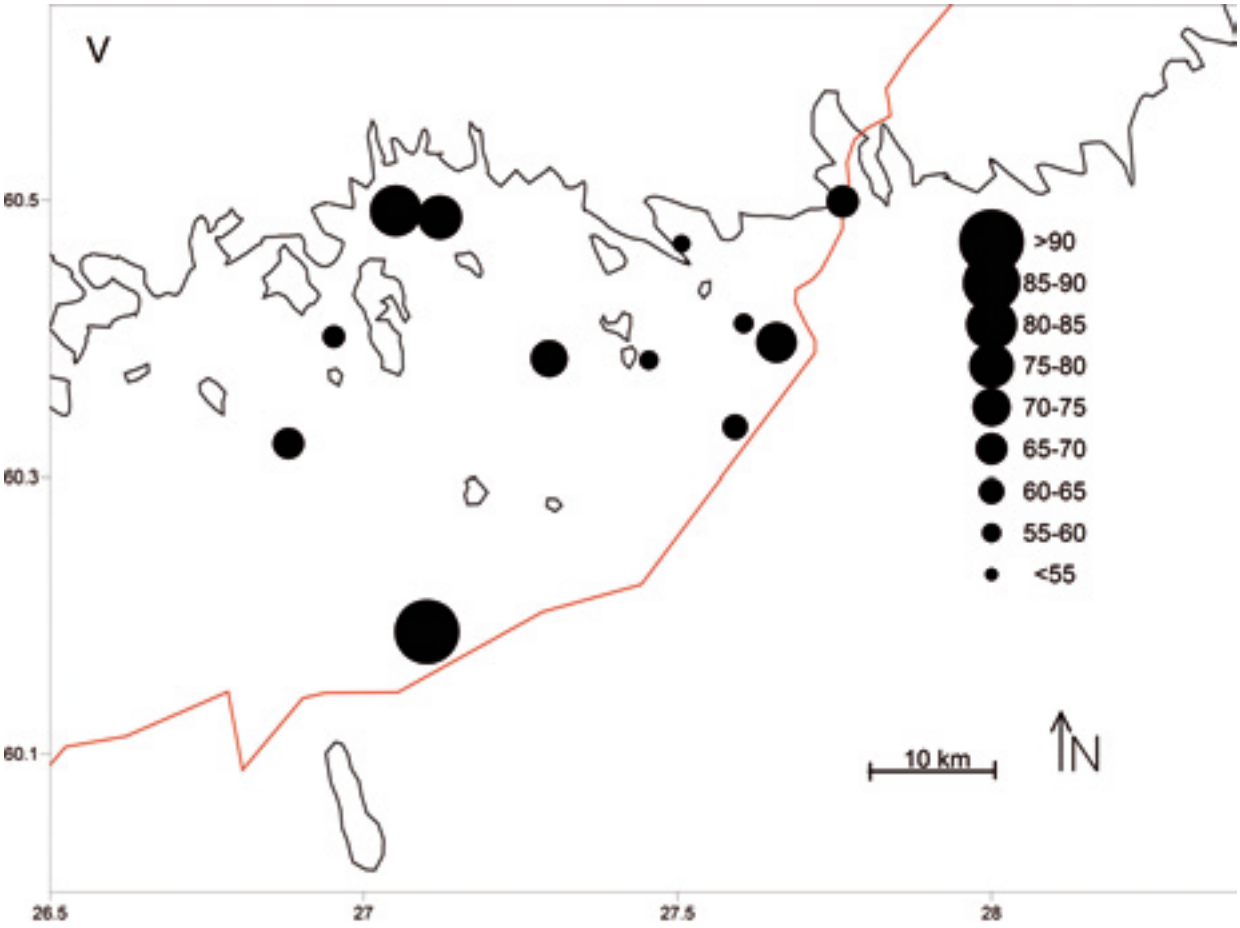

Figure 10. Distribution of vanadium in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

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.

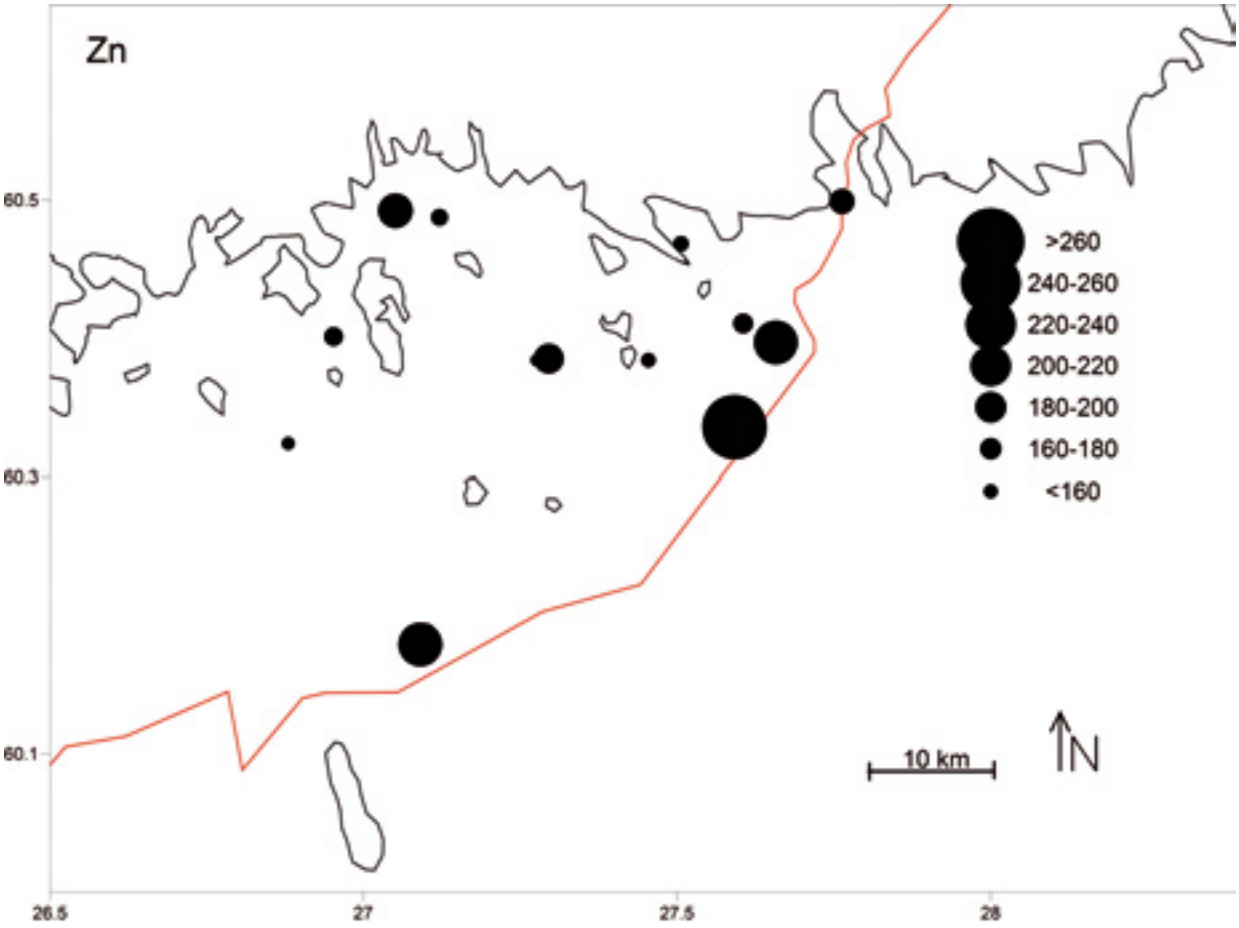

Figure 11. Distribution of zinc in the surface sediments (0–1 cm). Concentrations in mg kg^{-1}.

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

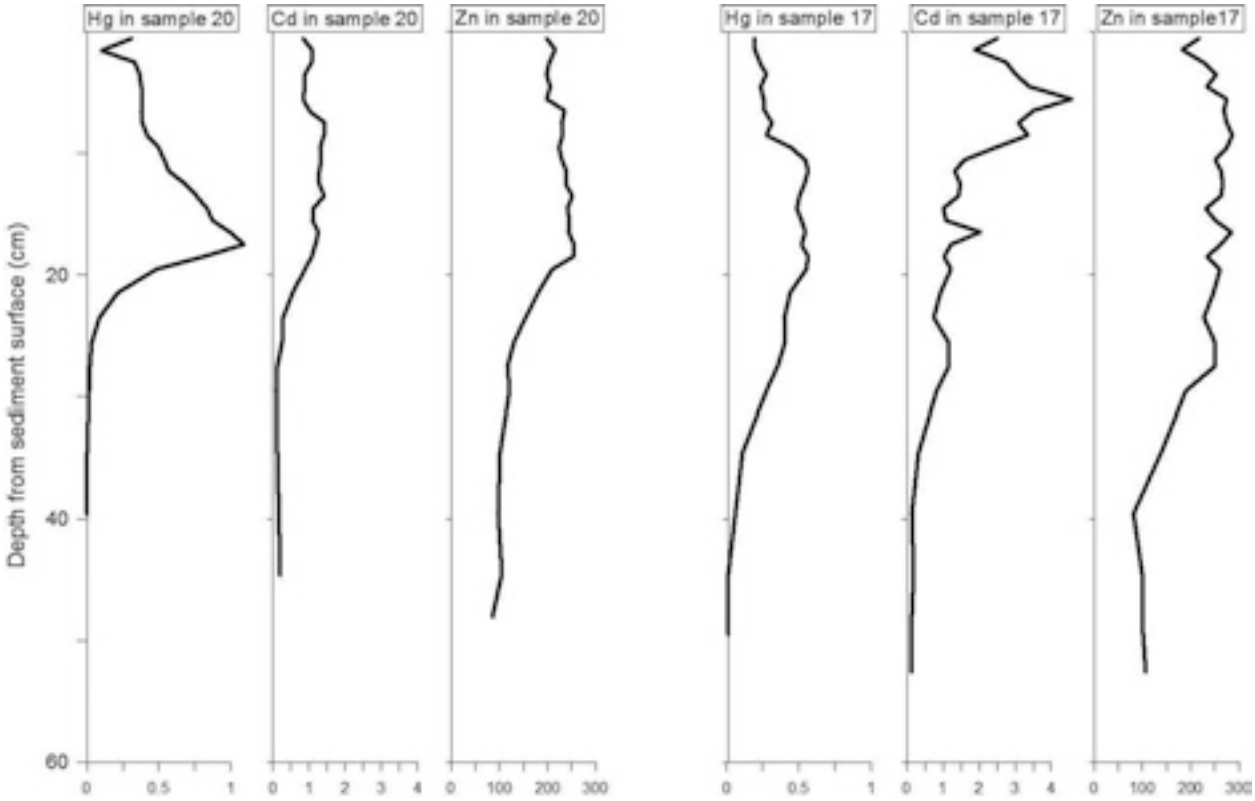

Figure 12. Vertical profiles of mercury (Hg), cadmium (Cd), and zinc (Zn) at stations 20 and 17. Concentrations in mg kg^{-1}.

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 that 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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