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**Sediment geochemistry studies in the Gulf of Finland and the Baltic Sea :
a retrospective view**

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Abstract Our recent knowledge of the chemistry of the seafloor of the Baltic Sea has been gained during the last century only and most of it during the last three to four decades. When thinking about the start of the industrialization it seems unfortunately late. However, fortunately the seafloor archives all environmental changes in the sedimentary column like pages in a book and they can be later observed and interpreted. The Geological Survey of Finland has performed seabed geochemistry studies for decades. The first studies were performed onboard cruises of the old research vessel *Aranda* and later on the new *Aranda* as well as on the surveys on our own vessels *Geola*, *Kaita*, and *Geomari*. A great part of the work has been done as collaboration in international research programmes, but especially the Marine Ecogeological Patrol by the A. P. Karpinsky Russian Geological Research Institute has been of great importance for Gulf of Finland studies and as a trigger for later studies in the Gulf of Finland as well as the Baltic Sea.

Keywords • geochemistry • methods • sampling • ¹³⁷Cs dating • sediment

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INTRODUCTION

The knowledge of the chemical character of the seabed of the Baltic Sea is not very old taken into account the time which has lapsed since the beginning of the industrialization in central Europe almost two centuries ago. In the northern Baltic Sea studies regarding sediment geochemistry were initiated by Stina Gripenberg (Thalassological Institute of Helsingfors) already in the 1920'ies. According to Gripenberg (1934) some Swedish and German expeditions had sampled bottom sediments of the Baltic Sea already since the 1870'ies, but no chemical examinations are mentioned. Her doctoral thesis (1934) "A study of the sediments of the north Baltic Sea and adjoining seas" is a compilation of the results of examination of seafloor sediments from field surveys during the period from 1924 until 1930 on board S/S *Nautilus* of the Finnish Institute of Marine Research. The study comprises some 130 samples from 81 monitoring

stations (F1–F81). The area covered the whole Baltic Sea north of latitude 57 degrees and 22 minutes, with the southernmost sample at the height of middle part of the island of Gotland. The obtained sediment samples were measured for water content, grain size distribution and salinity as well as the content of organic carbon, nitrogen and carbonates. Additional to the geochemistry observations also Gripenberg's sediment descriptions are interesting in our modern world with accelerating hypoxia in many sea areas as also Gripenberg observed hypoxia or anoxia in our sea areas almost a century ago.

SEDIMENT STUDIES IN THE BALTIC SEA

Later sediment studies were carried out more or less regularly by both Swedish and Finnish scientists, with exception to the break during and after WWII, but the first entirely geochemistry study published after the war, which was largely noted in scientific liter-

ature, was the study by Manheim (1961). In that study concentrations of major and minor elements including heavy metals were reported along two transects from Sweden in west to Lithuania (USSR) in east over the Baltic Proper, taken on board the Swedish hydrographic vessel *Skagerak* in summer 1959. This is the first study from the Baltic Sea where presence of MnCO_3 interpreted as rhodocrosite has been speculated. High molybdenum level (0.0035% DW) is another interesting observation from this cruise. Both Gripenberg (1934) and Manheim (1961) also reported Fe/Mn concretions from various sites in the northern Baltic Sea.

Since these pioneers many authors have reported on various characteristics and geochemistry of Baltic Sea sediments during the 1960'ies (Winterhalter 1966; Ignatius *et al.* 1968; Papunen 1968). The investigations of the recent soft surface sediments (gyttja clays) in the Baltic Sea started in the early 1970'ies after inventions of modern study sediment samplers which provided more or less undisturbed cores with good recovery (Niemistö, Voipio 1974; Boström *et al.* 1978; Suess 1979; Manheim 1982; Emelyanov *et al.* 1982; Emelyanov, Kharin 1988; Boesen, Postma 1988; Jakobsen, Postma 1989; Belmans *et al.* 1993). One such famous corer was the NIEMISTÖ corer (Niemistö 1974) with a later twin barrel version called GEMINI (Fig. 1), which was later modified at the GTK into the recent GEMAX corer. In the 1974 growing awareness of the environment and especially

the state of the Baltic Sea resulted in the creation of the Baltic Marine Environment Protection Commission, better known as HELCOM, with purpose of protection of the Baltic Sea environment.

STUDIES ON SEDIMENT GEOCHEMISTRY IN THE GULF OF FINLAND

Early daybreak

During early days of marine geology in the GTK chemical analyses were, except for some local studies, rather seldom used in routine work, excepting the analyses of organic content of the samples usually performed as analyses of loss on ignition, which were rather routinely performed for surface or near-surface sediments. Also in some cases from different sea areas analyses on iron-manganese concretions were performed (Winterhalter 1966). One of the first environment geochemistry projects as such performed by the marine geology unit of the GTK was the study of the Jätkäsaari harbour basin in Helsinki in 1990 (Rantataro 1996). These surveys were performed from the GTK vessels *Kaita* and *Geola*, however, in an area strongly affected by human activity.

The Marine Ecogeological Patrol (MEP)

The first more extensive GTK studies on environmental geochemistry of soft sea floor sediments in natural basins of the Gulf of Finland were conducted in context of the Russian "Marine Ecogeological Patrol" (MEP) programme in years 1993–1995 coordinated and successfully organized by the Russian Geological Research Institute VSEGEI. The MEP programme itself actually started already in 1990 and there was a collaboration agreement between the participating parties. The geochemistry programme under this agreement, however, didn't in practice and full capacity start before the 1993 cruise. These studies and cruises can be seen as a basis for all further marine environmental geochemistry work at the Geological Survey of Finland and are as such of more interest and more properly explained below.

The first MEP cruise was made on R/V *Professor Multanovskiy* on 2–7 August 1993 in the eastern Gulf of Finland, as a single leg from Helsinki and back. The leg was attended additional to the Russian-Ukrainian scientific team by five Finnish scientists, four from the Finnish Water and Environment Authority and the author of this article from the GTK. Altogether 12 stations between 27°00'66 E and 29°09'00 E as well as 59°52'04 N and 60°10'76 E were visited

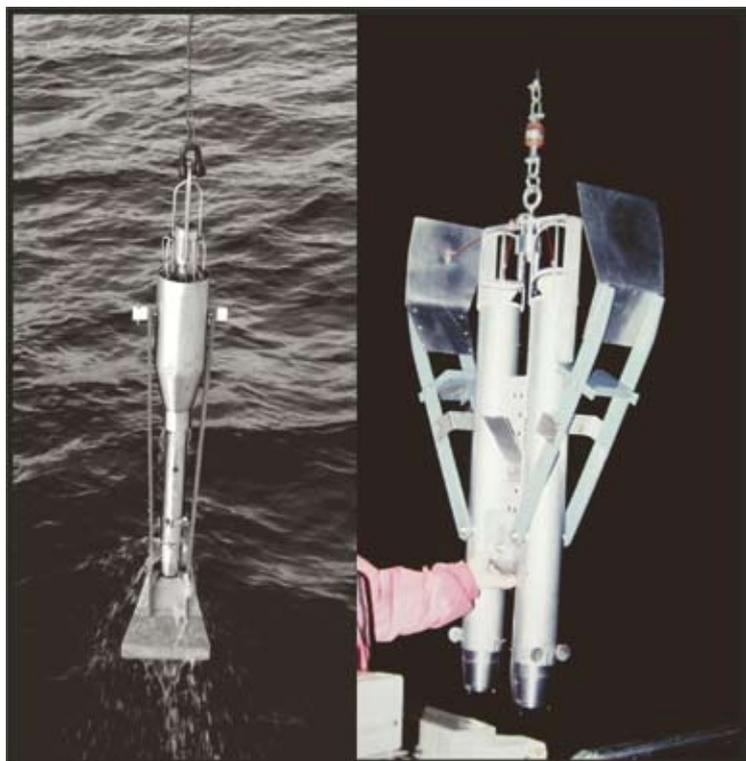


Fig. 1 The *Niemistö* and *Gemini* corers used during geochemistry studies of the GTK. Photos by Henry Vallius

and samples were taken for GTK from all of these stations (Fig. 2). All visited stations were located within Russian territorial waters. These were the early days of the Global Positioning System (GPS) and the Finnish delegation had a hand-held GPS receiver for best possible positioning of the sampling sites. During these days the precision of civil GPS without differential correction was, however, normally within ± 50 meters, but when the ship was anchored at the same location for an hour or two with the positioning on, the precision normally increased to within ± 10 – 20 meters.

At the same cruise one current profiler was moored south of the island of Suursaari (Gogland), close to station SL32. On the research vessel was also one submersible, the *RIF*, and one bathyscaphe or actually a towed submersible, the *THETIS*. The *RIF* (Fig. 3) was used several times during the first leg, and also the author of this article made a dive in the submersible ENE of the island of Lavansaari (Motshjnyj) on 4 August 1993, at $60^{\circ}06' N$, $28^{\circ}04' E$, near station F41. The dive was planned to start in a sedimentation basin and proceed to a till formation and up along the ridge. At the deepest part in the beginning of the dive the *RIF* hits the bottom at a depth of 54 meters b. s. l. in a soft sediment accumulation basin with abundant *Saduria entomon*, an evidence of oxic conditions at the sea floor. From here we aimed westward towards the moraine ridge that was observed on echo sounder from the mother ship before the dive. From the echo sounding the height of the ridge was measured to about 25 meters. At the rim of the accumulation area iron-manganese concretions were observed rather common on the sea floor, and soon it was observed the first boulder, guarded by a viviparous eelpout (*Zoarces viviparus*). In the next moment we entered the side of the moraine ridge, which mostly resembled of an ablation moraine with great difference in grain size, ranging from 1 cm to 3 m in size. With the largest boulders we had to be cautious as we didn't want to hit them too hard with our pressurized fuselage. The roundness of the boulders varied such that some of them were more rounded, but most of the boulders were actually rather angular. The more rounded boulders mainly represented the local sedimentary bedrock while there were a few easily iden-

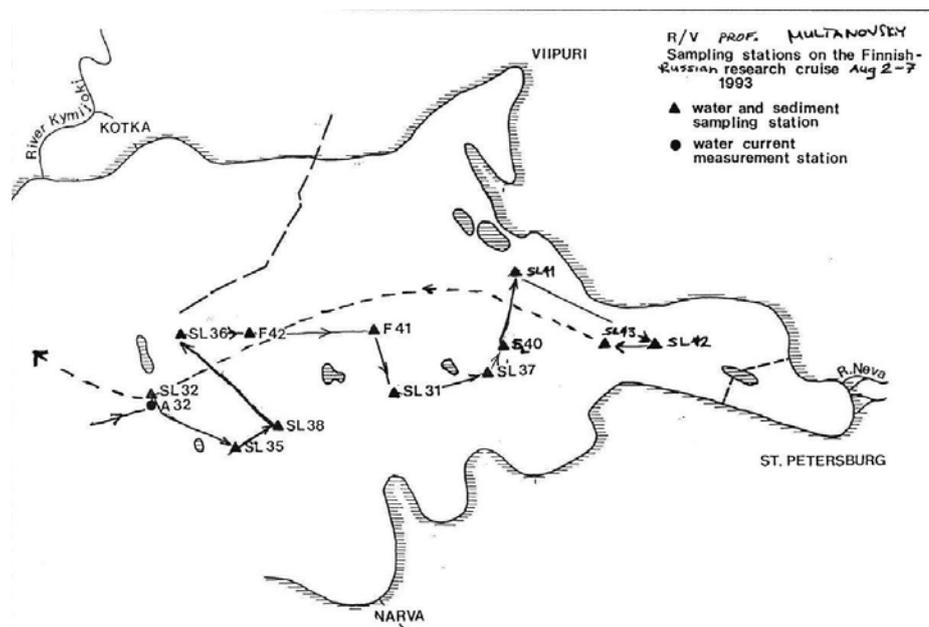


Fig. 2 A sketch of eastern Gulf of Finland with the route and sampling stations of the 1993 MEP cruise of R/V *Professor Multanovskiy* (from the field notes of the author)



Fig. 3 Submersible *RIF* on board mother ship *Professor Multanovskiy*. Photo: Henry Vallius

tifiable angular *rapakivi* boulders. Some of the larger were probably erratics on top of the more local and less transported ablation till. The diving site is located slightly on the distal side of the contact between crystalline basement and the sedimentary bedrock which is overlaying the basement. Between the boulders we sighted some Baltic herrings and a few more eelpouts as well as some remnants of fishnets and trawls stuck between larger boulders, which we obviously tried to avoid. The whole dive took slightly more than one hour and was very interesting from a geological point of view, especially as we also collected a couple of larger Fe/Mn concretions from the side of the accumulation basin where the surface of recent muddy clays turned into older postglacial/glacial clays.

On this cruise the soft surface sediments in the eastern Gulf of Finland were examined for their charac-

ter as well as their quality regarding heavy metals and harmful substances. Sampling was performed using a Niemistö corer, a Finnish built Limnos corer as well as a grab. The cores were sliced in subsamples using a rotary device. The samples taken by GTK were taken for determination of their content of heavy metals as well as nutrients and a sample thickness was chosen to be 10 mm down to 20 cm and below that 20 mm down to the bottom of the cores. All samples were stored in sealed and labelled plastic bags. The cooperation with the Russian and Ukrainian scientific crews worked very well, a reason why this Finnish–Russian cooperation continued until the MEP programme ended in 1995. The results of GTK work on the first MEP cruise have been reported in a couple of different papers (Vallius, Lehto 1998; Vallius 1999; Vallius 1999b; Vallius 2012; Vallius, Leivuori 1999; Vallius, Leivuori 2003).

The second MEP cruise was organized on 27 July to 5 August 1994 such that the Finnish scientists started their cruise on board the Finnish research vessel *Muikku* which sailed straight into Russian waters where the Finnish team planned to meet the Russian research vessel *Akademik Shuleikin* (Fig. 4), a sister ship to the previous year's *Professor Multanovskiy*. The Finnish scientific crew worked first for five days in Russian waters on *Muikku* after which we met the Russian vessel, which had been delayed for a couple of days because of technical problems. After that the Finnish team worked for six days on the Russian vessel after which the leg ended with a port call in Kotka, south-eastern Finland. During the cruise 29 stations were visited, 16 of them during the leg with the Russian vessel. In principle the same methods were used on this cruise as on the first cruise and sampling was also performed for the same purposes, except that a few stations were visited mainly in order to investigate occurrences of iron-manganese concretions. Also this time the expedition was equipped with a submersible, the *RIF*. Positioning was on this cruise assured by DGPS positioning.



Fig. 4 Research vessel *Akademik Shuleikin* in the eastern Gulf of Finland during MEP 1994. Photo: Henry Vallius

A lesson learnt from the first MEP cruise was that in order to gain results that are comparable over the whole Baltic Sea or even worldwide, it is better to analyze the obtained samples from total dissolution, instead of the partial leach which was used for the samples from the first cruise. Thus all samples from the second cruise were dissolved with a hydrofluoric acid – perchloric acid leach and measured for major and minor elements by ICP-AES/MS instruments at the chemistry laboratory of the GTK. Freeze drying of the sediment samples on the other hand was a standard procedure from the beginning. The same methods have been used since then. GTK results from the second cruise have been published in several papers (Vallius 1999; Vallius 1999b; Vallius 2012; Vallius, Leivuori 1999; Vallius, Leivuori 2003).

The third MEP cruise in the summer of 1995 didn't have a port call in Helsinki in the beginning of the cruise as GTK was the only participating institute from Finland, with only one cruise member. Thus the author of this paper travelled to St. Petersburg from where the cruise started. This time a clearly larger ship was chosen as MEP platform, the research vessel *Professor Logachev*, with a length over all of 105.5 meters, when the *Akademik Shuleikin* class vessels have a length over all of 72.6 meters. The cruise was planned to start on 30 May, but was delayed until the morning of 31 May due to technical problems. The weather was exceptionally good when the ship steamed out from St. Petersburg, calm, sunny with an air temperature of about 30 C degrees, and these conditions remained for about one week. Of the submersibles this time only the bathyscaphe *Tetis* was on board, but instead there were a couple of different kinds of ROV's and side scan sonars, which were commonly used during the cruise. The *Tetis* was only tested and checked on this leg, in order to be ready for a dive in Gotland Basin during the next leg (>200 meters depth) with GTK marine geologist B. Winterhalter, who participated in the second leg only.

Regarding the sampling instruments two major improvements were made. VSEGEI had leased a large box corer for studies on iron-manganese concretions and borrowed a *Gemini* corer for coring of soft sediments. Both these samplers provide clearly larger samples for examination and analyses. Otherwise methods during this cruise remained more or less unchanged from earlier years. Altogether 22 stations were visited, from all of which GTK got samples. However, some of them from sites with active formation of iron-manganese concretions and no accumulation of recent soft sediments. The *Gemini* corer, with substantially greater diameter, 80 mm instead of 50 mm, was a clear improvement especially regarding the geochemical analyses of the sediments as the old *Niemistö* corer didn't provide enough dry matter for analyses in sediments

with high water content. Now the cores could finally be analyzed from the top to the bottom for all necessary analyses. Only in a few rare cases with extremely high water content some analyses had to be omitted due to limited amount of dry matter. In such cases usually total carbon measurements were first omitted, secondly mercury, which also had its own method. Later this problem was finally eliminated with the evolution of the *Gemini* corer into the *Gemax* corer, with a 10 mm increase of the inner diameter of the core liner into 90 mm. This development work was concluded in cooperation between the manufacturer KART and the GTK in year 1998.

¹³⁷Cs dating of the cores

From the beginning of the MEP programme also accumulation rates at the different stations had been estimated by gamma spectrometry of ¹³⁷Cs both by Russian scientists on board the vessels as well as GTK scientists in own laboratory. Unfortunately the measurements at the GTK were rather unsuccessful in the beginning because of too small samples, which gave rather unreliable results. In this aspect the larger *GEMINI* corer provided satisfying samples for dating purposes. Additionally the ¹³⁷Cs curves from the cores give good estimate on the quality of the sampled sediment cores, such that disturbances in deposition or post-depositional disturbances are well visible in the curves. Due to the strength of the signal the gamma spectrometry method is very well usable in the Gulf of Finland and the Gulf of Bothnia along the trajectory of the fall out of the Chernobyl nuclear power plant accident. Results on accumulation rates have been published amongst other GTK results from the different cruises, but especially in Vallius (2015b). Other results especially from the third cruise have been published in several different papers (Vallius 1999; Vallius 1999b; Vallius 2012; Vallius, Leivuori 1999; Vallius, Leivuori 2003).

Extension of Finnish–Russian surveys

Overall the MEP cruises were very successful and gave for the first time a very comprehensive picture of the seafloor conditions in the eastern Gulf of Finland. The good cooperation between GTK and VSEGEI didn't finish with the MEP programme. Instead it started a fruitful co-operation in the Gulf of Finland on many shared cruises mainly on board Finnish research vessel *Aranda*, together with the shipmaster, Finnish Institute of Marine Research, usually also in Russian waters. Later the co-operation continued through new studies in the eastern Gulf of Finland and Neva Bay in connection with the two GTK–VSEGEI co-operation projects SAMAGOL and TRANSIT, which gave more insight into the seafloor of the eastern Gulf of Finland. SAMAGOL studies were in particular

published in the peer-reviewed special issue of the GTK Special Paper “Holocene sedimentary environment and sediment geochemistry of the eastern Gulf of Finland, Baltic Sea” edited by H. Vallius (2007), but some of the data has been used also in later studies, especially in combination with data from the later TRANSIT study. While the SAMAGOL study concentrated on the eastern Gulf of Finland the aim of the TRANSIT study was to investigate the offshore middle corridor from west to east through the entire Gulf of Finland. That data were mainly reported in a geochemistry study (Vallius 2012), but also in an assessment study on the northern Baltic Sea (Vallius 2014) as well as in a study on the quality of the offshore sediments in the Gulf of Finland (Vallius 2015a).

The Gulf of Finland Year 1996

Already during the MEP programme a trilateral Gulf of Finland project had been negotiated between the three neighbouring countries, the Gulf of Finland Year 1996. In order to gain information on the state of the gulf more information of the sea area and its sea floor was needed, especially in Estonian waters. Thus already two month after the last MEP cruise a cruise on R/V *Muikku* was arranged by the Finnish Environment Institute on 31 July– 4 August 1995. The data from this cruise were presented together with other available data at the Gulf of Finland Year 1996 final seminar and was published (Vallius, Leivuori 1999), and has been used as background data for several later papers on sediment geochemistry of the Gulf of Finland (Vallius 1999b; Vallius 2012; Vallius, Leivuori 2003).

BALTIC SEA STUDIES – THE BASYS PROJECT

As the most urgent investigations in the Gulf of Finland had been executed during the MEP programme as well as under the Gulf of Finland Year 1996 studies, the work was directed to the main Baltic Sea by the Baltic Sea System Study (BASYS), a large multimillion EU FP4 project which lasted from 1996 to 1999. Subproject-7 of BASYS “Paleoenvironment of the Baltic Sea” was coordinated by the Dr. Boris Winterhalter (GTK). Several cruises to the main Baltic Sea were conducted during the years 1996 to 1999 initiated by a cruise of the Finnish R/V *Aranda* in 1996, with a major cruise on board R/V *Petr Kottsov* on 22 July–2 August 1997 and supported by two R/V *Aranda* cruises each consecutive year until the end of year 1999.

On the R/V *Petr Kottsov* cruise tens of long sediment cores with different corers and about a hundred or more short sediment cores with a multicorer and a *GEMINI* corer were taken. The most impressive and important cores especially for palaeoenvironmental studies were taken with a *KASTENLOT* corer. For example the cubes for palaeomagnetic dating were mainly taken from the



Fig. 5 Subsampling of a *Kastenlot* core during a BASYS Subproject-7 cruise on board R/V *Petr Kottsov*. The cubes for palaeomagnetic dating are well visible in the sediment surface. Photo: Henry Vallius

KASTENLOT cores (Fig. 5). The different studies of the subproject-7 included studies on general marine geology, stratigraphy, mineralogy, environment and geochemistry. Also in this study manganese carbonates were observed in the sediment column just as almost 50 years earlier during the *Skagerak* cruise. The rather thin light carbonate layers were interpreted to correlate with saltwater inflow events from the North Sea through the Danish sounds (Alvi, Winterhalter 2001). Majority of the subproject-7 studies were reported in a special issue of the scientific journal *Baltica* (Vol. 14, 2001), amongst them a few studies on geochemistry and environmental geochemistry (Nytoft, Larsen 2001; Vallius, Leivuori 2001; Kunzendorf *et al.* 2001; Voss *et al.* 2001). Later also a few other studies were reported, such as a study by Vallius and Kunzendorf (2001) on sediment surface geochemistry of the three major Baltic Sea basins that were investigated during the BASYS cruises, as well as a study by the same authors (Kunzendorf, Vallius 2004) on rare earth elements (REE) in the deep basin sediments.

LATER INTERNATIONAL PROJECTS

The BASYS project was scientifically very successful, but in spite of that the financing from the European Union framework programmes for large marine scientific projects faded after the FP4. During the following years GTK participated only in a couple of metadata projects financed by the EU, the EUMARSIN and EUROSEISMICS projects. Meanwhile GTK staff worked with mapping of the coastal area of the Finnish parts of the Gulf of Finland, and area which had

been neglected in earlier work of Finnish research institutes with a marine scope. The field work of the coastal surveys were executed during years 2001 and 2002 and partly completed during the field work of the SAMAGOL project which lasted from year 2004 to year 2007.

These studies were very fundamental for the understanding of the sediments and palaeoenvironment of the coastal area. First data of these studies were published from the western part of the area where indications of permanent seafloor anoxia in coastal accumulation basins were reported (Vallius 2006). Maps with arsenic and heavy metal distribution in the modern soft surface sediments of the coastal area were later published by Vallius (2009) and an evaluation of the quality of the sediments based on American sediment quality guidelines a few years later (Vallius 2015b). The issue of the quality of the sediments has grown in importance during the last years mainly due to the increased activities at sea, which are affecting the seafloor, and knowledge of the state of the sediments is then crucial. A similar sediment quality evaluation was already earlier published (Vallius 2015a) on off-shore data from the Gulf of Finland which were obtained during the Finnish-Russian TRANSIT project during the years 2007 to 2010.

The lessons learnt from the different research programmes during the 1990's have successfully been adapted to later studies along the Finnish coast, such as the GEONAT project in the Kvarken area in the Gulf of Bothnia, the latest Finnish-Russian cooperation ENPI TOPCONS project, as well as the FINMARINET/VELMU project. Well worth mentioning are also the trilateral Finnish-Russian- Estonian cooperation studies under the Gulf of Finland Year 2014. During the second Gulf of Finland Year the scientists sampled at five sites exactly the same locations as had been sampled during the first Gulf of Finland Year in 1995 for comparison of real change in heavy metal load. The obtained data showed that Hg and Cd had decreased markedly and also the trend of Pb was found promising, while copper and zinc didn't show that good change (Table 1; Fig. 6). Thus a satisfying trend in general was observed for most studied elements. However, concentrations of As, Cd, Hg, and

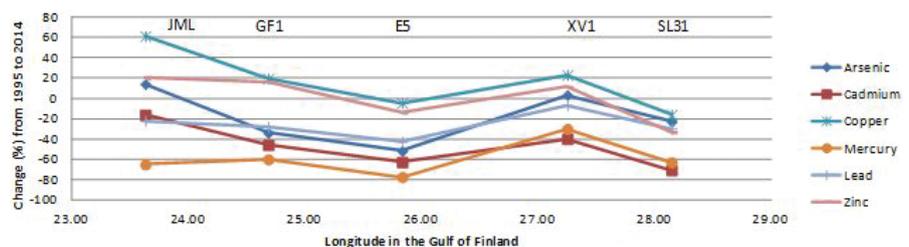


Fig. 6 Changes in heavy metal concentrations (% of change) of surface sediments (1–2 cm sediment depth) at five off-shore Gulf of Finland stations between sampling during Gulf of Finland Year studies of field seasons of 1995 and 2014.

Table 1 Changes in heavy metal concentrations (% of change) of surface sediments (1-2 cm sediment depth) at five Gulf of Finland stations between sampling during Gulf of Finland Year studies of field seasons of 1995 and 2014

Station	Latitude, degrees N	Longitude, degrees E	Water depth (m)	As change (%) 1995 - 2014	Cd change (%) 1995 - 2014	Co change (%) 1995 - 2014	Cr change (%) 1995 - 2014	Cu change (%) 1995 - 2014	Hg change (%) 1995 - 2014	Pb change (%) 1995 - 2014	Zn change (%) 1995 - 2014
JML	59.58	23.63	80	14.1	-16.2	16.3	1.4	61.5	-65.2	-22.2	20.1
GF1	59.71	24.69	83	-34.2	-46.1	11.6	-24.6	19.5	-60.2	-28.0	16.5
E5	59.75	25.83	73	-52.0	-63.0	-18.7	-9.4	-4.5	-77.7	-42.6	-13.9
XV1	60.25	27.25	63	3.3	-40.2	16.0	-4.1	23.1	-30.2	-6.9	11.4
SL31	59.96	28.15	40	-23.0	-71.0	-27.4	-15.2	-16.3	-63.1	-29.9	-33.5

especially Zn concentrations still occur at unacceptably high levels in certain areas of the Gulf of Finland sediments when compared to sediment quality guidelines (Vallius, 2015a, c).

CONCLUDING REMARKS

All in all knowledge of the sea floor and its geochemical characteristics in the Baltic Sea have improved markedly during the last decades. Use of sediment quality guidelines gives a good picture of the quality of the sediments, but no regional guidelines for the Baltic Sea are available. Unfortunately Norwegian guidelines (Bakke *et al.* 2010), which are the closest available, seem to be slightly problematic for some elements in the Baltic Sea, perhaps due to difference in the sample matrix. Nevertheless, regional guidelines for the Baltic Sea or the different Baltic Sea basins would be valuable. As biology now has been integrated with geology (and geochemistry) into a holistic approach the effects of contaminants in sediments should be evaluated also through routine biotests.

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REFERENCES

Alvi, K., Winterhalter, B., 2001. Authigenic mineralisation in the temporally anoxic Gotland Deep, the Baltic Sea. *In* Paleoenvironment of the Baltic Sea. *Baltica* 14, 74–83.

Backe, T., Källqvist, T., Ruus, A., Breedveld, G. D., Hyl-

land, K., 2010. Development of sediment quality criteria in Norway. *Journal of Soils and Sediments* 10, 172–178.

Belmans, F., van Grieken, R., Brüggmann, L., 1993. Geochemical characterization of recent sediments in the Baltic Sea by bulk and electron microprobe analysis. *Marine Chemistry* 42, 223–236.

Boesen, C., Postma, D., 1988: Pyrite formation in anoxic environments of the Baltic. *American Journal of Science* 288, 575–603.

Boström, K., Burman, J.O., Boström, B., Ponter, C., Brandlöv, S., Alm, B., 1978. Geochemistry, mineralogy and origin of the sediments in the Gulf of Bothnia. *Finnish Marine Research* 244, 8–35.

Emelyanov, E.M., Pilipchuk, M.F., Volostnykh, B.V., Khandros, G.S., Shaidurov, Y.O., 1982. Fe and Mn forms in sediment in the geochemical profile of the Baltic Sea. *Baltica* 7, 153–171.

Emelyanov, E. M., Kharin, G. S., 1988. Geological map of eastern and southeastern Baltic Sea. *In* The Baltic Sea (Ed. Boris Winterhalter), *Geological Survey of Finland, Special Paper* 6, 59–67.

Gripenberg, S., 1934. *A study of the sediments of the north Baltic Sea and adjoining seas*. Merentutkimuslaitoksen Julkaisuja/Havsforskningsinstitutets Skrifter 96, 1–231.

Ignatius, H., Kukkonen, E., Winterhalter, B., 1968: Notes on a pyritic zone in upper Ancyclus sediments from the Bothnian Sea. *Bulletin of the Geological Society of Finland* 40, 131–134.

Jakobsen, R., Postma, D., 1989: Formation and solid behavior of Ca-rhodochrochites in marine muds of the Baltic Deep. *Geochimica Cosmochimica Acta* 53, 2639–2648.

Kunzendorf, H., Voss, M., Brenner, W., Andrén, T., Vallius, H., 2001. Molybdenum in sediments of the central Baltic Sea as an indicator for algal blooms. *Baltica* 14, 122–130.

Kunzendorf, H., Vallius, H., 2004. Rare earth elements (REE) in deep basin sediments of the Baltic Sea. *Baltica* 17, 53–62.

Manheim, F.T., 1961. A geochemical profile in the Baltic Sea. *Geochimica Cosmochimica Acta* 25, 52–70.

Manheim, F.T., 1982. Geochemistry of manganese carbonates in the Baltic Sea : Stockholm Contributions in Geology, Symposium Vol. 2, 145–159.

Niemistö, L., 1974. A gravity corer for studies of soft sediments. *Merentutkimuslaitoksen Julkaisuja/Havsforskningsinstitutets Skrifter* 238, 33–38.

- Niemistö, L., Voipio, A., 1974. Studies on the recent sediments in the Gotland Deep. *Merentutkimuslaitoksen Julkaisuja/Havsforskningsinstitutets Skrifter* 238: 17–32.
- Papunen, H., 1968. On the sulfides in the sediments of the Bothnian Sea. *Bulletin of the Geological Society of Finland* 40, 51–57.
- Rantataro, J., 1996. *Anthropogenic impact on recent sediment in Jätkäsaari harbour basin: A comparison with the geochemistry of unpolluted glacial clay*. Geological Survey of Finland, Report of Investigation 134, 47 pp.
- Nytoft, H. P., Larsen, B., 2001. Triterpenoids and other organic compounds as markers of depositional conditions in the Baltic Sea deep basins during the Holocene. *Baltica* 14, 95–107.
- Suess, E., 1979: Mineral phases formed in anoxic sediments by microbial decomposition of organic matter. *Geochimica Cosmochimica Acta* 43, 339–352.
- Vallius, H., 1999a. Anthropogenically derived heavy metals in recent sediments of the Gulf of Finland, Baltic Sea. *Chemosphere* 38, 945–962.
- Vallius, H., 1999b. *Recent sediments of the Gulf of Finland: An environment affected by the accumulation of heavy metals*. Ph. D. thesis, Åbo Akademi University, 111pp.
- Vallius, H., 2006. Permanent seafloor anoxia in coastal basins of the Northwestern Gulf of Finland, Baltic Sea. *Ambio* 35, 105–108.
- Vallius, H., 2007. *Holocene sedimentary environment and sediment geochemistry of the Eastern Gulf of Finland, Baltic Sea*. Geological Survey of Finland, Special Paper 45, 70 pp.
- Vallius, H., 2009. Heavy metal distribution in the modern soft surface sediments off the Finnish coast of the Gulf of Finland. *Baltica* 22, 65–76.
- Vallius, H., 2012. Arsenic and heavy metal distribution in the bottom sediments of the Gulf of Finland through the last decades. *Baltica* 25, 23–32.
- Vallius, H., 2014. Heavy metal concentrations in sediment cores from the northern Baltic Sea: declines over the last two decades. *Marine Pollution Bulletin* 79, 359–364.
- Vallius, H., 2015a. Applying sediment quality guidelines on soft sediments of the Gulf of Finland, Baltic Sea. *Marine Pollution Bulletin* 98, 314–319.
- Vallius, H., 2015b. Sediment accumulation rates off the southern coast of Finland. *Baltica* 28, 81–88.
- Vallius, H., 2015c. Quality of surface sediments of the northern coast of the Gulf of Finland, Baltic Sea. *Marine Pollution Bulletin* 99, 250–255.
- Vallius, H., Lehto, O., 1998. The distribution of some heavy metals and arsenic in recent soft sediments from the eastern Gulf of Finland. *Applied Geochemistry* 13, 369–377.
- Vallius, H., Leivuori, M., 1999. The distribution of heavy metals and arsenic in recent sediments in the Gulf of Finland. *Boreal Environment Research* 4, 19–29.
- Vallius, H., Kunzendorf, H., 2001. Sediment surface geochemistry of three Baltic Sea deep basins. *Ambio* 30, 135–141.
- Vallius, H., Leivuori, M., 2001. The chemistry of the surface sediments of the North Central Basin, the Baltic Sea. *Baltica* 14, 108–114.
- Vallius, H., Leivuori, M., 2003. Classification of heavy metal contaminated sediments of the Gulf of Finland. *Baltica* 16, 3–12.
- Voss, M., Kowalevska, G., Brenner, W., 2001. Microfossil and biogeochemical indicators of environmental changes in the Gotland deep during the last 10,000 years. *Baltica* 14, 131–140.
- Winterhalter, B., 1966. *Pohjanlahden ja Suomenlahden rauta-mangaani-saostumista. Summary: Iron-manganese concretions from the Gulf of Bothnia and the Gulf of Finland*. Geologinen tutkimuslaitos, Geoteknillisiä Julkaisuja. 69, 1–77 pp.