Heavy metals in sediments of the Gulf of Finland: a review

Emelyan Emelyanov, Henry Vallius, Victor Kravtsov


Abstract The Gulf of Finland has during the last centuries been loaded with heavy metals of anthropogenic origin. Work with mapping of the chemistry of the sediments have been done in all surrounding countries during several decades, first in the Soviet Union and later in Russia and similarly in Finland. More recent sediment chemistry data from the last two decades was in this study combined into sediment chemistry maps added with some data from the commercial Nord Stream project. The result shows that zinc, copper and chromium are enriched in the eastern part of the Gulf of Finland, while mercury, cadmium and lead are showing the highest concentrations in the north-eastern part of the gulf.

Keywords • geochemistry • heavy metals • sediment • Gulf of Finland • Baltic Sea

INTRODUCTION

The Gulf of Finland is surrounded by three industrialized countries: Finland, Russia and Estonia. The largest port cities – St. Petersburg, Vyborg, Helsinki, and Tallinn as well as a few others (Primorsk, Ust-Luga) are located in different areas around the gulf (Fig. 1). In addition, there is a quite large amount of smaller ports, rather evenly distributed along the coasts of the gulf. The population density is very high, and the two capitals (Helsinki, Tallinn) are home to one million people, while St. Petersburg has more than five million inhabitants, in fact 5,225 million in 2016 according to Rosstat (2016) and the whole administrative district of St. Petersburg, the Leningrad Oblast has additionally over 1.779 million inhabitants (Rosstat 2016). The catchment of the Gulf of Finland is actively cultivated and there are well developed wood-processing industrial plants mostly located along the rivers with outlets in the Gulf of Finland. All these factors make the Gulf a pool with very high anthropogenic load. Industrial waste, loads from agricultural activity as well as from naval and merchant fleets sooner or later falls into the Gulf. The Neva River drains a densely populated metropolis – St. Petersburg into the small and rather shallow Neva Bay. Toxic elements from the river catchment and the city of St. Petersburg are loaded into the river and when entering the sea in the Neva Bay they are partly accumulating in the seafloor sediments.

The sedimentation in the Gulf was studied and reported by O. S. Pustelnikov (1992) and VSEGEI scientists (VSEGEI, 2010, Spiridonov et al. 2004, Sergeev et al. 2009, Spiridonov et al. 2007). According to Pustelnikov (1992) the Gulf of Finland covers an area of 20.6 thousand km². The average depth of the gulf is 38 meters, with a maximum depth of 123 meters. The water volume of the gulf is 1100 km³. The yearly average river runoff into the gulf is 114.1 km³. Salinity of the gulf varies between 9 PSU in the west to 2.2 PSU in the east. Sedimentary material is fed into the Gulf through the rivers Neva, Narva, Kymi-joki and a couple of other smaller rivers (Fig 1).
Typical clastic deposits (boulders, cobbles and gravelly deposits) are covering vast erosion near shore areas (VSEGEI, 2010) and in these areas are distributed usually quartz and feldspar sands as well as coarse silts, and in more deep areas (more than 50–60 meters) fine-silty mud, silty-pelitic, and pelitic muds are distributed (Emelyanov (Eed.) 2016). Muds typically contain 1–3% total organic carbon (TOC).

HISTORY OF RESEARCH IN THE GULF OF FINLAND

Arsenic (As) and heavy metals including zinc (Zn), copper (Cu), nickel (Ni), cobalt (Co), chromium (Cr), lead (Pb), cadmium (Cd), mercury (Hg), as well as some major components such as organic carbon ($C_{org}$), phosphorus (P), iron (Fe), manganese (Mn), calcium carbonate (CaCO$_3$), and amorphous silica (SiO$_2$$_\text{am}$) accumulating in the Gulf of Finland have been actively investigated for several decades in Soviet Union and Russia (Blazhchishin, Emelyanov 1977). The most complete summary of this subject was published by Pustelnikov (1992). Slightly later Emelyanov (1995) and Kravtsov and Emelyanov (1997) published data on dissolved and particulate forms of toxic elements in the water strata as well as in the bottom sediments. Data on high concentrations of trace elements in the sediments of the Neva Bay have also been published by VSEGEI (VSEGEI 2010; Info Bull. 2013, 2014). Simultaneously with the Russian research in the Gulf of Finland, such work was also carried out by Finnish scientists (Vallius, Leivuori 1999; Vallius, 2012).

In the two last decades (1984–2004) there were important works on dredging, port buildings and sedimentation in the eastern Gulf of Finland (Sergeev et al., 2009, Spiridonov et al. 2007). Important and large new ports and terminals were built in the Russian part of the Gulf of Finland (Ust-Luga, Primorsk and Bronka, Fig. 1). The significant increase of water depth within the dredging areas in the vicinity of the new ports disturb the dynamic equilibrium and sediment balance in the coastal zone (Sergeev et al. 2009).

The changing of geo-hydrochemistry characteristics in water column and bottom sediments changed in the dredged areas. In the previous cited publications, unfortunately, there were no data about the origin and concentrations of the heavy metals and As. Of the near-shore areas of the eastern Gulf of Finland, studies including these microelements were done by scientists of Sevmorgeo company (Shkatov et al. 2011). In these studies it was found out that during years 2005–2007 the near-bottom water in the Neva Bay was highly enriched in Zn and Pb, while their concentrations in years 2008–2010 were extremely low (Shkatov et al. 2011). The changes in time of the
concentrations of the mentioned microelements were studied also by Vallius (2014).

By comparison of the most recent data with data from earlier surveys it is possible to estimate changes in heavy metal accumulation and loads during the last decades in the different areas of the Gulf of Finland.

MATERIAL AND METHODS

In the Finnish sampling program the samples were taken with a GEMAX gravity corer with an inner diameter of 90 mm after thorough echo sounding investigations and the 1 cm thick subsamples were collected into sealed plastic bags and kept refrigerated until taken to the laboratory where the samples were pretreated before analyses. The chosen samples for chemical analysis of the Russian studies along the Nord-Stream pipeline were taken wet and dried at 105°C, then powdered in an agate mortar and the powder was subjected to chemical analysis. Besides the mentioned toxic elements (Zn, Cu, Ni, Co, Cr, As, Pb, Cd, Hg) the samples were determined for many major components, which are not reported here. The methods of chemical analyses were published in Emelyanov et al. (2002). In this article, authors compare ABIORAS (Kalinigrad) data with the data of the Geological Survey of Finland (GTK) (Fig. 2), which methods have been reported earlier (Vallius, 2012). There was a satisfying agreement between the results of the two institutes (Fig. 3). As the sediments along the Finnish coast of the Gulf of Finland are rather homogeneous and well known in quality the Finnish samples were not subjected to particle size analysis, thus a comparison between Finnish and ABIORAS particle size results is not possible and only ABIORAS particle size data are presented in this article. The samplings of bottom sediments along the Nord Stream route were carried out by Van-Veen grab sampler, as well as with a box-corer with an area of 0.16 m², and a height of 70 cm. The samples for the analyses were selected after a complete drain of water. The ABIORAS samples were analyzed for Zn, Cu, Co, Cr, Pb, Cd, and Ni by atomic absorption spectrophotometers.

The samples were prepared for chemical analyses using a method consisting of an acid decomposition in a platinum dish with perchloric, hydrofluoric, and hydrochloric acids heated in sandy bath (Emelyanov et al. 2002). Prior to analyses, 0.5-gram portions of sample were placed in a porcelain dish with their subsequent heat treatment in furnace at T = 300–500°C within 20–30-min period of time, in order to decompose organic compounds.

The obtained solutions were analyzed for trace elements using a C-115 spectrophotometer, including atomic absorption regime with air-acetylene combustion, and using emission regime with propane-air combustion (Khandros, Shaidurov 1980). Governmental (Soviet/Russian) standard samples of bottom sediments (CDO-1, -2, -3, CGD-1A, CT-1 et al.), were used in order to control the correctness of the ABIORAS laboratory analyses.

In the Finnish studies, the samples were taken ashore to the laboratory of the Geological Survey of Finland, where all samples were freeze dried and homogenized. The small amount of >2 mm material, usually parts of plants or benthic animals, was removed. The <2 mm fractions of the samples were totally dissolved with hydrofluoric acid - perchloric acid and instrumentally analyzed by ICP-MS or by ICP-AES depending on element. A part of the <2 mm fraction of the samples was also partially leached by a microwave assisted nitric acid leach (U.S. EPA 1990) as described by Niskavaara (1995). Hg was analyzed...
Fig.3 The concentration of heavy elements and As in the different sediment types along the pipeline Nord Stream, in mg/kg. Sediment types: 1 – gravel; 2 – sand; 3 – coarse silt; 4 – fine-silty mud; 5 – silty pelitic; 6 – pelitic mud; 7 – clay, 8 – samples of Nord Stream; 9 – samples of Geological Survey of Finland. For the comparison data of GSF are shown by symbol +.

Sediment types:

- gravel; △ sand; X silty aleurites; + fine silty mud; ○ aleuritic mud;
- pelitic mud; ◦ clay; ● ABIORAS (Nord Stream), ●+ - GS of Finland

Zinc is in this study found in a range of 27–315 mg/kg in the surface sediments (0–3 cm) of the Gulf.
of Finland. Elevated concentrations are confined to the eastern part of the Gulf of Finland, to the Neva Bay and the Gulf of Vyborg. In deep water about 10 areas with concentrations from 200 to 300 mg/kg of Zn were detected, as well as two small muddy areas containing up to 294 mg/kg of Zn, respectively (see Fig. 3).

Copper is found in a range from 4 up to 780 mg/kg in the surface sediments (0–3 cm) of the Gulf of Finland. As is the case with zinc the highest concentrations of this element are confined to the sediments at the exit of the Neva River, the Neva Bay – St. Petersburg (VSEGEI 2010), which well correlates with earlier reported concentrations by Vallius and Leivuori (1999). The muddy sediments in that area contain very high concentration of Cu, up to 780 mg/kg. Another area with contents of up to 134 mg/kg is located in the Gulf of Vyborg. Westward in the central parts of the gulf there are two small areas with relatively high contents of copper, one point containing 590 mg/kg Cu and a second point of 106 mg/kg Cu. Further west the copper contents level at 30–50 mg/kg with a few small spots reaching higher (up to 60–64 mg/kg). Three studied Nord Stream pipeline landfills with pelitic mud also contained 10–50 mg/kg of Cu.

Chromium has earlier been found to have highest concentrations in the Neva Bay outside the city of St. Petersburg (Vallius, Leivuori 1999). This could be verified also in the present study as the highest chromium concentrations in the surface sediments (up to 166 mg/kg Cr) are confined to the Neva Bay. Higher chromium contents (up to 113–123 mg/kg) were also found in a zone from Vyborg to the south-west. In the central part of the Gulf of Finland, no clear anomalies were found and only at a few individual stations with slightly increased contents of this element were detected. Baseline concentrations in the surface sediments (0–3 cm) range between 50–100 mg/kg.

There are three rather small areas of markedly elevated Ni contents in the sediments of the Gulf of Finland, in the Neva Bay (116 mg/kg), at one site near the edge of the outer Neva estuary, and a spot between Helsinki and Tallinn (170 mg/kg). Contents from 70 to 100 mg/kg are rather typical for Ni in the deeper waters of the Gulf.

In the mud of the central part of the Gulf of Finland, average contents of As are relatively low, round 5–10 mg/kg. Increased concentrations (10–30 mg/kg) of arsenic are found in a zone located in the eastern deep water Gulf of Finland. This zone presumably extends at least to the Neva Bay, as there at one station a concentration of 26 mg/kg As is measured. The zone might also extend north-east to the Vyborg Bay, but this can’t be verified by data from the present study. The maximum content of As (62 mg/kg) is found at a station in the main anomaly zone at longitude 26°00’N. The highest concentration of As observed in the study by Vallius and Leivuori (1999) is located at more or less the same longitude, only slightly more to the north – north-east.

Along the Nord Stream pipeline corridor a few sites with higher concentrations of As (10–52 mg/kg) were found scattered along the pipe-line route with no clear anomaly pattern.

Cadmium like As was studied only in the sampling traverse along the Nord Stream pipeline, as well as in the sediments off the northern coast of Gulf of Finland. The increased concentrations of Cd were without exception found in muddy sediments (Fig. 4). In contrast to the earlier mentioned elements, cadmium does not concentrate to the middle deep water part of the Gulf of Finland, but instead in the muddy sediments of the

**Fig. 4** The distribution of Cd (in mg/kg) in the surficial sediments (0–3 cm; 0–5 cm) of the Gulf of Finland
northern and north-eastern coastal region, as well as in the westernmost part of the gulf (Fig. 4), with the highest individual observation reaching 2.69 mg/kg. A similar distribution with highest concentrations in east and north-east was observed already by Vallius and Leivuori (1999).

Similar to Cd also Pb was studied only along the Nord Stream pipeline, as well as in the sediments off the northern coast of Gulf of Finland. According to the analyses it seems that the highest Pb concentrations are to be found along the northern coast of the Gulf of Finland as well as in the easternmost part of the gulf. At sites near Helsinki Pb concentrations up to 65 mg/kg were found. In the middle deepest part of the Gulf of Finland the Pb concentrations normally stay below 30 mg/kg, while along the northern coast as well as in the east the concentrations mostly exceed 30-40 mg/kg, at five separate stations even 50 mg/kg.

Mercury contamination in the Gulf of Finland is known to mostly reflect the input of Hg from the Kymijoki River. Verta et al. (2009) reported that more than 30 tons of mercury was emitted to the River Kymijoki between the 1940’s and 1971, which has been shown in many studies from the Gulf of Finland (Kokko, Turunen 1988; Vallius 2012). The concentrations of Hg in the sediments of the contaminated north-eastern part of the Gulf of Finland are very high. The high concentrations are to be found on both sides of the river moths: in the west and in the east. We don’t know in what form mercury is bound in the sediments, especially in the gravel and sand. We propose that a very thin film envelops gravel and sand grains. As a result, in the near-shore gravelly and sandy deposits the concentration of Hg are as high as in the muddy sediments. Also in this study the mercury anomaly outside Kymijoki River can be confirmed (Fig.5), even though Hg concentrations have been found to have decreased considerably during the last decades (Vallius, 2014). The highest surface concentration observed (0.58 mg/kg) is from one of the bays within one of Kymijoki outlets.

Average contents of the studied elements in the surface sediments (0-3 cm; 0-5 cm) of the Gulf of Finland, including all Finnish and Russian (as well as the Nord Stream) samples, are shown in Table 1.

Zn, Cu, As, Cr and Ni are in a good paired correlation with the granulometric fraction <0.01 mm of the surficial bottom sediments of the Gulf of Finland (Table 2). The more of fraction <0.01 mm in the samples, the higher content of element (see Fig. 3, Table 1). The microelements As and Hg do not correlate with this fraction: their highest contents are found in some samples of the gravel deposits, in sand and in the mud.

![Fig. 5](image-url) The distribution of Hg (in mg/kg) in the surficial sediments (0–3 cm; 0–5 cm) of the Gulf of Finland

<table>
<thead>
<tr>
<th>Sediment type *</th>
<th>Fractions &lt;0.01mm</th>
<th>Cu</th>
<th>Zn</th>
<th>Cr</th>
<th>Ni</th>
<th>Co</th>
<th>Pb</th>
<th>As</th>
<th>Cd</th>
<th>Hg</th>
<th>Sn</th>
</tr>
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<tbody>
<tr>
<td>Gr</td>
<td>15.75</td>
<td>21</td>
<td>46</td>
<td>35</td>
<td>28</td>
<td>23</td>
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<td>11</td>
<td>0.16</td>
<td>0.06</td>
<td>16.60</td>
</tr>
<tr>
<td>S</td>
<td>18.80</td>
<td>15</td>
<td>45</td>
<td>36</td>
<td>29</td>
<td>24</td>
<td>11</td>
<td>9</td>
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<td>Cs</td>
<td>20.10</td>
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<td>95</td>
<td>43</td>
<td>42</td>
<td>31</td>
<td>13</td>
<td>31</td>
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<td>-</td>
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<tr>
<td>Fsm</td>
<td>31.10</td>
<td>19</td>
<td>62</td>
<td>42</td>
<td>38</td>
<td>37</td>
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<td>Spm</td>
<td>56.20</td>
<td>34</td>
<td>120</td>
<td>42</td>
<td>43</td>
<td>36</td>
<td>16</td>
<td>8</td>
<td>0.34</td>
<td>0.06</td>
<td>3.00</td>
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<td>85.45</td>
<td>42</td>
<td>183</td>
<td>72</td>
<td>61</td>
<td>40</td>
<td>20</td>
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<td>39</td>
<td>14</td>
<td>11</td>
<td>0.23</td>
<td>0.02</td>
<td>3.15</td>
</tr>
</tbody>
</table>

\* Sediment type: Gr – gravel; S – sand; Cs – coarse silt; Fsm – fine silty mud; Spm – silty-pelitic mud; Pm – pelitic mud, Cl – clay, (according the classification of the Bezrukov & Lisitin, 1960)
DISCUSSION

Contamination of sediments by heavy metals

Recent studies confirm strong contamination of the Neva Bay during the last decades (Info Bull. 2014). The source of the toxic elements entering the Neva Bay and from there the Gulf of Finland is the metropolis of St. Petersburg and the Neva River. Kravtsov and Emelyanov (1997) observed that the zones of increased concentrations of both dissolved and suspended harmful substances begin in the outlet of River Neva at the city of St. Petersburg, stretch across the whole Neva Bay, outwards into the inner and outer Neva Estuary and occasionally northward close to Berezoyev Island.

Typically, the upper parts of the cores are more contaminated with heavy metals than the lowermost parts of the cores, but usually with a significant decrease in concentrations near the top of the core. The question is how long ago the accumulation of toxic elements into the sediments of the Gulf of Finland started. We do not know for sure, since without dating of the deep cores the age of the sediment in the cores, is not known. Authors can only assume that it started about 300–200 years ago with the beginning of the industrial era with the introduction of steam engines. Contamination of sediments by Pb and Cd started with the era of use of the combustion engine, i.e. with the introduction of motor vehicles automobiles about a century ago. Many other metals were introduced to the environment after the introduction of (petro-) chemical industries in the 20th century, while input of excess arsenic into the Gulf of Finland started after the introduction of pesticides in agriculture.

CONCLUSIONS

As a conclusion of the presented data we can note that there are some specific patterns in the spatial distribution of the heavy metals in the Gulf of Finland. The sea floor of Neva Bay and the Neva estuary are areas of accumulation of heavy metals in such a degree that these areas are anomalous regarding Zn, Cu and Cr, as the highest anomalies of these metals are to be found here. Hg exhibits a completely different anomaly pattern, as the main source of Hg in the Gulf of Finland is the Kymijoki River in south-eastern Finland, which is expressed in the Hg maps as an anomaly in the north-eastern part of the Gulf of Finland. Cd data are restricted to the central and northern part of the Gulf of Finland, where the highest anomaly is found in the east – north-east. Ni shows a couple of higher anomalies in the central part of the Gulf of Finland, slightly similar to As. Pb data are similar to Cd restricted to the middle and northern part of the Gulf of Finland, where Pb shows the highest concentrations in the east and north-east. It is quite obvious, that the patterns of the heavy metal anomalies are dependent on metal source, often rivers like the Kymijoki River and Neva River, as well as the local physico-chemical conditions.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. V. A. Sushin, the Fisheries Institute (AtlantNIRO, Kaliningrad), leader of sea studies on the Nord Stream project (agreement with the company Peter Gas, Saint Petersburg – “Northern-European gas pipe line. Sea sections of the Baltic Sea” No. 161 from 03.10.2005). Litho-geochemical studies

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The pair correlation (r) of the microelements with the granulometric fraction of sediment samples of the gas pipeline Nord Stream of the Gulf of Finland</th>
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<td>C_{org}</td>
</tr>
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<td>1</td>
</tr>
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<td>C_{org}</td>
<td>135</td>
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<tr>
<td>Fe</td>
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<td>107</td>
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<tr>
<td>Cd</td>
<td>107</td>
</tr>
<tr>
<td>Hg</td>
<td>107</td>
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</table>

* Fr.<0.01 mm – granulometric fractions
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