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Heavy metal distribution in the modern soft surface sediments off the Finnish coast of the Gulf of Finland

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Abstract This study is the first of its kind, as a systematic mapping of the whole coastal area of the Finnish part of the Gulf of Finland. This area was sampled with a relatively even spacing and the distributions of heavy metals and arsenic in the modern soft surface sediments are presented as circular symbol maps. Data on cobalt and molybdenum are reported for the first time from a total digestion from samples from this area. The sediments are strongly enriched by some of the studied elements due to the anthropogenic load, while others are only moderately present. High or relatively high levels of cadmium, copper, mercury, molybdenum, and zinc were found in the easternmost part of the study area.

Keywords *Baltic Sea, Gulf of Finland, geochemistry, heavy metals, sediment, pollution, concentration, contamination, cadmium, mercury, molybdenum.*

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INTRODUCTION

The Gulf of Finland is a sea area, which during the last half century has been strongly affected by the activities of the millions of inhabitants in the drainage basin of the gulf. Already in 2002 over 12.6 million people lived in the area (Hannerz, Destouni 2006), which easily can be seen in the condition of this shallow sea. Pollution is one problem as well as eutrophication, which has been caused by the strong loading of harmful substances and nutrients into the sea (HELCOM 2007, 2009). In this study, however, only the distribution of heavy metals in the seafloor sediments will be dealt with.

The offshore Gulf of Finland was in the 1990s rather well surveyed (Leivuori 1998; Vallius, Lehto 1998; Vallius, Leivuori 1999; Vallius 1999a, b; Leivuori 2000; Vallius, Leivuori 2003), but there was still relatively little knowledge about the environmental situation of the coastal zone of the Gulf of Finland. Virtually only the area around the outlets of River Kymijoki had been studied well as the area was known for high mercury contamination (Kokko, Turunen 1988; Anttila-Huhtinen, Heitto 1998; Verta *et al.* 1999; Pallonen 2001). Some local studies by regional authorities had also been made (Varmo, R. 1994; Miettinen *et al.* 1994), and in larger scale some evaluations of the overall situation with virtually no geochemistry data (National Board of Waters 1983; Pitkänen *et al.* 1994). Vaalgamaa (2008) has reported some data on copper and zinc trends in some coastal embayments in her study on human impact, which concentrated on eutrophication.

The Finnish part of the coast of the Gulf of Finland is ca. 250 kilometers long from west to east. In 1998 the Geological Survey of Finland (GTK) launched a project by which the whole coastal zone of the Gulf of Finland was to be mapped with a relatively coarse sampling density. The aims of the project were to acquire new information about the geology and geochemistry of the coastal zone and to describe the zone's environmental condition. After a pilot study, sampling was initiated in 2001 and commenced in late 2002. Additional information was gained from the SAMAGOL project, which during 2004 collected samples from the easternmost part of the Finnish coastline (Vallius 2007).

The aim of this paper is to report and describe the distribution of heavy metals along the coastline of the Gulf of Finland. Arsenic (As), and the heavy metals cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), mercury (Hg), molybdenum (Mo), nickel (Ni), lead (Pb), vanadium (V), and zinc (Zn) are presented here. Of these Co and Mo are reported for the first time from a total digestion from samples from the Gulf of Finland. Co distribution from off shore Gulf of Finland has earlier been reported from a partial leach by Vallius (1999a).

STUDY AREA

Bedrock geology

The area of this study lies completely within the bedrock area of Precambrian rocks (Fig. 1). The older rocks are of Svecofennian age and the younger

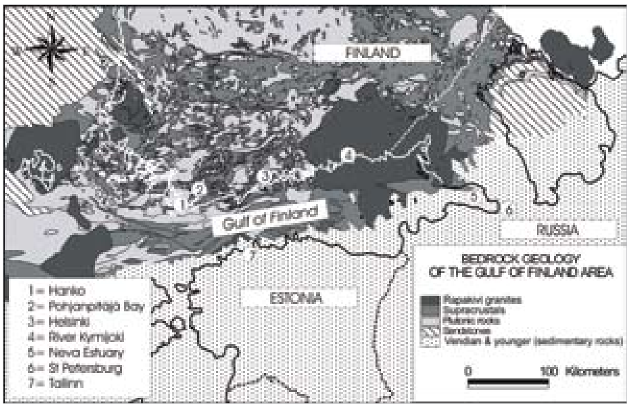

Fig. 1. Bedrock of the Gulf of Finland area (Vallius 1999b).

are rapakivi granites and associated rocks of post-Svecofennian age. Thus the time span of age is ca. 1.9 to 1.5 billion years. The western area consists mainly of late orogenic granites and supracrustals, as well as some metavolcanics, all of Svecofennian age, while the central part has more metavolcanics together with late and post-orogenic granites. The eastern study area comprises almost entirely of the large post-orogenic rapakivi massif of Vyborg. These three areas have slightly different geochemical composition compared to each other (Rasilainen *et al.* 2008) and this has to be taken into account when interpreting the geochemical anomalies of the seafloor sediments.

SEAFLOOR MORPHOLOGY AND QUATERNARY GEOLOGY

The coast of the Gulf of Finland is a most complicated pattern of islands and peninsulas divided by bays, sounds, and natural channels (Fig. 2). This pattern was produced by repeated glaciations during the Quaternary period. Especially on the eastern coast of the Gulf of Finland the bays tend to have a NNW – SSE direction, which was the last direction of ice movement during the Weichselian glaciation. In west the Gulf of Finland ends in the Hanko peninsula (see Fig. 1-1) which is

Fig. 2. An old picture from an inner bay of the western study area, which shows the complexity of the Finnish archipelago. Photo: J. J. Sederholm, 1906. GTK.

a part of the Salpausselkä ice marginal formation. In the western part of the coast of the Gulf of Finland the bays are usually rather small but often making up a network of sheltered bays in the archipelago. In the eastern part of the Gulf of Finland the bays are larger on average, but also there the inner bays are very well sheltered from the open sea. In the central part of the coast of the Gulf of Finland the bays are few in number, in general they are not very large and they are usually not very sheltered from sea either.

The most complicated archipelago of the coast of the Gulf of Finland is to be found in the western part of the coast where the islands are numerous and make up a mosaic of land between bays, sounds, and channels. In the eastern part of the coast the islands are on average clearly larger, they are not so indented as in the western archipelago, and they are not so numerous either. In the central part of the coast, there are only few islands in comparison to the western and eastern part of the coast, and in many places the mainland is in straight contact with the open sea. This is partly also the case in the easternmost part of the coast. This division of different types of archipelago in different parts of the coast is also reflected in bathymetry of the near coastal sea. The near coastal mud accumulation basins are on average smallest and most complicated in shape in the western archipelago, while in the eastern archipelago they are larger on average and also less complicated in shape. In the central part of the coast mud accumulation basins are on average rather small and partly scarce in number. This can also be seen as a limited number of samples from the outer part of the central coast.

There is also a general pattern of the accumulation basins as a function of distance from land. The accumulation basins in the innermost bays are usually rather large and they are present in virtually all bays, in the central archipelago accumulation basins are relatively small and fewer in number, while in the outermost area the accumulation basins again are larger but less in number than in the innermost bays. As a matter of fact the word "basin" does not always seem to be correct in the case of the outermost accumulation basins as they often do not form a basin (depression), but sometimes slopes or hills with modern accumulation of suspended matter. Normally one can find clays of different ages from glacial/late glacial, usually varved, clays to younger clays of different ages and Baltic Sea stages in the accumulation basins (Winterhalter 1992).

Water depth varies from zero at the coastline to 100 meters in the outermost parts of the study area. It also varies between the accumulation basins, which are separated from each other by submarine shallows made up of coarser material, such as gravel, sand, and especially glacial till which can be seen as different moraine formations. Sometimes bedrock penetrates the sediment as outcrops on different water depths.

MATERIAL AND METHODS

The samples of this study were taken as a part of the coastal mapping program of the GTK during a period from October 2001 to May 2004 as well as the SAMAGOL project between May 2004 and August 2004. Altogether 61 sites were sampled throughout the whole study area. All samples were taken from GTKs research vessels *Kaita* and *Geola*, except for one sample that was in August 2004 taken from research vessel Aranda. Standard sampling procedures were used during the whole project. At each sampling site the bottom was first investigated by echo sounding, in order to find the place best suitable for sampling. Often the seafloor was also examined with an underwater video camera. Sampling was performed using a twin barrel GEMAX gravity corer with an inner diameter of the core liner of 90 mm. The core liner is an acrylic tube with stainless steel core cutter, which allows inspection of the core through the liner. One of the two cores was sliced into 10 mm thick sub samples, which were packed in plastic bags, and immediately stored in +4° C. After the cruises all samples were taken ashore, freeze dried and sieved into < 2 mm fraction at the laboratory of the GTK. Arsenic and the metals cadmium, cobalt, chromium, copper, molybdenum, nickel, lead, vanadium, and zinc are reported from all 61 sites while mercury as more expensive to measure is reported from 39 sites.

All chemical analyses were made at the analytical chemistry laboratory of the GTK. The chosen 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.

QUALITY CONTROL

The analytical quality was checked with reference material samples. The reference materials QCNIST8704, CGBW07313 and QCMESS-2 were used such that at least two of these materials were analysed in every sample batch. Average recoveries for all included metals were normally well within +/- 10% of the certified values. Cadmium, however, seemed to be problematic with reference material MESS-2 (which recently has been replaced by MESS-3) having recoveries between 88 and 158% of the reference value. On the other hand it had very good recovery for reference material NIST8704, between 98 and 102% for all sample batches except one, which had a recovery of 110%. This implies that there might be some problems with the sample matrix of MESS-2 for our method. MESS-2 was also slightly problematic for zinc, having an average recovery of 133%. NIST8704 on the other hand got zinc recoveries of 94 to 103% for all sample batches except one, which had a recovery of 43% only. That is clearly an error in analysis, but it is the only erroneous element in this batch and the batch had samples from five cores only. Strangely enough it is impossible to see any zinc anomaly created by these five samples, the southernmost samples between longitude 24.0 and 24.5 degrees east (see map, also Fig. 13).

RESULTS AND DISCUSSION

The results of the chemical analyses of the soft surface sediments (0-1 cm) are here presented as circular symbol maps in order to facilitate comparison of different elements in different regions. In the case of As one sample is shown as surface concentration value only, not as a circular symbol, for reasons explained later.

Arsenic

Arsenic is a metalloid, which trioxide (As2O3) is strongly poisonous. Because of its poisonous character it has been used in some pesticides. It is also rather commonly used in electric industry (Emsley 1989). The main sources of anthropogenic arsenic in nature are wood preservatives, pesticides and fertilizers as well as releases from smelters and metal industry (Loukola-Ruskeeniemi, Lahermo 2004).

It seems that arsenic does not very well reflect the regional geology, but instead, especially the higher concentrations, reflect anthropogenic distribution of the element (Fig. 3). The concentrations, however, are normally not very high, as the mean and median are 9.72 mg kg-1 and 7.73 mg kg-1, respectively (Table 1). On the other hand the highest value found was as high as 68.4 mg kg-1. That sample is exceptional, as the second highest value measured was 19.1 mg kg-1 only. The strongly anomalous sample was taken from Pohjanpitäjä Bay (Fig. 1-2), in the westernmost part of the study area.

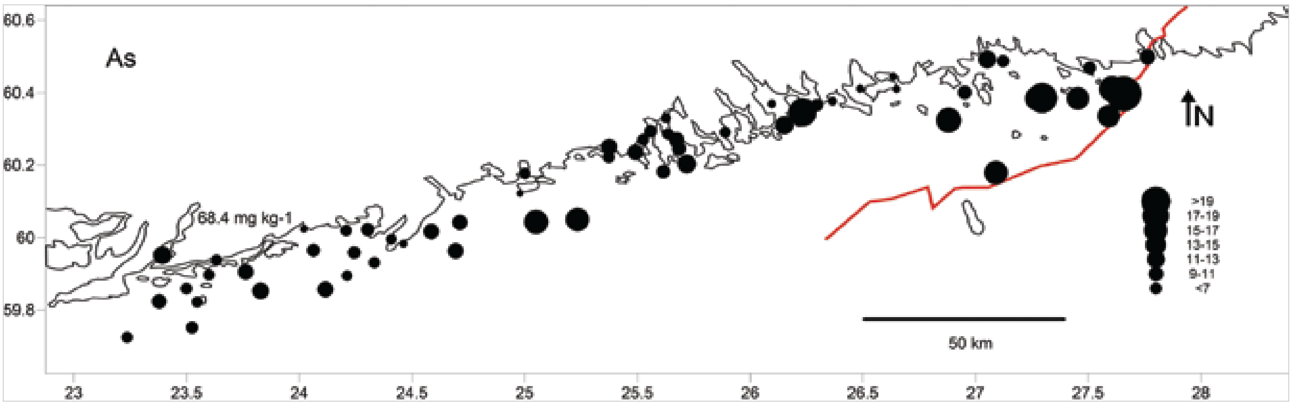

Fig. 3. Distribution of arsenic in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

Arsenic in that sample is probably to a much greater amount of anthropogenic origin than in the other samples. The bay where the sample is taken is rather large, but there is only a narrow sound to the open sea, which reduces water exchange considerably. It is not easy to point out the exact source of this arsenic, but knowing that there are old metal industries in Fiskars and Billnäs as well as the port of Skuru, all of them located close to the northern end of the bay, it gives a good hint of the source. This extreme sample is not shown as a symbol on the map (Fig. 3), as the resolution of the rest of the map would strongly decrease if this "outlier" would be shown. Instead the value (68.4 mg kg-1) is shown on the right side of the sampling site.

The data of the present study can be compared for example with the study of Vallius and Leivuori (1999) from the offshore Gulf of Finland, where the mean and median values (both 14 mg kg-1) are almost twice as high as the values of this study and the highest value of that study was 28 mg kg-1. This indicates that the coastal sediments are on average slightly cleaner in arsenic than the offshore sediments or that the loading has decreased from the early 1990'ies.

The distribution of arsenic does not vary very much in the central and western part of the coast, except for a couple of slightly higher values in the central part, but in the easternmost part of the coast, near the Finnish – Russian border there seems to be a clear arsenic anomaly, the origin of which is unknown. When speaking about arsenic it is worth to remember that its distribution is always strongly controlled by the local redox-conditions (Leivuori, Vallius 2004).

Cadmium

Cadmium is an element, which is of low value for most life forms, although it acts as a micronutrient for some lower organisms. It is toxic and carcinogenic for most organisms in higher concentrations (Emsley 1989). The natural background concentrations of cadmium are rather low, but the anthropogenic load has increased the concentrations of cadmium in the environment considerably.

The distribution of cadmium in the seafloor sediments of the study area does not seem to correlate with any geological provinces, instead it seems to be controlled by the anthropogenic load (Fig. 4). In the marine environment cadmium is in oxic conditions, like in the Neva Estuary (Fig. 1-5) and the shallow Eastern Gulf of Finland, easily mobilized (Rosenthal *et al.* 1995), and does not necessarily reflect local sources. Instead for example Vallius and Leivuori (2003) state that cadmium in the Gulf of Finland is at least partly

Table 1. Descriptive statistics of arsenic and heavy metals in the surface (0-1 cm) of the modern soft sediments of the Gulf of Finland (mg kg-1, DW).

	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn	Hg
Mean	9.72	0.85	14.9	75.1	43.5	2.47	37.3	39.0	83.3	170	0.10
Median	7.73	0.70	14.7	77.6	42.4	1.64	36.5	37.1	83.8	168	0.07
Mode	6.79	0.52	14.5	72.5	41.1	0.97	35.6	33.4	70.5	180	0.06
Standard Deviation	8.25	0.52	3.30	16.0	10.0	2.49	7.40	8.31	17.8	31.5	0.06
Minimum	4.35	0.30	8.32	45.0	27.6	0.57	19.8	25.7	49.4	92.9	0.04
Maximum	68.4	2.69	25.4	111	76.3	13.6	54.8	65.1	122	260	0.32
Count	61	61	61	61	61	61	61	61	61	61	39

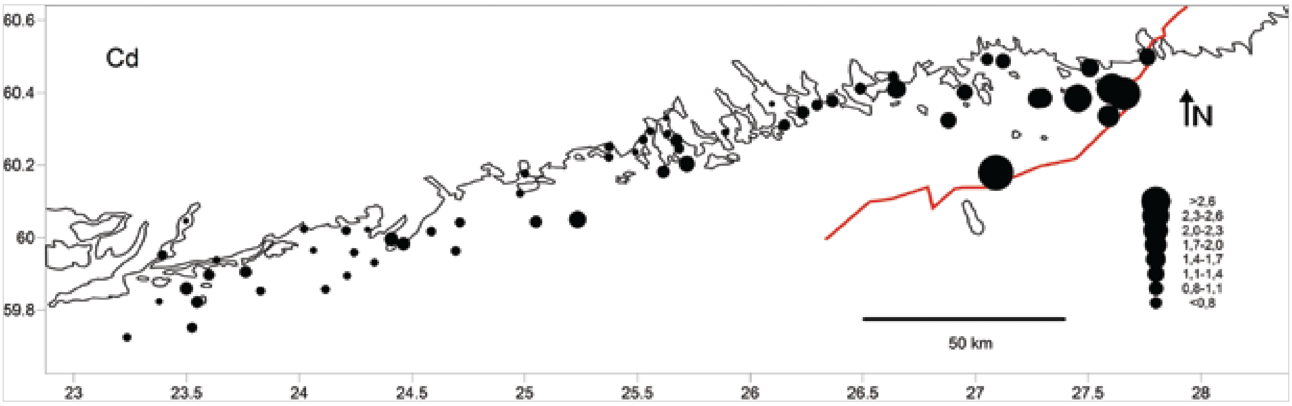

Fig. 4. Distribution of cadmium in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

transported from more distant sources. Because of the Coriolis force and the topography of the Gulf of Finland the currents along the northern coast are on an average directed from east to west. Thus at least part of the cadmium close to the Finnish – Russian border, are transported from east.

Concentrations along the coast are high (Table 1), and especially the concentrations in the eastern part are so high (2.5 mg kg-1 – 2.7 mg kg-1), that they clearly exceed the highest values of the offshore study (Vallius, Leivuori 2003) 2.19 mg kg-1. The mean and median values of the present study 0.85 mg kg-1 and 0.70 mg kg-1, respectively, are on the other hand clearly lower than the mean and median values of the offshore study (Vallius, Leivuori 2003), 1.23 mg kg-1 and 1.28 mg kg-1, respectively. Thus the mean and median concentrations of cadmium in the present study are lower than what was found in the offshore Gulf of Finland in the 1990'ies, while on the other hand the highest concentrations are clearly higher than in the 1990'ies. However, as the highest concentrations in the study by Vallius, Leivuori (2003) were found in the easternmost part of the Gulf of Finland, in Russian territory, it cannot be interpreted, that the sediments of the present study along the Finnish coastline are clearly lower in cadmium than during the 1990's, as concentrations there were lower than the mean and median concentrations already then. Instead the high concentrations in the easternmost Gulf of Finland raised the mean and median values of the whole gulf to excess. However, as the highest concentrations in the present study are clearly higher than the maximum concentrations of Vallius and Leivuori (2003), it can be estimated, that at least locally the cadmium concentrations are rising.

The most striking feature of the distribution of cadmium in the present study is the high anomaly in the easternmost part of the coast (Fig. 4).

Cobalt

Cobalt is a rather common metal in the nature. It is known as an essential element for life in minor amounts. At higher levels of exposure, however, it shows toxic effects similar to many other metals (Emsley 1989).

The anomaly pattern of cobalt in the study area probably reflects geology more than an anthropogenic signal, as the central area is anomalous (Fig. 5). In the bedrock of this area shales and amphibolites are rather common. These rocks contain cobalt in relatively high amounts (Rasilainen *et al.* 2008). In the rapakivi areas of the eastern coast as well as in the bedrock of the western coast cobalt concentrations are rather low. There is a possibility of an anthropogenic signal in Helsinki (Fig. 1-3) region as three samples there are slightly anomalous, this is, however rather speculative (Fig. 5). The only sample, which stands out from the map, is the sample from Pohjanpitäjä Bay (Fig. 1-2), in the westernmost part of the study area (Fig. 5). That sample is probably to a greater amount of anthropogenic origin than the other samples (cf. arsenic). The bay where the sample is taken is rather large, but there is only a narrow sound to the open sea, which reduces water exchange considerably.

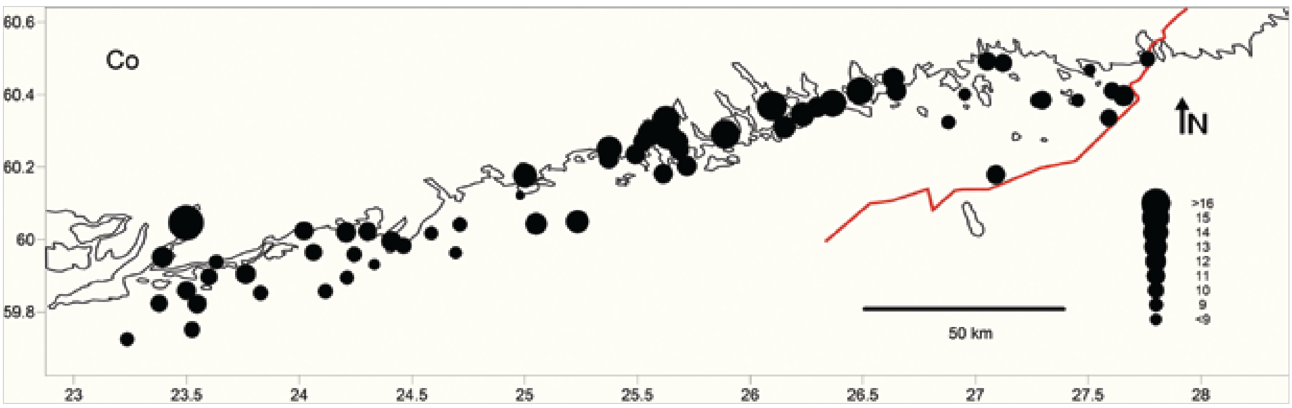

Fig. 5. Distribution of cobalt in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

There is only one earlier study of cobalt distribution in the Gulf of Finland (Vallius 1999a), but the measurements were made from a partial leach, thus a comparison to the present study is not possible. However, when compared with the till geochemistry data from southern Finland (Koljonen 1992), the mean and median values of the present study, 14.9 mg kg-1 and 14.7 mg kg-1, respectively, are practically on the same level as in Koljonen's data. It can thus be speculated that the seafloor sediments of the southern coast of Finland are not badly contaminated by cobalt. Cobalt is used in many industrial processes, thus also the anthropogenic part of the accumulated cobalt origins from many sources, and no single point sources can be indicated.

Chromium

Chromium is a rather common metal, which is essential for humans, but similar to many other metals it can also be toxic in higher concentration or in certain compounds (Emsley 1989). The anomaly pattern of chromium is similar to cobalt. The samples from the central shale and amphibolite areas are anomalous in relation to the rest of the study area (Fig. 6). Moreover the eastern rapakivi area is depleted in chromium. The central anomaly indicates that local geology is at least partly visible in the geochemistry of the soft seafloor sediments. The concentrations of chromium in the study by Vallius, Leivuori (1999) are on all levels higher than concentrations published in the present study (Table 1). Mean and median values in the present study are rather low (75.1 mg kg-1and 77.6 mg kg-1, respectively), and they are thus clearly below the mean and median values of Vallius and Leivuori (1999) from the offshore Gulf of Finland, 87 mg kg-1 and 84 mg kg-1, respectively. Also the maximum concentration found in the present study 111 mg kg-1 are clearly below the maximum of 138 mg kg-1 (Vallius and Leivuori 1999). Thus it seems that the surface seafloor sediments of the beginning of the first decade of the 21st century are clearly cleaner than the sediments of the early 1990's. As a matter of fact the concentrations are not very much higher than the average chromium concentrations in the fine fraction of till in southern Finland (Koljonen 1992).

Copper

Copper is commonly known to be essential for life but toxic in higher concentrations just as most other metals (Emsley 1989). The distribution pattern of seafloor copper is bimodal (Fig. 7), as the bedrock of the western and central parts of the coast seems to be reflected in the copper anomaly, while seafloor copper concentrations increase eastward, where the bedrock, especially in the main rapakivi area, is known to be depleted in copper (Rasilainen *et al.* 2008). The mean and median values of this study (Table 1), 43.5 mg

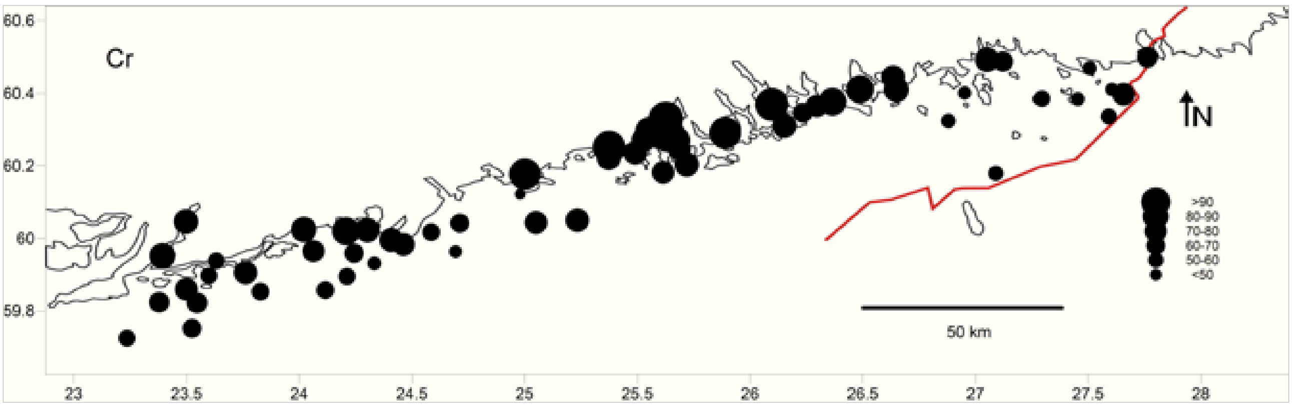

Fig. 6. Distribution of chromium in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

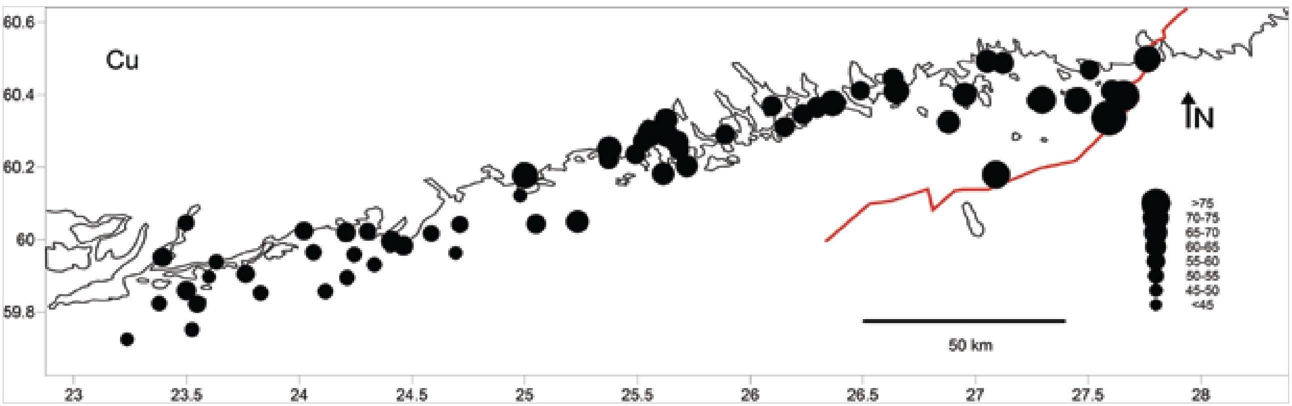

Fig. 7. Distribution of copper in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

kg-1 and 42.4 mg kg-1, respectively, are practically on the same levels as the values of the offshore sediments (Vallius, Leivuori 2003), where both mean and median values were 43 mg kg-1. Still the maximum value of the present study, 76.3 mg kg-1, clearly exceeds the maximum value of the study by Vallius and Leivuori (2003), 63 mg kg-1. Those sites in the present study which exceed the maximum value of the earlier study (Vallius, Leivuori, 2003) are situated close to the Finnish – Russian border, which gives reason to believe that copper has a similar origin to cadmium, and that it is at least partly transported from east (Fig. 7). The copper concentrations of this study show out to be on an average twice as high as the values of copper in the fine fraction of till in Southern Finland (Koljonen 1992). This gives reasons to believe that the seafloor copper is to a greater extent of anthropogenic origin than for example cobalt and chromium.

Mercury

Mercury normally occurs in very small concentrations in nature and thus the main part of the mercury found in the soft seafloor sediments is of anthropogenic origin. Mercury is of no value for any life forms and it is toxic or very toxic, depending on compound (Emsley 1989). The mean and median values of this study (Table 1), 0.10 and 0.07 mg kg-1, respectively, are clearly lower than the values reported from the offshore sediments of the Gulf of Finland, 0.18 mg kg-1 and 0.17 mg kg-1, respectively (Vallius, Leivuori 2003). Also the maximum concentration of this study 0.32 mg kg-1 is lower than the maximum by Vallius and Leivuori (2003), 0.39 mg kg-1. The sample with the highest mercury concentration was taken from eastern Gulf of Finland, from the Russian sector (Vallius, Leivuori 2003). The samples from the present study (Fig. 8), which showed the highest mercury concentrations, are taken from sites near the outlets of River Kymijoki (Fig 1-4), which is known to be badly polluted by mercury (Kokko, Turunen 1988; Anttila-Huhtinen, Heitto 1998; Verta *et al.* 1999; Pallonen 2001). In spite of that the offshore sample from Russian waters by Vallius and Leivuori showed higher mercury concentration than these samples. The samples of the present study are, however, not from the exact river outlets, and thus the concentrations are not as high as possible. This has been verified in a later study by the author of this study, where clearly higher concentrations were found in the river mouths (up to 0.50 mg kg-1 and more). That data will, however, be published later. Remarkable for the anomaly pattern of mercury is that the highest concentrations of mercury are to be found in the coastal area near River Kymijoki (Fig. 8), and not near the Finnish – Russian border, as is the case for example with cadmium and copper (Figs 4, 7).

Molybdenum

Molybdenum is an element, which is essential for most life forms and moderately toxic in higher concentrations (Emsley 1989). It is a rather rare element in nature, also in this study its mean and median values 2.47 mg kg-1 and 1.64 mg kg-1, respectively, are relatively low (Table 1).

There are no earlier reports on molybdenum distribution in the Gulf of Finland surface sediments, thus the results of the present study cannot be compared with other results. There is however one study (Kunzendorf *et al.* 2001) from the main Baltic Sea. The circular symbol map (Fig. 9) of molybdenum shows, that molybdenum values close to the Russian border are clearly higher, as a matter of fact several times higher than the mean and median values of the dataset. The maximum concentration is as high as 13.6 mg kg-1, but additional to that sample there are several samples close to the border where the concentrations exceed 8 mg kg-1. As the concentrations are higher in offshore areas only, especially close to the Russian border (Fig. 9) it is not very plausible that the molybdenum would originate from the rapakivi massif, especially as the molybdenum concentrations in the tills of this area are not very high in molybdenum (Koljonen 1992). It is more plausible that this molybdenum anomaly is of anthropogenic origin. As the anomaly is located close to the border, as there are no higher concentrations near

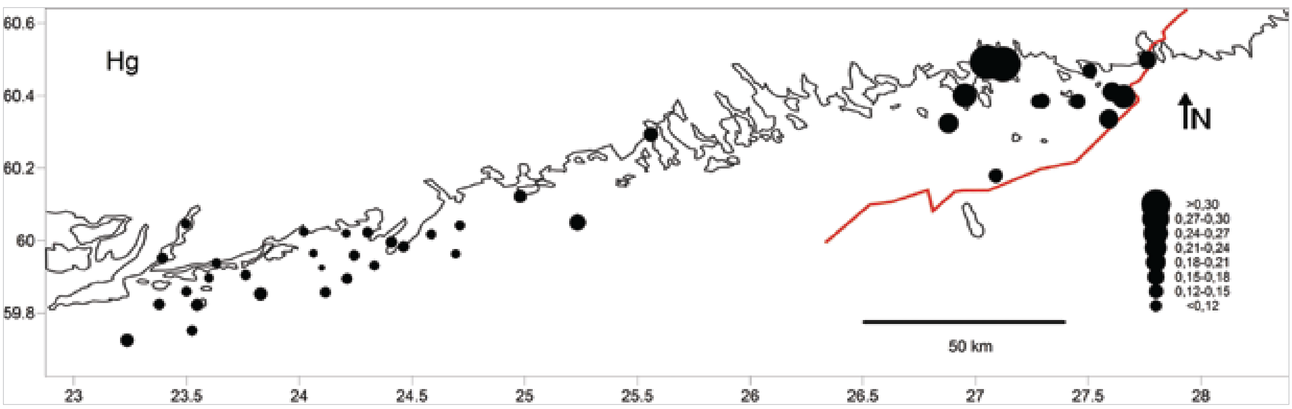

Fig. 8. Distribution of mercury in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

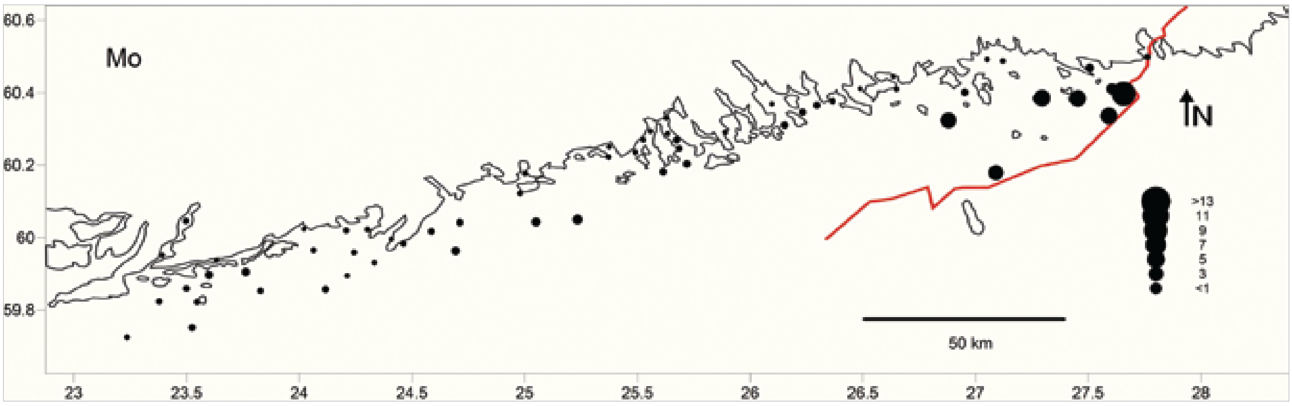

Fig. 9. Distribution of molybdenum in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

the coast, and as there are no known Mo-sources in the archipelago itself, we can assume that at least part of this molybdenum originates in Russia. When comparing the molybdenum concentrations of the present study with the study by Kunzendorf *et al.* (2001) it can be seen that the concentrations of molybdenum in the coastal Gulf of Finland are still rather low in comparison with the highly enriched molybdenum concentrations in the deeper cores of the main Baltic Sea.

Nickel

The importance of nickel at least for higher life forms is uncertain and it is harmful or toxic to humans depending on concentration and compound (Emsley 1989). The map of nickel reflects, just like cobalt and chromium, the shale and amphibolite areas of the central coast, where these metals are present in slightly higher concentrations (Fig. 10). The mean and median values for nickel in the present study (Table 1), 37.3 mg kg-1 and 36.5 mg kg-1, respectively, are clearly below the corresponding values of the offshore data by Leivuori (1998), which both were 42 mg kg-1. Also the maximum concentration found in the present study, 54.8 mg kg-1, is slightly lower than in the offshore study by Leivuori (1998). Thus the coastal sediments are today probably slightly cleaner of nickel than the offshore soft surface sediments in the 1990'ies. When comparing the nickel data of this study with the data of the fine fraction of till in southern Finland, it can be seen that nickel concentrations of the present study are clearly higher than the values by Koljonen (1992). It can thus be expected that the soft surface sediments of the northern coast of the Gulf of Finland are moderately contaminated by anthropogenic load of nickel.

Lead

Lead is widely known to be toxic and of no good for any organisms (Emsley 1989). It seems that this metal has no physiologically relevant role in the body. The concentration map of lead shows two clear anomalies, one outside the capital city of Finland, Helsinki (Fig. 1-3), and another one close to the Finnish – Russian border (Fig. 11). Neither of these correlates with any known geological features, it can thus be expected that they are mostly of anthropogenic origin. The mean and median values of the present study (Table 1), 39.0 mg kg-1 and 37.1 mg kg-1, respectively, are clearly lower than the values reported by Vallius and Leivuori (2003) from the offshore Gulf of Finland. Also the highest measured concentration of the present study is clearly lower than the maximum of the Vallius and Leivuori (2003) study, 88 mg kg-1. The coastal surface sediments are thus today clearly

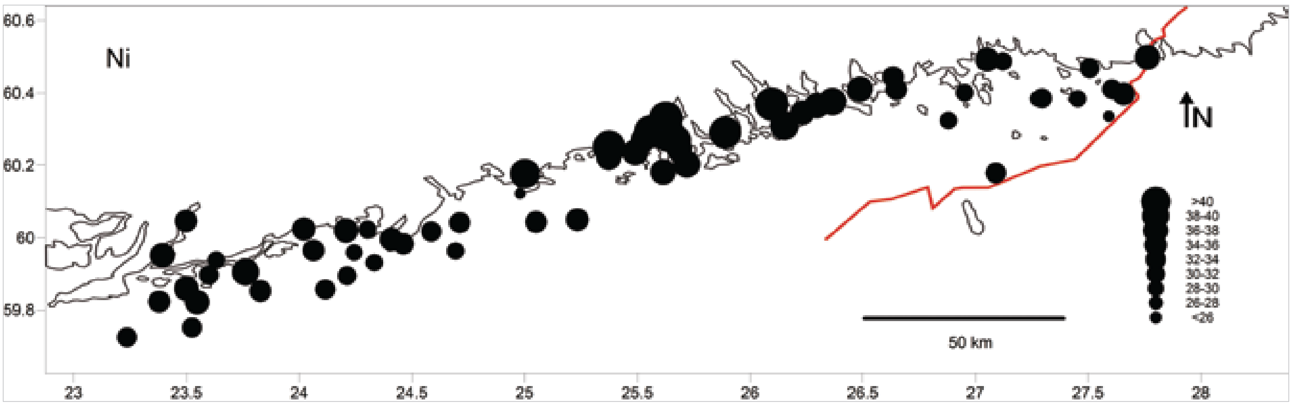

Fig. 10. Distribution of nickel in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

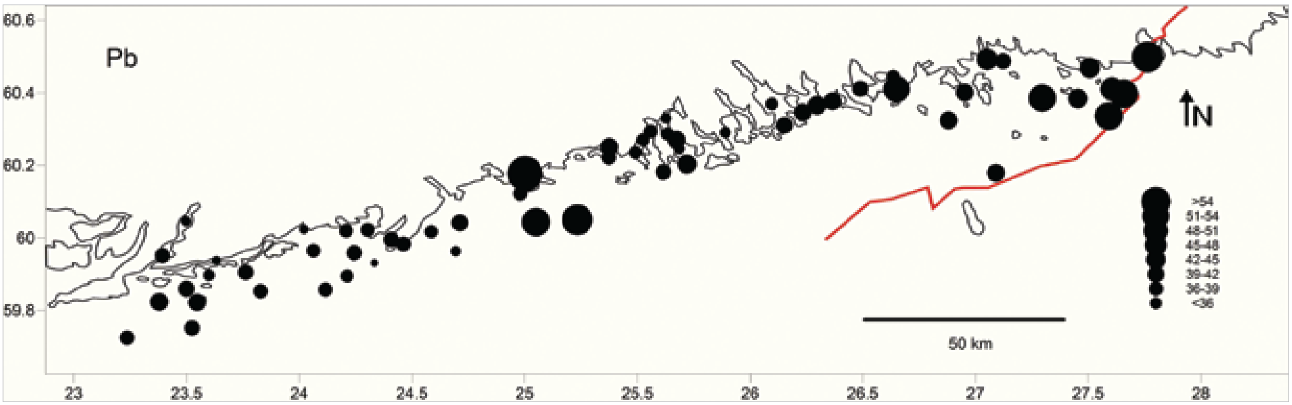

Fig. 11. Distribution of lead in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

cleaner in lead than the offshore surface sediments of the 1990'ies. This was actually expected as Vallius and Lehto (1992), Vallius and Leivuori (1999), and Pallonen (2004) reported decreasing levels of lead in the seafloor surface sediments from the end of last century. That decrease is most probably attributed to the decrease in lead emissions due to the ban of use of lead as fuel additive (Vallius, Lehto 1998). If we, however, compare the data of the present study with the data from till fines by Koljonen (1992), it can be seen that the lead concentrations of the present study still exceed the concentrations in till fines multifold. Thus it can safely be stated that sediment lead is still mainly of anthropogenic origin.

Vanadium

Vanadium is an essential trace element for many life forms but as most metals it is also toxic in some compounds and high concentrations (Emsley 1989). The anomaly pattern of vanadium resembles slightly of that of cobalt, chromium, and nickel, as there is an anomaly in the area of shales and amphibolites of the central coast (Fig. 12). Like chromium vanadium seems to be depleted in the eastern rapakivi area. The mean and median values of this study (Table 1), 83.3 mg kg-1 and 83.8 mg kg-1, respectively, are slightly higher than the corresponding values (76 mg kg-1 and 77 mg kg-1) of Leivuori (1998) from the offshore Gulf of Finland. The maximum concentration of the present study, 122 mg kg-1, on the other hand, exceeds clearly Leivuori's (1998) maximum value of 96 mg kg-1. As the highest concentrations of this study are measured from samples close to the coast it raises the question, has vanadium concentrations increased in the coastal area from the 1990'ies or were they higher already then? That question is impossible to answer by reference to older data as such do not exist. The vanadium data from the study by Koljonen (1992) shows that average values in till fines are on an average on the same level as in the present study, but when looking at the maps by Koljonen (1992) it can be seen that vanadium values near the coast are especially low (less than 60 mg kg-1). This indicates that vanadium in the Gulf of Finland sediments still is to a rather large extent of anthropogenic origin.

Zinc

Zinc is very essential for life and harmful or toxic only in high concentrations (Emsley 1989). Zinc is anomalous in the whole eastern half of the study area (Fig. 13) and the highest concentrations 217 mg kg-1 and 260 mg kg-1 (Table 1) were found close to the Finnish - Russian border. Additionally one rather high concentration (245 mg kg-1) was found close to Helsinki (Fig 1-3). When comparing the mean and

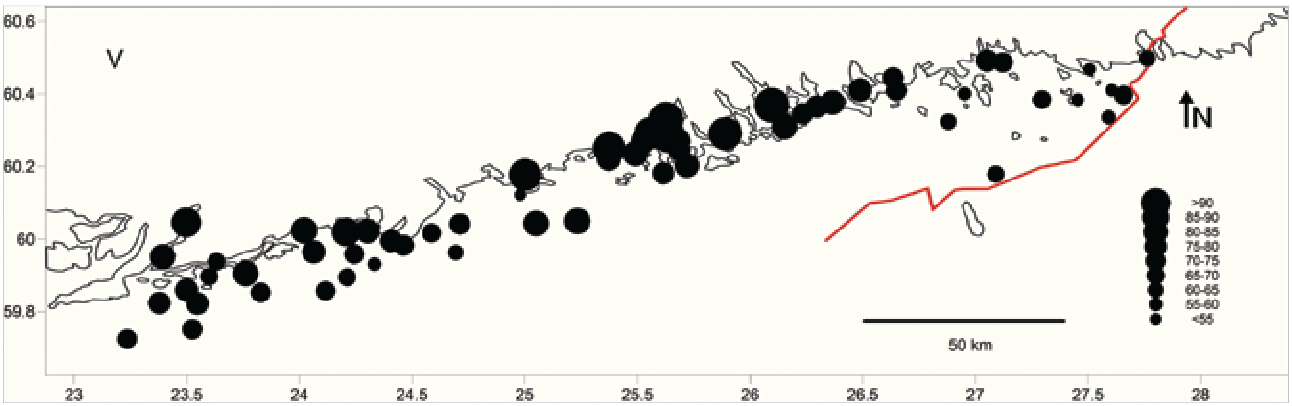

Fig. 12. Distribution of vanadium in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

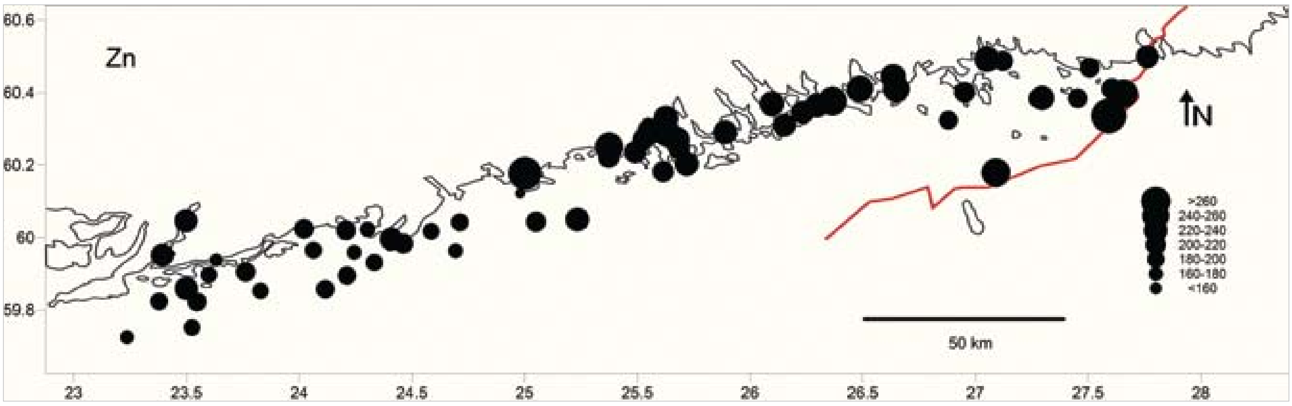

Fig. 13. Distribution of zinc in surface soft sediments of the Finnish coast of the Gulf of Finland. Units in mg kg-1 DW.

median values of this study, 170 mg kg-1 and 168 mg kg-1, respectively, with the corresponding offshore data (Vallius, Leivuori 2003), 199 mg kg-1 and 183 mg kg-1, it can be seen that the average concentrations of the present study are on a clearly lower level. Also the maximum concentration of the present study, 260 mg kg-1 is clearly lower than the maximum concentration reported by Vallius and Leivuori (2003), 391 mg kg-1. As virtually all the sites with highest concentrations in the study by Vallius and Leivuori (2003) were situated in the Russian territory of the Gulf of Finland only, that is, outside and to the east – southeast of the area of this study, it can be presumed that the offshore concentrations of zinc close to the present study area have been on an average on the same level as today, or only slightly higher. Comparison with Koljonen's (1992) data on till fines shows that the concentrations in the seafloor sediments are almost three times higher. Thus it seems that zinc in the coastal seafloor sediments is mainly of anthropogenic origin.

The erroneous zinc values that were discussed in the quality chapter earlier are from samples from the westernmost Gulf of Finland, thus the symbols of those samples should be slightly smaller, highlighting even more the anomaly of the easternmost coast.

CONCLUSIONS

This study is the first of its kind, as a systematic mapping of the whole coastal area of the Finnish part of the Gulf of Finland. As the area was sampled with a relatively even spacing the results of the distribution of heavy metals in Finnish coastal Gulf of Finland can be considered rather reliable. Only the outer part of the central coast lacks samples as a result of lack of any larger basins of recent sedimentation in the area.

The studied elements can clearly be divided in three or four main groups depending on concentrations and distribution patterns. Compared to the rest of the study area cadmium, mercury, and molybdenum show strongly elevated concentrations in the easternmost study area, along the Russian border. Mercury however shows even higher concentrations near the eastern part of the studied coastline. This is easily understandable as the source of mercury is in the River Kymijoki sediments. The sources of cadmium and molybdenum are not easy to point out, but it seems that these metals are to a large extent transported from east, as can be expected from the anti-clockwise pattern of the main currents, caused by the Coriolis force. These elements are also the mostly human induced elements in the sediments of the study area.

Copper and zinc, and partly also arsenic and lead are slightly similar to cadmium, mercury and molybdenum by showing maximum concentrations at the Finnish-Russian border, but the contrast to the rest of the study area is much weaker. Copper and zinc show rather high concentrations in the central, near shore part of the study area, which is the area with abundant metavolcanics and other supracrustal rocks. It thus seems that the Cd, Hg, and Mo anomalies are controlled by human impact, while Cu and Zn anomalies are also geologically controlled.

Arsenic and lead show elevated concentrations at the Finnish–Russian border, but they both also show an anomaly at longitude 25°, which is the Helsinki region (Fig. 1-3). This anomaly cannot be clearly explained, but it seems that it might be human induced. In contrast to Cu and Zn these two elements do not show any clear anomaly in the central near-shore area. Their anomalies thus seem to be a mixture of natural and anthropogenic origin.

The rest of the studied metals show quite identical anomaly maps, showing rather low concentrations in the easternmost rapakivi area, clearly elevated concentrations in the central near–shore areas, and rather even values in the other areas. They thus seem to reflect local geology. Co, Cr, Ni and V thus can be interpreted to be mostly of natural origin, with a human induced addition.

Of the studied elements at least cadmium, copper, mercury, molybdenum, and zinc show highly or relatively highly elevated concentrations in the surface sediments of the easternmost part of the study area, a not so satisfactory situation, especially as also this part of the Gulf of Finland probably will during near future be involved in different kind of submarine activities, affecting the seafloor. The heavy metals can in unfavorable conditions be released into the water column from suspended sedimentary matter. All submarine activities affecting the seafloor in this area should be carefully considered.

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