Development of Guidelines for Environmental and Geochemical Assessment of Marine Bottom Sediments in Peter the Great Gulf

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Abstract. The current system of assessment of bottom sediments quality in the Russian Federation is based on overseas standards and/or reference concentrations of pollutants. The use of foreign standards contradicts the legislation of the Russian Federation, and the use of reference concentrations leads to ambiguity of estimates due to the heterogeneity of bottom sediments and natural variability of the content of controlled substances. This paper presents the analysis of existing approaches to assessing pollution of bottom sediments, and the results of theoretical and experimental research, calculations, assessing pollution of bottom sediments of the Zolotoy Rog Bay in Peter the Great Gulf. The necessity for adoption and capture in a regulatory document of regional background concentrations of pollutants in bottom sediments is shown. Guidelines are proposed for environmental assessment of the pollution level of bottom sediments in Peter the Great Gulf, based on the use of integral characteristics and criteria for assessing the degree of pollution of bottom sediments depending on the type of use of the water area.

1. Introduction
With the increase of intensity of the economic development in Primorsky Krai (Russian Federation) and the exploitation of coastal waters it becomes necessary to comprehensively study the marine environment, including the waters of Peter the Great Gulf. An effective and reliable method for assessing the ecological state of a water body is to monitor the level of pollution of bottom sediments. However, the method is significantly complicated by many different methodological approaches and individual author's developments that are used in the world, including Russia. Bottom sediments were researched by experts in various areas of science and technology. Despite considerable attention to the study of bottom sediments and the availability of a massive amount of accumulated data, the problem of assessing the degree of pollution of the sediments with priority pollutants remains one of the most controversial, and it is far from being resolved. At present, there are no standardized characteristics of the quality of bottom sediments in terms of pollutants concentration in Russia, which is the main reason for the lack of uniformity in methodological approaches to the study of bottom sediments. The lack of clear criteria significantly reduces the possibility of a reasoned conclusion on the results of a research of the ecological state of bottom sediments. The practical significance of this work lies in the development of assessment methods and quality criteria for marine bottom sediments, which will
make it possible to reliably and uniformly obtain information on the status of diverse water bodies in the territory of the Primorsky Krai.

2. Research materials and methods
Coastal waters of the Peter the Great Gulf in the Sea of Japan were chosen as the research objects. These waters are used in different ways and suffer from varied anthropogenic pressure: the Zolotoy Rog Bay is a port; the Uglovoy Bay is a recreation area; the Kitovy, Minonosok and Krakovka bays are used for sea-farming). The staff of the School of Engineering of Far Eastern Federal University (FEFU) carried out environmental studies of these objects [1, 2], and the results formed the basis for the development of a methodology for assessing the ecological and geochemical state of bottom sediments of water areas that differ in types of economic activity.

In this work, we used the data on the composition of bottom sediments obtained during comprehensive engineering surveys of the Zolotoy Rog Bay (in the Peter the Great Gulf) in 2017. The data on the content of pollutants in bottom sediments of the bay are compared with the standards and reference concentrations of these pollutants according to official regulatory documents and literature sources (table 1). It can be seen that the values of permissible concentrations chosen as standards (instead of missing maximum permissible concentrations) can vary quite significantly.

Table 1. Comparison of the content of pollutants in bottom sediments of the Zolotoy Rog Bay with applicable standards and reference concentrations.

| Pollutant        | Regulation values | Reference concentrations | Literature sources |
|------------------|-------------------|--------------------------|--------------------|
|                  | [3] | [4] | [5, 6] | Primorsky Administration for Hydrometeorology and Environmental Monitoring | State ecological monitoring | FEFU, 2017 | [9] | [10] | [11] |
| Copper, mg/kg    | 35  | 35  | 132   | 63                    | 12.7                  | 47.2    | 11.3 | 8    | 28    |
| Cadmium, mg/kg   | 0.8 | 0.8 | 2     | 1                     | 0.3                   | 1.3     | 0.06 | 0.1  | 0.2   |
| Lead, mg/kg      | 85  | 85  | 130   | 61                    | 26.7                  | 48.2    | 8.5  | 20   | 35    |
| Zinc, mg/kg      | 140 | 140 | 220   | 137                   | 89.6                  | 131.9   | 45.6 | 30   | 100   |
| Arsenic, mg/kg   | 29  | 29  | 10    | -                     | 10.1                  | 14.0    | 32.4 | -    | -     |
| Iron, g/kg       | -   | -   | -     | 29.7                  | 17.0                  | 44.6    | 10.5 | <1.5 | >3.5  |
| Chromium, mg/kg  | 100 | 100 | -     | -                     | 13.9                  | 79.2    | -    | 20   | -     |
| Nickel, mg/kg    | 35  | 35  | 80    | 16                    | 12.7                  | 28.2    | 12.8 | 15   | 45    |
| Mercury, mg/kg   | 0.30| 0.30| -     | 0.40                  | -                     | 0.17    | 0.04 | 0.05 | -     |
| Oil products, mg/kg | 50  | 180 | -     | 306                   | 59                    | 668     | -    | 30   | -     |

The choice of a reference value for assessing the ecological state of bottom sediments is problematic [12]. The use of standards specified for soils (maximum permissible concentrations and approximate permissible concentrations) [5, 6] does not allow for a reliable assessment of the ecological and geochemical state of the bay and is incorrect due to the difference in the genesis and physicochemical characteristics of bottom sediments and soils [13]. Existing regulatory acts of the Russian Federation [14, 15] require that the quality assessment of bottom sediment was carried out relative to the reference concentrations of pollutants, but do not provide a clear definition of the reference concentration, offering three options for determining the reference: concentration of pollutants in bottom sediments of ecologically clean water areas; concentration of pollutants in bottom sediments at the same station at a depth of not less than 20 cm; reference indicators according to long-term observations in the same water area. In addition, due to the natural variability and heterogeneity of the geochemical background, the accepted reference concentrations are largely random values. The
use of permissible concentration has an advantage: this is a specific value, set by a regulatory
document (albeit a foreign one) – the “Neue Niederlandische Liste” well known in our country [3].
Therefore, permissible concentrations are widely used, although this is contrary to Russian law.

Unfortunately, the regulatory document [15] does not require the determination of a regional
geochemical background, as for soil assessment. We would like to emphasize that, based on these
guidelines, regions have the right to develop and approve regional indices of average pollutants
content in bottom sediments, taking into account geochemical characteristics of a particular territory.

The data on the contents of specific heavy metals in bottom sediments of the Zolotoy Rog Bay are
presented in figure 1. Comparative assessment demonstrates the ambiguity of conclusions about the
level of bottom sediments contamination, depending on the choice of standard or reference
concentration.

Figure 1. Comparative assessment of the content of heavy metals in bottom sediments of the Zolotoy
Bay.

In Russian and world practice, the pollution is mainly assessed using individual indices, which
makes it possible to determine the levels of maximum pollution to a water body, but does not provide
an understanding of the general picture. For environmental assessment of a water body, it is necessary
to obtain an integrated characteristic of the pollution level of bottom sediments [13]. Unlike other
natural environments, integrated assessment is not required for bottom sediments by a regulatory
document, therefore, researchers use different approaches. In order to assess bottom sediments, a
technique was used similar to that adopted for soils. The total pollution index ($Z_c$) from guidelines by
Yu.E. Saet [16] (also known as Saet’s summary index) was used as criteria for assessing
the technogenic impact on bottom sediments. It is calculated by the formula:

$$Z_c = \sum_{i=1}^{n} K_c - (n - 1)$$

where $K_c$ is the concentration index (the ratio of the content of the chemical element in the evaluated
object to its reference content); and $n$ is the number of elements taken into account (only substances
whose contents exceeds reference values are included in the calculation).
When calculating $Z_c$, there is no uniformity in accounting for chemical elements with different $K_c$ [17]. On the one hand, all elements can be taken into account, including those depleted compared to the reference [18], which, in essence, contradicts the concept of pollution. On the other, only accumulating elements can be taken into account using the boundary criterion $K_c > 1$ recommended by Saet. The obtained $Z_c$ values were differentiated according to four pollution levels of the scale for assessing the degree of pollution of water systems [16]: weak $Z_c < 10$, moderate $Z_c = 10-30$, strong $Z_c = 30-100$, very strong $Z_c > 100$. Another important methodological issue is the list of monitored indices. Initially, integrated assessment techniques, including the Saet’s method, were used to assess soil contamination with heavy metals. However, in modern conditions, the intensity of the content of organic pollutants can be high, beyond the scope of self-purification of a water body. The results of calculating the geochemical associations parameter for the water area of the Zolotoy Rog bay and the difference in conclusions about the degree of contamination of bottom sediments, depending on the choice of priority pollutants, are demonstrated in figures 2 and 3.

**Figure 2.** The results of the calculation of ecological-geochemical state of the Zolotoy Rog Bay based on the total pollution index $Z_c$ excluding (above) and including oil products (below).

The calculations of $Z_c$ showed using different values of reference concentrations produces results that interpret the same situation either as a norm or as an anomaly. Therefore, in order to assess the ecological state of bottom sediments based on the calculation of the total pollution index, it is
necessary to specify regional reference concentrations of pollutants in sea ground, as they will provide a unified approach to assessing the quality and pollution of bottom sediments. The assessment of bottom sediments pollution was carried out using the contamination factor $C_f$ (characterizes the pollution of the water area by individual substances) and the degree of contamination $C_d$ (reflects the total pollution of the water body with the substances under study), proposed by Hakanson [19]:

$$C_d = \sum C_f$$

where $C_f$ is the contamination factor.

$$C_f = \frac{C_f}{C_0}$$

where $C_f$ is the concentration of substances in bottom sediments; $C_0$ is the reference concentration of the substance.

To assess the pollution of toxic substances in the water of the Zolotoy Rog Bay $C_f$ values were determined for eight heavy metals (Cu, Pb, Cd, Zn, As, Cr, Ni, Hg) and oil products. The values obtained were ranked from $C_d < 9$ (low pollution level) to $C_d \geq 36$ (high pollution level). The calculation results (figure 3) show high pollution level of bottom sediments at all sampling points ($C_d > 36$).

![Figure 3](image-url)  
**Figure 3.** Degree of contamination ($C_d$) of bottom sediments in the Zolotoy Rog Bay taking into account oil products.

The analysis of existing methodological approaches to assessing the state of bottom sediments has confirmed the acceptability of the approaches used in various environmental and geochemical assessments. However, different criteria underlying each methodology provide different critical values for assessing the degree of contamination. A methodological approach to assessing the quality of bottom sediments in Peter the Great Gulf should be based on the development of clear gradations of environmental and geochemical estimates of bottom sediments, the group of parameters used, among which are: the total pollution index [16], the use of uniform background concentrations for Peter the Great Gulf, gradation according to the hazard level.

3. Results and discussion

The algorithm for the guidelines of assessment of the quality of bottom sediments in Peter the Great Bay Gulf reduces to the following:
1. It is necessary to specify and capture in a normative document the regional geochemical background of the content of substances in bottom sediments of Peter the Great Gulf. Due to the fact that reference concentration values for chemical elements are presented in a wide range according to different literature data, it is proposed to accept the monitoring data of the FSBI “VNIIOkeangeologia” (2012-2014) [7, 8] as a unified standard for assessing the pollution of marine bottom sediments in the region.

2. Adopt the guidelines for environmental assessment of bottom sediments pollution for selected priority controlled indices and for integrated pollution indices, based on the results of theoretical and experimental studies, regional geochemical background and application of integral criteria. Use the total pollution index as an integral criterion, by analogy with the index specified for soils [18].

**Table 2.** Estimation scale of bottom sediments pollution hazard based on the total pollution index \((Z_c)\) and types of economic activity.

| Bottom sediments pollution category | \(Z_c\) value | Possible use of bottom sediments |
|------------------------------------|---------------|---------------------------------|
| Clear \(K_r<1\), does not exceed the reference for all indices | Dredging with the possibility of subsequent use for land reclamation, dumping in water bodies without restrictions | Use of water bodies for recreational purposes (recreation, tourism, sports) | Use for any kind of sea-farming |
| Weak \(<10\) | Use for land reclamation, with placement at officially authorized dumping sites | Use of water bodies for recreational purposes (recreation, tourism, sports) | Use for any kind of sea-farming |
| Moderate \(10-30\) | Use for land reclamation, with placement at officially authorized dumping sites with the addition of clean soil (gravel) | Use after dumping sandy or gravel soil with repeated quality control | Use with restriction, subject to analysis for the content of pollutants in the products |
| Strong \(30-100\) | If excavated, the sediments should be dumped outside the bay, in areas with intensive sediment removal into the open sea (Gamov canyon in the Sea of Japan) | Restriction on a water body / use for swimming is considered impossible | Use for sea-farming is prohibited |
| Very strong \(Over 100\) | If excavated, the sediments should be treated as wastes and dumped at specialized landfills | Restriction on a water body / use for swimming is considered impossible | Use for sea-farming is prohibited |

3. Priority pollutants should include heavy metals (Cd; Cr; Cu; Pb; Ni; Zn; As; Hg) and oil products. The list of controlled parameters is supplemented by specific indices.
4. The assessment of ecological and geochemical state of bottom sediments is carried out on the basis of the well-known guidelines by Yu.E. Saet. The ranking of soil pollution levels proposed in the guidelines should be supplemented with the fifth grade – “clear bottom sediments” (table 2), corresponding to the natural content of pollutants in bottom sediments (pollutants concentrations are at or below the regional geochemical background), by analogy with the criteria for soils [16].

5. Conclusions about the ecological state of bottom sediments and managerial decisions made on the basis of bottom sediments quality assessment are determined by the type of economic activity and the purpose of the water body (table 2).

4. Conclusions

The use of various initial parameters and methods for the assessment of pollutants in bottom sediments leads to incomparable results and contradictory conclusions, as shown on the example of the Zolotoy Rog Bay. The guidelines proposed for the environmental assessment of bottom sediments pollution levels are based on the regional geochemical background and the use of integrated criteria. It is proposed to use the regional geochemical background values for Peter the Great Gulf as a unified standard for assessing pollution levels of marine bottom sediments in the region. Criteria for assessing the degree of pollution of bottom sediments are developed depending on the type of use of the water area.

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