ICES CM 1996/R:3

THE LOAD OF ANTHROPOGENICALLY DERIVED HEAVY METALS IN RECENT SEDIMENTS OF GULF OF FINLAND

Henry Vallius

Geological Survey of Finland, Betonimiehenkuja 4,
FIN-02150 Espoo, Finland

Abstract-The load of heavy metals in Recent soft sediments in Gulf of Finland have been studied through gravity corer sampling during repeated cruises. All cores were chemically analysed for total concentrations. For the determination of the anthropogenically derived part of the samples they were partially leached using microwave assisted nitric acid digestion. This technique leaches almost all matter except for silicates. It gives the best average for the anthropogenically contaminated part of the element concentrations. Totally some 30 elements were analysed by ICP-MS and ICP-AES techniques. Most of the profiles were dated using gammaspectrometry, thus determining the Chernobyl peak of 137-Cs. The horizontal distribution of heavy metals in surface sediments show high concentrations especially in eastern Gulf of Finland close to St. Petersburg. The pattern differs depending on element. Some metals, especially those that are bound to oxides, deposit under oxic conditions close to the source. Others are under similar conditions kept in solution or released from already deposited matter and they migrate farther off. The vertical profiles (10-50 cm) of the partially leached, anthropogenically derived part of the heavy metals show different trends in different parts of the study area. All metals show high levels in the upper part of the sediment profiles in Russian territory. There is however for some metals a slowly decreasing trend in the topmost part of the profiles. This good recent trend can partly be explained by the decrease in industrial production in Russia and partly due to better sewage cleaning in St. Petersburg.

Keywords: Heavy metals, contamination, Recent sediments, Gulf of Finland, distribution.

Henry Vallius: Geological Survey of Finland, Betonimiehenkuja 4, 02150 Espoo, Finland [tel: +358 9 46 931, fax: 358 9 462 205, e-mail: Henry.Vallius@gsf.fi]

INTRODUCTION

The Gulf of Finland is a rather shallow bay of the Baltic Sea (figure 1). Since almost 15 million people live in its drainage area, it has strongly been affected by industrial pollution, agriculture and sewage from cities. St. Petersburg is the largest city in the area, its sewage is combined with polluted water from Neva River and this water is affecting the water and sediment of Neva Bay, Neva Estuary and in some extent also the whole Gulf of Finland. Awareness of the environmental situation in the Baltic Sea and especially in the Gulf of Finland encouraged to this study of metal contents in Recent soft sediments in the Gulf of Finland. In order to get a good picture of the situation several cruises were needed. Most of the material was collected during three cruises of MEP (Marine Ecological Patrol), organized by All Russia Geological Research Institute (VSEGEI). Additional sediment profiles were collected on cruises of R/V Aranda of the Finnish Institute of Marine Research and of R/V Muikku of the Finnish Environment Agency. Altogether 55 stations were sampled in Russian, Estonian and international waters. Basins within the Finnish economical zone will be included in the sampling programme during 1996.

SAMPLING MATERIAL

The surfaces of the sedimentary basins in Gulf of Finland are usually fine grained (silt-clay). The topmost part of this sediment (2-4 cm) is usually composed of loose, brown and oxidized

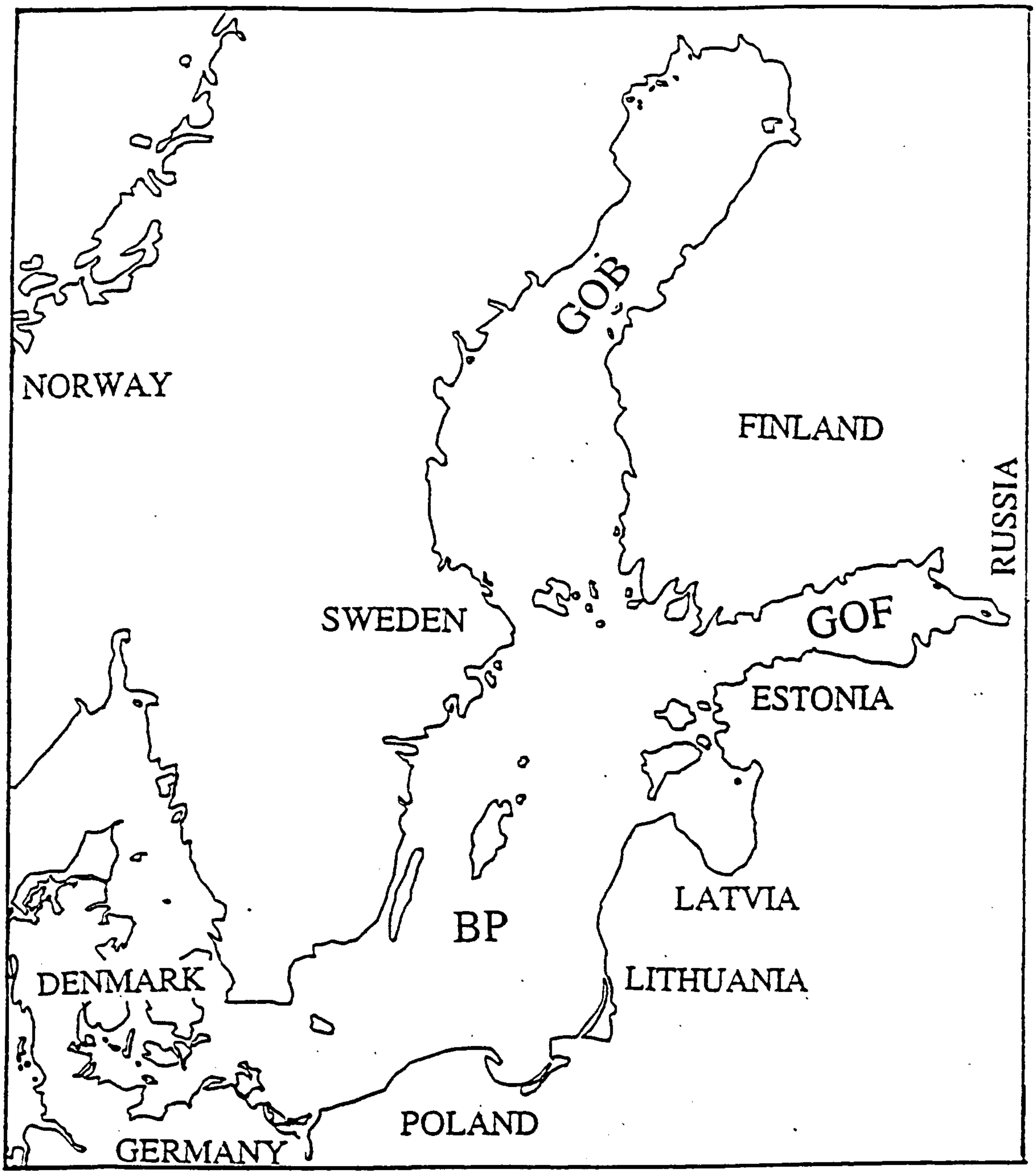

Figure 1. Baltic Sea. Gulf of Finland (GOF), Gulf of Bothnia (GOB) and Baltic Proper (BP) indicated.

fine muddy material. Below this the sediment is reduced, grey to dark grey or sometimes black indicating presence of sulphides (Åker et al. 1988). Sometimes blue glacial clay is present in the lowest parts of the profiles. The grain size of the recent sediments is to > 90% composed of clay, silty clay, clayey silt or silt.

The surfaces of the basins in whole Gulf of Finland are oxic although the oxide content is low in some spots (FIMR 1994, 1995, 1996a,1996b). The oxic layer in the surface of the sediment column is usually 0.5 cm to 4 cm thick. Below that the sediment is totally anoxic. It is important for the stability of the elements that these conditions remain unchanged (Petersen et al. 1996).

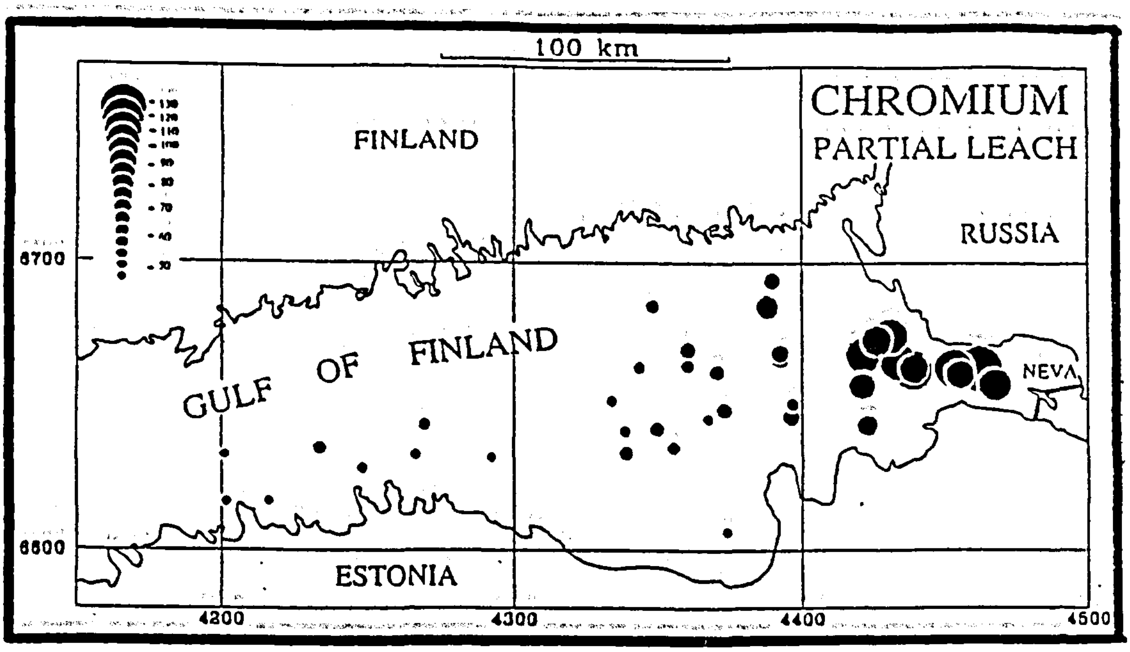

Figure 2. Partial leach – anthropogenic load of chromium (mg/kg) in surface sediments of the Gulf of Finland. Finnish national coordinate system.

METHODS

Sampling was done from the research vessels using different kinds of gravity corers. In all cases the sediment cores were sliced in 1 cm slices and immediately after that stored in -20°C. Most of the cores were also dated using gammaspectrometry and thus determining the ^{137}Cs-peak of the 1986 Chernobyl nuclear power plant accident (Kyzyurov et al. 1994). The frozen samples were later freeze dried in laboratory before chemical analysis. All samples were analysed by ICP/MS and ICP/AES for some 30 elements from total dissolution (hydrofluoric acid-perchloric acid) and partial leach (microwave assisted nitric acid digestion = EPA method 3051)(U.S. Environmental Protection Agency 1990). Mercury was determined using cold vapour AAS method (FIMS-analyser). The partial leach gives an average of the anthropogenically derived part of the metals since that leach does not solve silicates. In this paper only the partially leached 'anthropogenic' load is reported.

RESULTS

Horizontal distribution

Metals from different sources have clearly been enriched in the surface of the sea bottom of the whole Gulf of Finland. The horizontal distribution of the metals in recent, soft sediments in the Gulf of Finland is controlled by physical and chemical properties of the emitted metals, by currents and by the physical and chemical conditions in each individual area. Many metals deposit quite close to the source like in the inner and outer Neva estuary. There the area of sedimentation starts at 20 metres depth level. Most chromium (figure 2) and cobalt are under

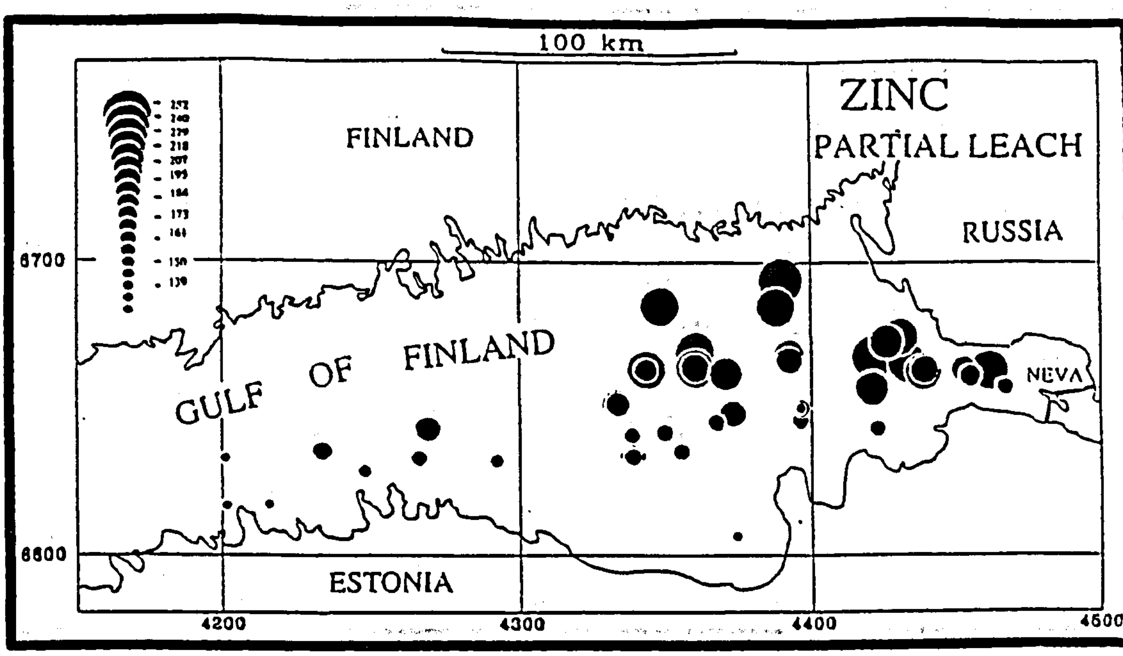

Figure 3. Partial leach – anthropogenic load of zinc (mg/kg) in surface sediments of the Gulf of Finland. Finnish national coordinate system.

oxic conditions bound to oxides and they deposit rapidly in the estuary. Part of the mercury and lead deposit in the Neva estuary but part is spread out in the eastern Gulf of Finland. Cadmium, copper, zinc (figure 3) and nickel start depositing in the estuary but under oxic conditions they are mostly transported out to the open gulf. Since the bottom topography of the eastern Gulf of Finland hinder currents from flowing out in any other direction than NW from the outer Neva Estuary the highest concentrations of the mobile metals will usually be found on the northern side of the gulf (figure 3). Part of the metals are of course introduced to the water system from other sources, like Vyborg bay and Kotka area.

Vertical distribution

The average trend for all metals in the vertical profiles show an increased input during the last 40 - 60 years with a slight decrease of some metals during the last decade. This decrease can more clearly be seen in Neva Bay area than at stations out in the open sea. The enrichment factors for many metals in the 3 - 15 cm part of the sampled sediment profiles vary between 2 and 5, which means 2 to 5 times higher metal contents compared to the older sediments beneath, that are representing background. Some specific metals like mercury (figure 4) and cadmium show enrichment factors up to 10. Fortunately mercury has decreased during the last decade, but unfortunately cadmium has not significantly in more than a few areas.

Iron, manganese and partly arsenic are so mobile that the vertical profiles can not be used for trend analyses.

DISCUSSION

The anthropogenic impact can clearly be seen in the topmost part of the sediment profiles. The horizontal and vertical distribution varies depending on element. Some elements, like cadmium and copper, are clearly more mobile and migrate easily far out to the sea while

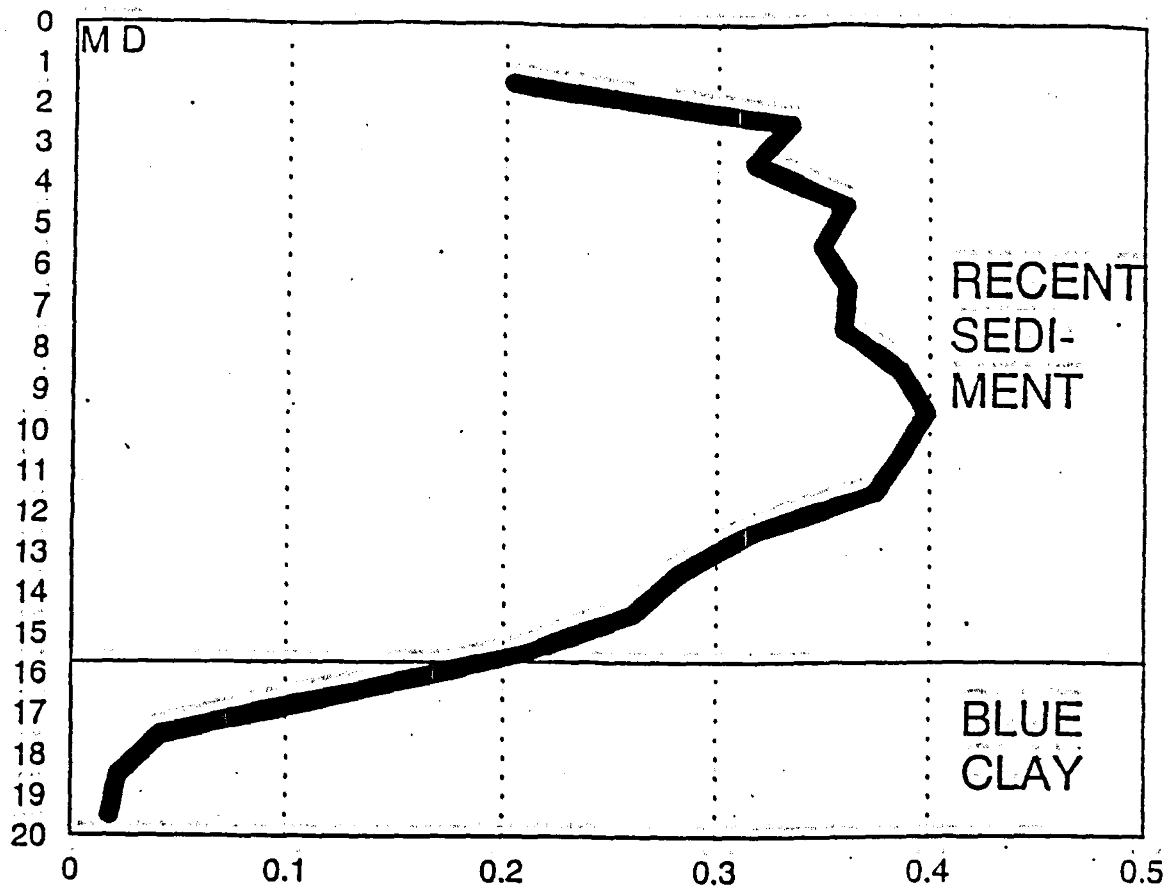

Figure 4. Mercury contents ($\mu g/g$) in vertical section from surface to 20 cm depth in soft, recent sediment at station V14. Data from 0-1 cm is missing.

some, deposit close to the river mouth. The vertical profiles indicate changes in metal emissions. Off the coast these profiles show only weak decrease during the last years. The profiles in the Neva estuary show a slight decrease of some metals during the last decade. This can partly be explained by the decrease in industrial production due to the economic depression in Russia and partly by improvement in sewage cleaning in St. Petersburg since the Central Aeration Plant started operation in the beginning of the 1980-ies. Dilution by organic matter caused by the strong algal blooms during the last decade might have a minor role here. The trend in metal contents in the soft sediments of Gulf of Finland is ''good'' what comes to their content of anthropogenically derived metal contents. If the economic situation in Russia does not change the industrial production will not increase. That will keep the emissions down, but it will on the other hand also hinder investments in better, pro-environmental machinery and establishments.

The situation is now quite stagnant and satisfying as long as the metals are trapped in the sediments. The bottom conditions can however change from oxic to anoxic within some years if anoxic bottom waters are introduced to the Gulf of Finland from main Baltic Sea where some of the deeper basins are totally anoxic and hydrogen sulphide is predominant.

In the vertical columns cadmium, zinc, lead and copper remain fixed as long as the conditions remain anoxic.

Within ten years the flood protection dam of St. Petersburg at Kotlin island will be operating. After westerly storms when the gates have been closed, the dam has to be opened within 24 hours. Before the gates are open the water level inside the dam will probably be higher than outside the dam because of the amount of water transported by Neva river. The opening of the gates will cause strong currents and erosion of the bottom, which will release metals from the sediments into the aquatic system.

If the sediment surface conditions in any part of Gulf of Finland change into anoxic the metals that are oxide bound (Co, Cr) will be strongly released into the water system. This is however not very probable to happen in eastern part of Gulf of Finland where the levels of these metals are highest.

REFERENCES

Åker, K., Eriksson, B., Grönlund, T. and Kankainen, T. 1988. Sediment stratigraphy in the northern Gulf of Finland. Geol. Surv. Finland Spec. Pap. 6, pp. 101-117.

FIMR 1994. Finnish Institute of Marine Research, Annual report 1994.

FIMR 1995. Finnish Institute of Marine Research. Cruise report of R/V Aranda, cruise 2/95.

FIMR 1996a. Finnish Institute of Marine Research. Cruise report of R/V Aranda, cruise 6/96.

FIMR 1996b. Finnish Institute of Marine Research. Cruise report of R/V Aranda, cruise 7/96.

Kyzyurov, V., Mikheev, Y., Niemistö, L., Winterhalter, B., Häsänen, E. and Ilus, E. 1994. Shipboard determination of deposition rates of recent sediments based on Chernobyl derived Cesium-137. Baltica, Vol. 8, pp. 64-67.

Petersen, W., Wallman, K., Li, P., Schroeder, F. and Knauth, H.-D., 1992. The influence of diagenetic processes on the exchange of trace contaminants at the sediment - water interface *In* Calmano & Förstner (eds.) Sediments and Toxic Substances - Environmental Effects and Ecotoxity. Springer, Berlin.

U.S. Environmental Protection Agency (EPA), Washington, DC 20460, Revision 0 November 1990. Method *3051*, Microwave assisted acid digestion of sediments, sludges, soils and oils.