Assessment of the Pollution Level of Bottom Sediments in the Zolotoy Rog Bay (Vladivostok City, Primorsky Krai)

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Abstract. The paper presents the results of assessment of the ecological state of bottom sediments in the Golden Horn Bay based on the integral index of pollution with heavy metals. According to the total pollution index, bottom sediments in major part of the show an average pollution level on Saet’s scale. The most polluted are bottom sediments in the areas adjacent to wharf walls. A significant contribution to pollution of bottom sediments is made by copper, lead, cadmium and zinc. It was found that such substances as cadmium and lead did not enter the bay with wastewater in the period of 2011-2016, which indicates the accumulation of these pollutants in bottom sediments from wastewater that was entering the bay in an earlier period.

1. Introduction

The monitoring of the ecological state of individual water areas in the Peter the Great Gulf shows a significant level of anthropogenic pollution. The sources of pollution are river runoff, industrial and domestic discharges, surface runoff from contaminated soils as a result of economic activity \cite{1, 2}. The Golden Horn Bay (Vladivostok city) suffers the most severe impact of the economic activities of Vladivostok city’s enterprises and the communal sphere \cite{3}. Along with petroleum hydrocarbons, heavy metals such as copper, lead, zinc, cadmium and nickel contribute the most to the pollution level. There is a trend for improvement of the ecological state of the bay (based on data from 2011-2016), which is associated with the transfer of a significant part of municipal wastewater to wastewater treatment plants. The analysis of statistical reports on waterworks (Federal statistical form “2-TP”) showed that heavy metals were virtually absent in wastewater during this period (figure 1). Pollution with oil is subject to significant temporal variations, which is associated with water exchange with adjacent clean areas of the Peter the Great Gulf and destruction of oil products as a result of biohydrochemical transformations \cite{4}. In general, the quality of water over the indicated period changed from extremely polluted to polluted or moderately polluted \cite{5}.

The bottom sediments analysis is of great importance in assessment of the ecological state of the bay. Pollutants entering with wastewater are transformed into insoluble forms in the aquatic environment, deposited into bottom sediments and accumulated over a long period of time. In contrast to the water mass, there is currently no improvement in the status of bottom sediments \cite{3}. The surface layer of bottom sediments is a source of secondary pollution of the sea, it has a negative impact on the ecosystem of the bay, and it can be seen as an object of accumulated environmental damage. In order to assess the environmental hazard of polluted bottom sediments, various calculated integral indicators are used. There were very few such assessments for the Zolotoy Rog Bay. However, it is precisely the...
assessment of pollution of bottom sediments based on the calculation of various indices using scales of pollution that can be of significant importance when developing measures to eliminate sources of accumulated environmental damage or reduce their negative impact.

Figure 1. The dynamics of the input of pollutants with wastewater into the Golden Horn Bay.

2. Research materials and methods
This work uses the results of comprehensive surveys of the bottom, water area and coastal zone of the Zolotoy Rog Bay, carried out by the staff of Far Eastern Federal University in 2017.

The sampling of bottom sediments in the Zolotoy Rog Bay was carried out during the expeditionary research at 18 stations shown in figure 2. In addition to the stations located in the middle part of the bay, bottom sediments were additionally sampled at stations located in close proximity to pollution sources (stations No. 1H-12H) and three background stations (No. 16, 17, 18) located seaward from the entrance to the Golden Horn Bay.

Figure 2. Geographical location of the Golden Horn bay and stations of hydrological, hydrochemical, geochemical and hydrobiological monitoring. Not pictured: stations No. 17 (Alekseyev Bay) and 18 (Amur Bay).
Bottom sediments were taken with Van Veen grab samplers in accordance with the requirements of GOST 17.1.5.01-80 [6] to obtain an aggregate sample. Additionally, at six stations (No. 2, 4, 6, 8, 10, 12) bottom sediment samples were collected using GOIN samplers maintaining the vertical distribution of pollutants in the layers, and separating the surface layer (0-5 cm), near-surface layer (depth 5-10 cm), and a layer from the bottom of the column (the core height was 10 cm).

The content of pollutants was determined using atomic absorption spectrophotometry (heavy metals) [7] and infrared spectrophotometry (petroleum hydrocarbons) [8].

During the state monitoring, the ecological state of bottom sediments is assessed mainly by comparing the content of pollutants with acceptable values established in the framework of Russian-Dutch cooperation program PSO 95/RF/3/1 “Removing polluted bottom sediments in St. Petersburg” [9].

One of the most well-known criteria for assessing the technogenic impact on bottom sediments is the total pollution index (\(Z_C\)), which is an indicator of adverse effects on public health [10].

The total chemical pollution index is defined as the sum of the concentration coefficients \(K_{C_i}\), individual components of the pollution according to the formula:

\[
Z_C = K_{C_1} + \cdots + K_{C_i} + \cdots + K_{C_n} - (n - 1)
\]

The concentration coefficient of the \(i\)-th polluting component is equal to the ratio of the excess of the content of this component over the background value. When calculating the total pollution index, \(K_{C_i} < 1\) values are excluded, as they do not affect the ecological state of bottom sediments.

The pollution of water bottom sediments based on the \(Z_C\) index is assessed using Yu.E. Saet’s method [11] (table 1).

When calculating the integral pollution index, concentrations of pollutants in bottom sediments of the Zolotoy Rog Bay, calculated according to observations of 2012-2016 (obtained from the Federal Institution “Primorskaya UGMS”), were taken as “background” values. The aggregate values of pollutant concentrations at background stations No. 16-18 were used only for indicators that were not assessed during the state monitoring. The assessment of pollution level of bottom sediments was carried out according to the method by Yu.E. Saet, the rating scale is presented in table 1.

### Table 1. Indicative scale of the assessment of water systems pollution.

| Pollution level | \(Z_C\) of toxic elements in bottom sediments | The content of toxic elements in water |
|-----------------|---------------------------------------------|---------------------------------------|
| Weak            | Below 10                                    | Slightly elevated relative to the background |
| Average         | 10–30                                       | Elevated relative to the background; occasional excess of the MPC |
| Strong          | 30–100                                      | Many times higher than the background; stable excess of the individual MPC levels |
| Very strong     | Over 100                                    | Almost constant presence of many elements in concentrations above the MPC |

3. Results and discussion

The composition of bottom sediments in the Zolotoy Rog Bay is characterized by a wide range of pollutants and their high concentrations, significantly exceeding the threshold values at which the abundance of benthos and species diversity decrease [12, 13]. A sedimentary “oil bitumen” layer has formed at the bottom of the bay, reaching 0.7-1.5 m in different areas [14]. Strong pollution of bottom sediments with metals is typical for the Golden Horn Bay. The average annual concentrations of heavy metals in the bottom sediments of the studied water area in the period from 2011 to 2016 significantly exceed background values for metals such as copper, zinc, lead, cadmium, mercury, and iron [6].
The results of calculations of the total pollution index of bottom sediments are presented in figures 3 and 4, separately for the middle part of the bay and sections located near the wharf walls. According to calculations, most bottom sediments of the middle part of the bay show average pollution level (10<Z<30). The bottom sediments in the apex of the bay (stations No. 2-4) show strong pollution level. Moving towards the exit from the bay, the pollution level of bottom sediments decreases. At the same time, a relative increase in the pollution level of bottom sediments is observed at stations No. 10-12, however, it does not exceed the “average pollution level”.

![Figure 3](image-url)

**Figure 3.** Assessment of the ecological state of the middle part of the Golden Horn Bay by the total pollution index of bottom sediments.

A slightly different pollution trend is observed for bottom sediments taken off the wharf walls (figure 4). Most bottom sediments are also characterized by average pollution level. However, with the exception of stations No. 1 and No. 1H, in the apex part of the bay a stronger pollution level is typical for its middle part compared to areas adjacent to the mooring walls, which seems strange and can be explained by dredging and cleaning of the bottom by wharfs’ owners. A strong pollution level of bottom sediments was observed in the area of two stations (No. 4H and 11H) located in the coastal zone adjacent to the central part of the city, where there is only one wastewater discharge (urban wastewater). A very strong pollution level of bottom sediments was found at station No. 8H, in the area of wharfs belonging to Federal enterprise Directorate for Construction in the Far Eastern Federal District, although there are no organized wastewater discharges in this bay area.

![Figure 4](image-url)

**Figure 4.** Ecological state assessment of areas in the Zolotoy Rog Bay adjacent to wharf walls according to the total index of bottom sediment pollution.
In general, comparative analysis of the pollution of bottom sediments in the Zolotoy Rog Bay showed that, moving away from the apex part, there is a sharp increase in pollution of bottom sediments near wharf walls relative to the pollution level in the middle part of the bay. Further to the exit from the bay, the pollution level of bottom sediments both in the middle part and near wharf walls decreases.

To assess the depth of bottom sediments pollution in the bay, samples from several layers were studied together with the aggregate sample. The results of pollution level assessment for various sediment layers are presented in figure 5.

![Figure 5. Total pollution index for different sediments layers in the Zolotoy Rog Bay.](image)

Only at stations No. 6 and No. 12 the pollution level decreases from average (10<Zc<30) to weak (Zc<10) with the increase of sediments layer depth. At station No. 4, on the contrary, an increase in the pollution level of bottom sediments was observed along the depth of bottom sediments layers. At stations No. 2 and No. 10, the middle layer turned out to be the most polluted. The results obtained did not allow us to find a pattern in the change of pollution level of bottom sediments with the depth, which also indicates that they were disturbed mechanically.

4. Conclusions

Based on the results of integrated assessment of the ecological state of bottom sediments in the Golden Horn Bay, the following characteristic features were identified:

- the largest part of the bay water area is located in the zone of average pollution of bottom sediments. Areas adjacent to wharf walls and located mainly in the apex part of the bay are in the zone of strong and very strong pollution of bottom sediments. The specified zone is the most environmentally neglected;
- the pollution level of bottom sediments decreases further to the exit from the bay;
- priority pollutants of bottom sediments are copper, lead, cadmium and zinc;
- cadmium and lead pollution is caused by accumulation of these pollutants in bottom sediments from wastewater that was entering the bay in an earlier period.

The use of the bottom sediment pollution index made it possible to identify areas of significant anthropogenic pollution in the Zolotoy Rog Bay not by individual pollutants, but by their complex impact, which is an important aspect in addressing the issue of bottom sediment management in developing a program for the elimination of accumulated environmental damage.
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