Arsenic and heavy metal distribution in the bottom sediments of the Gulf of Finland through the last decades

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Abstract The Gulf of Finland is known to have been under rather hard stress from the anthropogenic loading of harmful substances for many decades. The emissions are known to have decreased slightly during the last two decades, but can that decrease be seen also in the sea floor sediments? In this study, heavy metal data from the early 1990s are compared with new research data from 2007–2009. Concentrations of most metals have decreased in the sea floor sediments through the last one and one-half decade. The situation is improving in general despite a drawback on cadmium; those concentrations have remained at levels much too high, with virtually no decrease in trend through the years. Lead and mercury on the other hand seem to have decreased even more than expected, which is a very good sign, given the harmfulness of these metals.

Keywords • Heavy metals • Distribution • Arsenic • Carbon • Environment • Contamination • Pollution • Sediment • Gulf of Finland

INTRODUCTION

The Gulf of Finland is known to have been under rather hard stress from the anthropogenic loading of nutrients and harmful substances. In this study, arsenic and heavy metal accumulation trends during the last decades were analyzed based on a transect of surface cores along the deepest, middle part of the Gulf of Finland from west to east. The results of this study, whose samples were taken during 2007–2009 are discussed based on the earlier knowledge of the distribution of heavy metals in the Gulf of Finland (e.g. Vallius 1999 a, b, c; Vallius 2007; Vallius 2011; Vallius, Lehto 1998; Vallius, Leivuori 1999; Vallius, Leivuori 2003; Leivuori 1998; Leivuori 2000; Leivuori, Vallius 2004). Also, total carbon will be discussed, as many heavy metals have an affinity to carbon. About one third of the deeper bottoms of the Gulf of Finland are covered with modern recently accumulated clays. These so called ‘gyttja clays’ are rich in organic material with rather large specific surface areas, and as a consequence, they easily trap heavy metals from the hydrosphere. Thus these sediments record well the changes in the deposition of heavy metals into the seafloor, and the analyses of cores from these modern sediments give a good estimate of changes in the emission of heavy metals in the different sea areas. By comparing these most recent data with data from earlier surveys, it is possible to estimate changes in heavy metal loads during the last decades in the different areas of the Gulf of Finland. The studied transect can thus be seen as a baseline study of the situation of the gulf in 2007-2009.

The study area covers the middle corridor of the Gulf of Finland from west to east, reaching from about 23 degrees longitude to 28 degrees longitude (Fig. 1). The length of the sampling transect of the eleven sites is 290 kilometres. In spite of being situated in the middle of the gulf, regarded as the deepest parts of the Gulf of Finland, the water depths of the sampling sites are rather shallow, ranging from 35 meters to 77 meters, with a median depth of 64 metres (Table 1). This is explained by the fact that the whole Gulf of Finland is relatively shallow, with an average depth of 35.5 meters only (Vallius 1999b).
MATERIAL AND METHODS

This study is a synthesis of the sediment surface geochemistry done as a result of the field work of the TRANSIT project, performed by the Geological Survey of Finland (GTK, Geologian Tutkimuskeskus). It is a follow-up study of the bilateral SAMAGOL project (2004–2007) which was arranged by the GTK and the A. P. Karpinsky Russian Geological Research Institute (VSEGEI). The study area of the SAMAGOL project covered the easternmost part of the Gulf of Finland only, while the TRANSIT project has concentrated on all off-shore parts of the gulf in Finnish and Russian waters. The samples of this study were taken between the years 2007 and 2009. Most of the samples were taken during cruises of the GTK vessel Geomari, but some of the eastern samples were also taken during two cruises of the Finnish research vessel Aranda (Table 1). Samples discussed in this study are from the off-shore areas only, from Finnish and Russian waters. Because of various practical reasons, the sampling sites of this study do not exactly coincide with the sampling sites of the previous studies, thus only statistical comparisons of mean and median values of the datasets can be considered justified.

In all cases, the sea floor was first examined by echo sounding in order to check the suitability of the sediment for sampling, as the aim was to always sample modern muddy, clayey sediments – so called ‘gyttja clays’. At all chosen sites, the sea floor was sampled using a twin barrel gravity corer, the GEMAX-corer with an inner diameter of the core liner of 90 mm. The core liner is an acrylic tube with a stainless steel core cutter, which allows an inspection of the core through the liner. Sample lengths varied between 35 and 65 centimetres, which gives satisfactory temporal resolution through the 20th century. One core was always sliced into 10 mm thick subsamples and stored in plastic bags which were kept on board in +4 C degrees temperature. The other core was vertically split, photographed and described. Standard description forms of the GTK were used.

After freeze drying, all subsamples were homogenized and sieved to a <2mm fraction in order to remove unnecessary objects such as plant or animal remains. The sample material itself is in fact up to 95% of a < 65µm fraction, which is why no other sieving is necessary. Before the chemical analyses, the samples of a few profiles were analyzed at the GTK for $^{137}$Cs in order to find the level of the 1986 Chernobyl peak. The method is based on gamma spectrometry using an EG&E Ortec ACETM-2K spectrometer with a 4” NaI/ Ti detector. The $^{137}$Cs curve of these analyses marks the depth of the sediment accumulated from the trajectory of the Chernobyl nuclear power plant accident of April 1986. The eastern Gulf of Finland received most of the deposition of the Chernobyl fallout in the Baltic Sea (Ilus 2007), which makes this dating method very successful in the Gulf of Finland area.

All chemical analyses were done in the chemistry laboratory of LABTIUM. In the laboratory, the samples were weighed for wet weight, freeze dried, and weighed for dry weight before sieving. Arsenic and the metals cadmium, cobalt, chromium, copper, mercury, nickel, lead, and zinc as well as total carbon are reported from all 11 sites. The samples were totally digested with hydrofluoric - perchloric acids followed by elemental determination using inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectrometry (ICP-AES), depending on the element. Mercury was always measured with an Hg-analyzer through pyrolytic determination. Leipe et al. (2010) estimated the muddy sediments of the Gulf of Finland to contain 0.7 percent of inorganic carbon on average. As virtually all carbon in the Gulf of Finland is of organic origin; no specific analysis for organic carbon was performed. Instead total carbon was analyzed by a LECO CNS analyzer.

The analytical quality was checked with standard reference materials. The reference materials QC-
NIST8704 and QCMESS-2 were used in every sample batch. Recoveries of QCNIST8704 for all reported heavy metals in all sample batches were normally well within +/- 10% of the certified values. One recovery of lead in one sample batch was 87.3 percent, which still is a rather satisfactory recovery. For QCMESS-2 there were some slightly higher deviations from the certified values. This is especially true for cadmium, which had recoveries between 87.5 and 150.0 percent. This implies that there might be some problems with the sample matrix of QCMESS-2 for the method used by the LABTIUM laboratory. The good recoveries for reference material QCNIST8704, however, assure that the analytical quality is good and that the results can be used for such a baseline study.

The results of the chemical analyses are presented as circular symbol maps of the topmost slices (0-10 mm) of the cores in order to facilitate comparison of the variability of different elements in different regions. Vertical profiles are also presented in order to see the change in temporal trends of the elements. This is further verified through comparison with data from earlier studies.

**RESULTS**

**Horizontal distribution**

In this section, the horizontal distribution of arsenic, carbon, and the heavy metals cadmium, cobalt, chromium, copper, mercury, nickel, lead, and zinc will be presented, and the distribution pattern will be discussed. The surface concentrations are compared with previous data from the early 1990s (Vallius, Leivuori, 1999) as well as with data from a coastal study by Vallius from 2001 - 2004 (Vallius 2009). As already mentioned, all data are comparable due to standard sampling and sample handling methods, laboratory practices, and certified standard reference materials in every sample batch.

Arsenic is known to have rather low concentrations in the Gulf of Finland, which has been shown by Leivuori (1998, 2000), Leivuori and Vallius (2004), Vallius (1999a, 1999b, 2007, and 2009), Vallius and Lehto (1998), and Vallius and Leivuori (1999). In this study, the surface concentrations of arsenic did not reach high concentrations either (Fig. 2, Tables 1 and 2). The samples close to the Finnish–Russian border (sites 8 and 9) showed concentrations of 22.1 mg kg⁻¹ and 27.8 mg kg⁻¹, which are considered to be rather low concentrations. The rest of the samples had still lower concentrations. Arsenic can not be seen as a major contaminant of the gulf, and according to the results of this study, the concentrations of arsenic have remained at the same rather low level as they were in the early 1990s (Table 2).

Cadmium is known to be one of the worst contaminants in the sediments of the Gulf of Finland (Vallius 1999a, b; Vallius 2007; Vallius 2009; Vallius 2011; Leivuori 2000; Vallius, Leivuori 2003). The highest cadmium concentrations in the early 1990s were found in the eastern Gulf of Finland (Vallius, Leivuori 1999). When looking at the cadmium concentrations of this study, it seems, however, that the cadmium peak anomaly (sites 6–9, Fig. 3) is located more to the west compared with the earlier study. This implies that the surface anomaly has moved west. On the other hand, the average concentrations are slightly lower than in the early 1990s (Table 2), which might indicate a westward movement of the highest contaminated material from the east, but that cannot be verified with the rather small present dataset. According to HELCOM (2010), however, the load of cadmium through the Neva River was in 2006 to be almost 30 tons annually, close to the annual average during the last decade. It is the highest input of cadmium from any river to the Baltic Sea (HELCOM, 2010) and makes up the majority of all reported riverine cadmium input into the Gulf of Finland. That input should be possible to see on a cadmium anomaly map of the Gulf of Finland, but the

![Fig. 2 Arsenic concentrations (mg kg⁻¹) in surface (0-1 cm) soft sediments of the Gulf of Finland.](image-url)
main cadmium anomaly is actually located closer to the central part of the Gulf of Finland (Fig. 3). It may be that the cadmium, in the present hydrographical conditions, is moving farther west from its source in the Neva River area than from earlier decades. The finalized Kotlin flood protection dam has been thought to hinder the movement of matter from the Neva Bay into the Gulf of Finland. Could it instead be that most particulate matter and heavy metals in dissolution are forced into the new deep shipping channels and out through the main gates of the dam? Heavy metals and other hazardous substances would thus more easily be moving into the Gulf of Finland; this could be seen as the transport of cadmium over a longer distance before settling onto the sea floor with the sedimentary matter.

Cobalt concentrations in the surface sediments are on average close to the concentrations reported in earlier studies, except at two sites near the Finnish–Russian border (sites 8 and 9), where the cobalt concentrations are clearly higher (Fig. 4). In fact, the highest value of 35.8 mg kg⁻¹ is almost 50% greater than the highest concentration (25.4 mg kg⁻¹) found in the coastal study by Vallius (2009; Table 2). It thus seems that there is a point source of cobalt somewhere close to those two sites. Cobalt was not reported in the earlier study by Vallius and Leivuori (1999), so comparisons with the early 1990s are not possible. Nevertheless, it seems that cobalt concentrations are at a rather acceptable level, except in the Finnish–Russian border area.

Except for the easternmost site, the chromium concentrations of this study can not be considered very high (Fig. 5). The concentration of 95.2 mg kg⁻¹ chromium at the easternmost site is rather high but still clearly under the maximum concentration (111 mg kg⁻¹) found in the coastal study by Vallius (2009) and almost 50% lower than the maximum concentration.
Fig. 3 Cadmium concentrations (mg kg⁻¹) in surface (0-1 cm) soft sediments of the Gulf of Finland.

Fig. 4 Cobalt concentrations (mg kg⁻¹) in surface (0-1 cm) soft sediments of the Gulf of Finland.

Fig. 5 Chromium concentrations (mg kg⁻¹) in surface (0-1 cm) soft sediments of the Gulf of Finland.
of 138 mg kg\(^{-1}\) of the early 1990s study by Vallius and Leivuori (1999; Table 2). Also, the average chromium concentrations of this study are clearly lower than the average in the study by Vallius and Leivuori (1999). It thus seems that chromium concentrations in soft surface sediments have decreased in the Gulf of Finland during the one and one half decade between the study of Vallius and Leivuori (1999) and this study. The lowest chromium concentrations are found in central parts of the Gulf of Finland (sites 5–7).

Copper concentrations are moderate, on average (Fig. 6). Most surface sediment values from central and eastern Gulf of Finland fall close to the mean and median values (43 mg kg\(^{-1}\)) of the off-shore Gulf of Finland study by Vallius and Leivuori (1999), while all values in the western Gulf of Finland are at clearly lower levels than those reported in 1999. The average concentrations as well as the maximum concentration of this recent study are however at clearly lower levels than in the earlier studies of the gulf (Table 2). Accordingly, it is probable that copper concentrations on average have decreased in the surface soft sediments of the Gulf of Finland. A striking feature is that the copper concentrations at sites 7–10 are at almost exactly the same level, 48 mg kg\(^{-1}\). These are also the highest measured copper concentrations in this study. As a consequence, earlier studies (Kokko, Turunen 1988; Anttila-Huhtinen, Heitto 1998; Verta et al. 1999; Pallonen 2001; Vallius 2009; Vallius 2011) have shown rather high concentrations in the surface sediments of the eastern – north eastern Gulf of Finland. That is also the case in this study (Fig. 7), but what is remarkable is that the mercury concentrations in these last off-shore samples are at much lower levels than in any earlier studies. The maximum concentration of this study, 0.10 mg kg\(^{-1}\), is comparable with the average level of the coastal study by Vallius (2009; Table 2), and about half of the average level of the earlier off-shore study by Vallius and Leivuori (1999). Mercury has thus decreased significantly during the one and one half decade that has passed since the study by Vallius and Leivuori (1999).

Nickel was not investigated in the earlier off-shore study by Vallius and Leivuori (1999), but instead by Leivuori (1998), whose data was added to the data in Table 2. In that publication, nickel is said to have decreased from east to west, although no map was presented. In the present study, the distribution of nickel is, however, bipolar, such that there are two anomalies, one in the west, increasing from site 1 to site 4 and another anomaly in the east, increasing eastward from site 8 to 11 (Fig. 8). The highest concentration, 40.7 mg kg\(^{-1}\), was found at site 4, in west central Gulf of Finland. Even that concentration can not be seen as an alarmingly high value. In comparison to the coastal study by Vallius (2009) and a summary study by Vallius (2011), the average values are at the same level, although the extremes in the coastal study are at different levels (see Table 2).

Lead is an interesting metal in the sense that the use of lead in fuel was abandoned in Finland in the 1990s and in the rest of the European Union –of particular interest, Estonia – in 2003. Thus, it should be possible to see a decrease in lead concentrations in the sediments...
between the earlier studies and this recent one. This can be verified (see Table 2), as the average soft surface sediment values have decreased by 20% since the early 1990s and the maximum values have decreased even more. Earlier, the highest concentrations were to be found in the eastern Gulf of Finland; in this recent study, those concentrations are lower, but still amongst the highest in the study (Fig. 9). It thus seems that
there are still rather high lead emissions from Russia, either from gasoline or from other sources. A couple of relatively high concentrations are, however, found in the central and western Gulf of Finland as well.

Zinc was in a 1990s study by Vallius and Leivuori (2003) shown to have its highest sediment surface concentrations in the eastern- north eastern Gulf of Finland. The anomaly pattern of the recent study, however, shows the highest concentrations in the central Gulf of Finland, with an increasing trend from east to west up to site 4 and with moderate concentrations in the east and the lowest values at the three westernmost sites (Fig. 10). In the earlier off-shore study by Vallius and Leivuori (1999), zinc concentrations were at a clearly higher level than today with average levels above 200 mg kg$^{-1}$. As recent average concentrations are at a level of less than 160 mg kg$^{-1}$ (Table 1 and 2), it can be calculated that there is a decrease in zinc concentrations of almost 25% in the sediment surface since the early 1990s, which can be seen as a good trend. Actually only one observation (site 4) reaches the mean of the earlier data with a concentration of 201 mg kg$^{-1}$ (Table 2).

**Relationship between carbon and some of the heavy metals**

Carbon concentrations have been found to be high in the eastern Gulf of Finland. Leipe et al. (2010) noted high particulate organic carbon (POC) contents and the highest POC accumulation rates of the whole Baltic Sea in the off-shore areas of the eastern Gulf of Finland. A strong carbon anomaly in that area is also shown in this study (Fig. 11), which correlates rather well with the anomalies of the heavy metals cadmium and zinc. The relationship between carbon and heavy metals could be explained by metal affinity to organic carbon as well as with the character of the organic rich sediment; such sediment often is made up of very fine material with large specific surface area of the particles. Large specific surface area can be assumed to be proportional to the ability of binding metals to the particle from the water phase. The fact that the highest carbon contents are found in the central eastern Gulf of Finland and not in the Neva Estuary itself is mostly explained by the few and rather small areas of accumulation in the estuary. The suspended matter is instead transported westward to areas where accumulation is possible. Due to the Coriolis force, the currents follow the northern coast on their way westward and sedimentary matter is accumulated as soon as favourable conditions develop. Simultaneously, there are free metals in the water column ready to settle on accumulating matter, while a portion of the metals have been bound to the particles earlier during transport.

The carbon concentrations in the anomalous area are at a level between 8 and 10%, which certainly can be considered high. In the rest of the gulf the carbon concentrations are at relatively normal levels for surface soft sediments, between 4 and 6%. But, because of the high anomaly, the mean and median concentrations for the whole transect are high, 7.4% and 7.9% respectively.

**Temporal trend and vertical distribution**

According to the findings of all the studied elements, clear trends of deposition could be found as evidenced from the data of the early 1990s to the recent survey. Looking at the statistics of the recent surface data in comparison to earlier surface data (Fig. 12) it can be seen that the mean and median, as well as the maximum values of all elements except arsenic, have decreased clearly compared to the data of the early 1990s study. While the average concentrations for most metals have decreased approximately 10–20%, the average
for mercury has decreased by 60%. The same pattern applies for the maximum values except that the change has been more profound (Fig. 12), with several tens of percents of decrease in maximum values for many of the metals, and with a decrease of 60% of the maximum value of zinc and 70% decrease of the maximum concentration of mercury. This is a very promising result; still an even better trend of decrease would be desirable. Arsenic is the element for which virtually no decreased is recorded, on the other hand arsenic has never been problematic in the Gulf of Finland and levels have been low earlier, thus a clear decrease cannot be expected. Cadmium, on the other hand, has decreased only a little on average, approximately ten percent, and the maximum value has decreased only 7% in one and one half decade, which can not be seen as a very satisfactory decrease as cadmium was already known in the 1990s to be the worst contaminant of the Gulf of Finland (Vallius, Leivuori 1999; Vallius, Leivuori 2003). Chromium, copper, nickel, and lead exhibit a uniform change in the last one and one half decades, such that average concentrations of these metals have decreased approximately 15–25% and the maximum values 23 to 38%, which can be seen as a relatively satisfying change, especially as the change has been greatest in lead concentrations. Of all studied elements, the change in mercury concentrations has been by far the best, which is very good when considering the harmful effects of mercury. On the other hand, decreases can hardly be detected in cadmium concentrations, a slightly alarming situation, as Vallius and Leivuori (1999, 2003), already then thought it to have a not-so-promising trend.

The decrease in surface concentrations between the earlier survey data and the recent study can also be verified by vertical profile data of which an example is the vertical profiles of cadmium, chromium, lead, zinc and mercury from site 8 (Fig. 13). There, all the metals decrease clearly toward the sediment surface except cadmium, which increases towards the surface, two to three topmost centimetres excepted. Even those uppermost centimetres are on an excessively high level. As expected from what was said earlier, mercury, zinc,
and lead have had the greatest decrease, but the decrease in chromium has been strong as well. Cadmium once again stands out to be the problematic element. If the topmost centimetres are neglected, virtually no decrease can be recorded since 1994. If we, however, assume that there is a real decreasing trend in cadmium starting, then this can be seen as a good sign.

CONCLUSIONS

The situation concerning heavy metals in the sediments of the Gulf of Finland is improving in general with a drawback on cadmium. As expected, and partly already observed in the early 1990s, lead has decreased remarkably, mainly due to the ban on lead additives in car fuel in Finland and rest of the European Union. Mercury has decreased more than was ever expected, and levels are now much better. It remains to be seen if there will be in near future any remediation in the case of cadmium as the cadmium concentrations of today are too high.

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