Evaluation of Pollution Level in Zolotoy Rog Bay (Peter the Great Gulf, the Sea of Japan)

Y Kazachkova, L Lazareva, V Petukhov
Engineering School, Far Eastern Federal University, 8, Sukhanova St., Vladivostok 690950, Russia
E-mail: redcurious@yandex.ru

Abstract. The results of the hydrochemical research of water and bottom sediments of the Zolotoy Rog Bay in July 2015 are presented below. It is shown that, as a result of a large amount of polluted sewage entering the Zolotoy Rog Bay, the concentrations of organic substances (BOD5) and petroleum hydrocarbons in the water exceed the MPC. The concentrations of heavy metals in soils exceed both the background level and the level of permissible values. As a result of the calculation of the bottom accumulation (CBA) coefficient for oil hydrocarbons, the situation in the Zolotoy Rog Bay can be classified as an ecological disaster. According to the total pollution index (Zc) of heavy metals, the bottom sediments of the Zolotoy Rog Bay are characterized as strongly and very strongly polluted.

1. Introduction
Among the coastal sea waters of the city of Vladivostok, one of the largest industrial ports of Russia, the Zolotoy Rog Bay experiences the strongest anthropogenic impact. This marine area is fully involved in the economic life of the city. The discharge of a large volume of industrial domestic waste water (without cleaning 60%) and spills of petroleum products resulting from the operation of maritime transport lead to contamination with a wide range of chemicals in the considered water area [1,2]. The presence of any man-made pollution in the Zolotoy Rog Bay not only brings harm to the environment and human health but also does not meet domestic and world standards of environmental quality. As a result of the adoption of the law on the free port of Vladivostok [2], the port itself becomes Russia's landmark for the Asian Pacific countries. Therefore, it is important to assess the ecological status of this water object.

2. Research materials and methods
The Zolotoy Rog Bay extends into the Murav'ev-Amursky peninsula for about 7 km. The banks are artificially levelled virtually all along their length and fortified by walls equipped with quays and piers, and expanded for port facilities [3]. To the low bank of the bay peak the valley of the Obyasneniya river comes along the banks of which a significant number of enterprises, motor depots and warehouses of fuels and lubricants are located.

To assess the ecological status of the Zolotoy Rog Bay, the samples of sea water and sediments were taken in November 2015. The sampling of water was carried out from the surface (1-1.5 m) and bottom (1.5-2 m from the bottom) layers by the Niskin bathometer in accordance with GOST 31861-
The soil samples were selected by the portable Wang Win scoop according to GOST 17.1.5.01-80 [5]. Sampling stations were selected with the aim of maximum coverage of the investigated water area.

The heavy metal concentrations were determined by means of atomic absorption spectrophotometry [6]. The measurement of the content of petroleum hydrocarbons in the seawater was carried out by the fluorimetric method [7]. To determine the concentrations of petroleum hydrocarbons in soils, infrared spectrophotometry was used [8].

The assessment of the anthropogenic impact degree of the controlled sources of wastewater discharge in the Zolotoy Rog and the river was carried out according to the materials of the water resources department of the Amur River Basin Water Authority for Primorsky Krai. Based on the data of the 2-TP forms for 2012-2015, the volume of wastewater was determined and the mass of pollutants received into the investigated water area was calculated.

3. Results and discussion

The water area under consideration was most heavily impacted in the 1960s-1980s in connection with the construction of a shipyard, docks, cargo terminals and Vladivostok CHPP-2 [9]. At the present time, as a result of sewage from industrial enterprises and municipal services, including the Obysneniya river, storm drain from the city's territory and emergency spills of oil products, The Zolotoy Rog Bay is one of the most polluted marine areas of the Russian Federation [1]. Figure 1 shows the main sources of industrial and domestic wastewater entering the Zolotoy Rog Bay and the Obysneniya river, as well as the stations for water and bottom sediments sampling.

![Figure 1. Location of the sources of negative impact and sampling stations in the Zolotoy Rog Bay.](image)

The volumes of wastewater discharge into the Zolotoy Rog Bay and the Obysneniya river are shown in Figure 2. It can be seen from the Figure that the main volume of waste water falls at Vladivostok CHPP-2 and KGUP “Primorskiy Vodokanal”, the total discharge of CHPP-2 and KGUP “Primorskiy Vodokanal” is about 95% of the water users in the water area of the Zolotoy Rog and the Obysneniya river. The large volumes of CHPP-2 discharges are associated with the seawater intake from the Ussuriisk Bay, its use for cooling the exhaust steam and the subsequent discharge of the heated normative pure water into the Obysneniya river. The largest runoff of untreated wastewater is accounted for KGUP “Primorskiy Vodokanal”.

The proportion of wastewater treated to normative indicators is low. The reason for the massive discharge of untreated sewage into the Zolotoy Rog is the insufficient capacity of the existing treatment facilities or their defective condition.
The results of calculating the mass of pollutants (Table 1) of water users discharging sewage into the Zolotoy Rog Bay in 2016 indicate that the greatest mass of discharges falls on organic matter (BCO) and petroleum hydrocarbons. The share of iron is the largest in the metals’ content.

| Company name                          | Mass of pollutants, kg/year |
|---------------------------------------|-----------------------------|
|                                       | BCO | OP  | Fe     | Cu   |
| OOO “Dalretrans”                      | 40   | 0    | 0.78   | 0.073 |
| OAO “Vladavto”                        | 2,547 | 14   | 2.4    | 0.048 |
| OAO “Commercial Port of Vladivostok”  | 5,556 | 1.51 | 90     | 1.4   |
| “Fishing Port of Vladivostok”         | 3,410 | 105  | 180    | 0.27  |
| “Arenda”                              | 715   | 8.5   | 0.514  | 0     |
| OOO “Vladivostok Sea Terminal”        | 139   | 1,280 | 1.7    | 0     |
| OOO “Trans-Eco”                       | 18.8  | 0.6   | 0.0043 | 0     |
| CR “Dalzavod”                         | 9,140 | 1,090 | 50     | 1.3   |
| OAO “Dalcomholod”                     | 12    | 1    | 0.333  | 0.006 |
| OOO “Ecoservis-FE”                    | 10    | 0    | 0      | 0.58  |
| KGUP “Primorskiy Vodokanal”           | 808,000 | 9,380 | 9.3    | 100   |
| CHPP-2                                | 321,209 | 1,308 | 38.9   | 0.192 |
| “Dalzavod-Terminal”                   | 37    | 0    | 0      | 0     |
| OOO “Femsta”                          | 148   | 6    | 7.86   | 0.42  |
| OAO VF “ERA”                          | 2,870 | 0    | 51     | 0.52  |
| OOO “Sollers-FE”                      | 130   | 0    | 2.06   | 0.05  |
| **Total mass of pollutions**          | **1,153,981.8** | **13,194.61** | **434.88** | **105** |

To fully characterize the ecological status of any water body and assess the prospects for its use for fishery, recreational and other purposes, the information on the contamination of water and bottom sediments is necessary [10]. The small size of the water area of the Golden Horn Bay (length about 7 km, width is not more than 1 km, surface area is 4.44 km²), a large number of pollutants and weak
circulation of water lead to contamination of the water column and accumulation of pollutants in soils [11].

The determination of BCO₅ is used to assess the content of biochemically oxidizable organic substances and as an integral indicator of water contamination. The results of pollution of the waters of the Zolotoy Rog Bay with easily oxidized substances according to BCO₅ are shown in Figure 3.

Figure 3 shows that the content of pollutants in the BCO₅ in the waters of the investigated water area is not uniform. Permissible concentration exceeding is observed at the Station No. 3 in the central part of the Zolotoy Rog Bay and at the Station No. 5 in the watery part of the water area. The same results of the MPC exceeding are observed according to the state monitoring system (GOS) [1]. High values of BCO₅ in the water of the investigated water area are associated with the recurring release of household sewage from the enterprise of KGUP “Primorsky Vodokanal”. In Fig. 1 it can be seen that a large number of domestic sewage discharges of the given enterprise are entering the Obyasneniya river, which, under the conditions of low water exchange in the Zolotoy Rog Bay, lead to an increased concentration of easily oxidizable organic substances in the water of the central and the middle part of the bay.

The iron share in the sewage waters of the enterprises 1.2–7.4 times exceeds the MAC. The water discharged after the cooling of the turbines CHPP-2 which is considered to be normative clean also exceeds the MAC for iron by 4.8 times. Nevertheless, we did not reveal the excess of MAC for heavy metals in the water of the Zolotoy Rog Bay, see Table 2.

| No. of station | Concentration of metal, 10⁻²mg/dm³ |
|----------------|----------------------------------|
|                | Cu     | Fe      | Pb      | Hg     |
| 1              | 0.06 / 0.07 | 0.72 / 1.0 | 0.14 / 0.18 | 0.0031 / 0.0039 |
| 2              | 0.03 / 0.05 | 0.77 / 0.99 | 0.18 / 0.14 | 0.0027 / 0.0079 |
| 3              | 0.12 / 0.05 | 1.7 / 1.1 | 0.15 / 0.17 | 0.00022 / 0.0021 |
| 4              | 0.01 / 0.02 | 2.4 / 1.2 | 0.17 / 0.19 | 0.0013 / 0.0014 |
| 5              | 0.07 / 0.03 | 3.5 / 2.5 | 0.17 / 0.18 | 0.00049 / 0.00095 |
| MPC, mg/dm³   | 0.005 | 0.05 | 0.1 | 0.0001 |

The iron share in the sewage waters of the enterprises 1.2–7.4 times exceeds the MAC. The water discharged after the cooling of the turbines CHPP-2 which is considered to be normative clean also exceeds the MAC for iron by 4.8 times. Nevertheless, we did not reveal the excess of MAC for heavy metals in the water of the Zolotoy Rog Bay, see Table 2.

The results of the assessment of oil hydrocarbon contamination in the waters of the Zolotoy Rog Bay are shown in Table 3. It can be seen from the table that in the water the maximum permissible concentration limit for petroleum hydrocarbons is observed virtually throughout the entire water area. The Station number 1, located at the exit from the Zolotoy Rog Bay, Fig. 1, is characterized by the lowest concentrations of petroleum hydrocarbons due to good water exchange with more open waters.
of the bay. Due to a poor solubility of petroleum hydrocarbons in the seawater [12], in the near-bottom water layer of the investigated water area, the content of petroleum hydrocarbons is lower than in the surface layer.

Table 3. Content of petroleum hydrocarbons in the water of the Zolotoy Rog Bay.

| № station | Surface horizon | Near-bottom horizon |
|-----------|-----------------|---------------------|
|           | Concentration, mg/dm³ | Part of MPC | Concentration, mg/dm³ | Part of MPC |
| 1         | 0.049           | 0.98          | 0.033          |
| 2         | 0.081           | 1.62          | 0.041          | 0.82       |
| 3         | 0.056           | 1.12          | 0.045          | 0.9        |
| 4         | 0.218           | 4.36          | 0.067          | 1.34       |
| 5         | 0.061           | 1.22          | 0.056          | 1.12       |

According to the state monitoring data, the maximum concentration of petroleum hydrocarbons in the surface layer of the waters of the Zolotoy Rog Bay in 2015 was 5.2 MPC (0.26 mg/dm³) and was recorded in its central part [13].

According to our visual observations of the surface condition of the sea waters of the Zolotoy Rog Bay, the entire water area is very often covered with oil film and floating debris.

The study of bottom sediments gives the most integrated assessment of the pollution of aquatic ecosystems since most pollutants sink to the bottom and are sorbed by bottom sediments.

The bottom sediments of the Zolotoy Rog Bay are represented by gray ooze. This circumstance, as well as limited water exchange with the high seas and numerous sources of pollution, contribute to the accumulation of heavy metals in the bottom sediments.

Currently, for marine sediments, there are no normatively fixed maximum permissible HM concentrations. Therefore, to assess the pollution of the bottom sediments by HM, we compared them with:

- background values (BV) [14];
- permissible levels of concentration (PL) in accordance with foreign norms (Neue Niederländische Liste) [15].

Data on the HM content in BS, as well as the ratio of mean concentrations of HM to the background concentration and PL, are presented in Table 4.

Table 4. Heavy Metals in BS the Zolotoy Rog Bay, mg/kg.

| Metal | Cu | Fe | Pb | Hg |
|-------|----|----|----|----|
| BV [14], mg/kg | 10 | 15,000 | 10 | 0.02 |
| PL [15], mg/kg | 35 | – | 85 | 0.3 |

| № station | Concentration of metal, mg/kg |
|-----------|-------------------------------|
|           | C¹ | C² | BV³ | C⁴ | PL⁵ |
| 1         | 116.3 | 11.6 | 3.3 | 54,883 | 3.6 | 143.6 | 1.4 | 0.38 | 19 | 1.3 |
| 2         | 251.4 | 25 | 7.1 | 60,717 | 4 | 248 | 2.9 | 1.04 | 52 | 3.5 |
| 3         | 262.2 | 26 | 7.4 | 57,464 | 3.8 | 284.5 | 28.4 | 3.3 | 1.33 | 66.5 | 4.4 |
| 4         | 150.5 | 15 | 4.3 | 58,669 | 3.9 | 194 | 19 | 2.2 | 1.81 | 90.5 | 6 |
| 5         | 139.7 | 13.9 | 4 | 55,528 | 3.7 | 119.5 | 11.9 | 1.4 | 0.89 | 44.5 | 3 |

¹ - concentration of heavy metals in the bottom sediments, mg/kg.
² - the ratio of the actual concentration of metal in the sample to the content at the background station.
³ - the ratio of the metal content to the PL value; - PL is absent).

Table 4 shows that for copper the greatest excess of both the background concentration and PL is observed in the bottom sediments of the central part of the Zolotoy Rog Bay (Station No. 3) and at the Station No. 2 in the vicinity of the trade and fish ports, see Fig. 1. The Vladivostok Commercial Sea
Port and the company “Primorsky Vodokanal” make a big contribution to pollution by copper as they account for the largest part of the input of the element in question with wastewater, see Tabl. 1. In addition, the banks of the bay are equipped with quays and piers which also contributes to pollution. A high content of iron in soils is observed throughout the entire area of the bay. The greatest mass of input, and, consequently, the contribution to pollution, of this metal is accounted for by such enterprises as KGUP “Primorsky Vodokanal” and CHPP-2, Tabl. 1. In 2016, the supply of iron with the wastewater of CHPP-2 decreased by 39 tons compared to 2012. In 2012–2016 the mass of iron discharge from the Kuzbass State Unitary Enterprise "Primorsky Vodokanal" was 10 tons / year, Figure 4.

Among other water users, iron in drains is more present in such enterprises as Vladmorrybport, VICP, VP ERA, and CSD Dalzavod, Table 1.

The central part of the investigated water area at the Stations No. 2–3 is also characterized by a high degree of accumulation in lead and mercury soils, see Table 4. The high content of lead in the bottom sediments is most likely due to a long-term pollution when this element was widely used in batteries and as an additive to fuel transport [2]. To the accumulation of mercury in the bottom sediments of the water area in question, the activity of the Dalzavod enterprise was the most significant because it was used in large volumes in the technological cycles of the company.

The calculation of the total pollution index of HM (Zc) [16] was carried out for all sampling points of all the metals analyzed (formula 1):

\[
Z_c = \left(\frac{1}{n} \sum_{i=1}^{n} K_{ci}\right) - (n - 1), \text{ mg / kg}
\]

where \(K_{ci}\) is the concentration coefficient calculated as the ratio of the metal concentration \(Ci\) in the BS to its concentration in the background; \(n\) – number of metals.

### Table 5. The values of the total pollution index HM BS of the Zolotoy Rog Bay.

| Station | 1   | 2   | 3   | 4   | 5   |
|---------|-----|-----|-----|-----|-----|
| Zc (unit) | 45.2 | 102.8 | 124.7 | 128.4 | 74  |

According to the total pollution index (Zc) of heavy metals, the bottom sediments of the Zolotoy Rog Bay are characterized as strongly and very strongly (stations 2–4) polluted, Table 5.

For petroleum hydrocarbons in all samples of the bottom sediments of the investigated water area, Figure 5, there is a significant (up to 202.2) excess of PL.

The bulk of petroleum products enters the water area of the investigated facilities with sewage from KGUP “Primorsky Vodokanal” and CHPP-2 “Table 1”.

Figure 4. Iron supply (t / year) in the water area of the Zolotoy Rog Bay and the Obyasneniya river (2012–2016).
To determine the rate of accumulation of petroleum hydrocarbons in the bottom sediments, taking into account changes in their concentration in the marine environment, the values of the bottom accumulation coefficient (CDA) were calculated. The results of the calculation are shown in Table 6.

Table 6. Characteristics of the content of petroleum hydrocarbons in the bottom sediments of the Zolotoy Rog Bay.

| Station | 1   | 2   | 3   | 4   | 5   |
|---------|-----|-----|-----|-----|-----|
| $C_{bs}$, mg/kg | 1,556 | 5,513 | 10,112 | 9,334 | 5,074 |
| $C_{water}$, mg/dm$^3$ | 0.041 | 0.061 | 0.051 | 0.143 | 0.058 |
| $KDA$, unit | 37,951 | 90,377 | 198,274 | 65,273 | 87,483 |

According to the criteria for assessing the pollution of surface water bodies [17], the current situation in the Zolotoy Rog Bay for this type of pollution can be classified as an ecological disaster. Anthropogenic pollutants released into water bodies have a negative impact on marine ecosystems and, once certain concentrations have been reached, may lead to the loss of marine biological species. Such consequences are particularly likely in urban and industrial ports [18]. Regardless of the source of pollutants (precipitation from the atmosphere, flow with run-off of rivers, domestic wastewater, etc.), they are absorbed by suspended fine mineral and organic particles in the marine environment concentrated in hydro dynamically calm basins where silt deposits accumulate [19]. According to the literature, reversible changes in benthic communities begin when the concentration of petroleum hydrocarbons is $10^{-100}$ mg/kg. Beginning at the concentration of $1,000^{-4,000}$ mg/kg, a significant decrease in the abundance and species diversity of benthos occurs as well as a 50% loss of animals because of toxicological experiments [20]. In the Zolotoy Rog Bay, according to our data, the concentrations of petroleum hydrocarbons vary from 1,556 to 10,112 mg/kg (31 PL–202.2 PL), Figure 5.

4. Conclusion
On the basis of the conducted studies, it is established that MPC excess in the water is observed in BCO$_5$ in the central part of the Zolotoy Rog Bay at the place of sewage disposal by KGUP “Primorsky Vodokanal”; in oil hydrocarbons - in the places of parking of sea vessels of the port facilities. In the marine bottom sediments of the water area under consideration, petroleum hydrocarbons, heavy metals (copper, iron, mercury, lead) are accumulated in considerable quantities. As a result of the calculation of the KDA coefficient for petroleum hydrocarbons, the situation in the Zolotoy Rog Bay can be classified as an ecological disaster.

It is determined that the trade and fishing port, ship repair yard, small-sized and large-capacity fleet as well as discharges of untreated industrial domestic sewage have a negative impact on the ecological state of the water area in question.
Reference

[1] 2014 Quality of Marine Waters According to Hydrochemical Indicators (Moscow: Nauka) p 200
[2] Hristoforova N 2012 Modern Ecological State of Peter the Great Bay, Sea of Japan (Vladivostok: Publishing house of the Far Eastern Federal University Press) p 440
[3] 1984 Sailing Directions of North-Western Shore of the Sea of Japan / General Directorate of Navigation and Oceanography (Moscow: Ministry of Defense of the USSR) p 375
[4] 2013 GOST 31861-2012 Water General Requirements for Sampling (Moscow: Standartinform)
[5] 2002 GOST 17.1.5.01-80 Nature Protection (JMPR). Hydrosphere. General Requirements for Sampling of Bottom Sediments of Water Objects for Their Pollution Analysis (Rev 1) (Moscow: IPK Publishing House of Standards)
[6] 1993 Manual on Chemical Analysis of Marine Waters (app. the decision of the Committee of Hydrometeorology and Environmental Monitoring, Ministry of Environment of the Russian Federation dated 28.04.1992) RD 52.10.243-92 (St.-Petersburg: Gidrometeoizdat) p 262
[7] PND F 14.1:2:4.128-98 Quantitative Chemical Analysis of Waters. Method of Measurement by Massing Concentration of Oil Products in Samples of Natural, Drinking and Waste Water Fluorimetric Method Using Liquid Analyzer “Fluorat-02”
[8] PND F 16.1:2.2.22-98 Quantitative Chemical Analysis of Soils. Technique of Execution of Measurements of Mass Fraction of Oil Products in Mineral, Organogenic or-Gano-Mineral Soils and Sediments by the Method of IR-Spectrometry
[9] Petrenko V 2000 Global and Local Features of Technogenesis on Primorye Coast (Sea of Japan) Reports of the Workshop on the Global Change Studies in the Far East (Vladivostok) Vladivostok pp 26–37
[10] Ogorodnikova A 2001 Ecological and Economic Evaluation of the Impact of Coastal Sources of Pollution on the Natural Environment and Bioresources of Peter the Great Bay (Vladivostok: TINRO-center) p 193
[11] Galyshova Y 2009 Biological Effects of Organic Pollution in Coastal Marine Ecosystems of the Russian Part of the Sea of Japan Izvestiya TINRO vol 158 pp 209–20
[12] Beskid P 2011 Characteristics of Process of Transformation of Oil in Marine Environment and Their Impact on Operations of Liquidation of Emergency Floods of Oil The Operation of Maritime transport 1(63) pp 71–5
[13] 2016 Report on Environmental Situation in Primorye in 2015 The Administration of Primorsky Krai (Vladivostok) p 269
[14] Kalinchuk V 2010 Complex Chemico-Ecological Study of Coastal Zone of North-Eastern Part of the Russian Island Vestnik DVO RAN 5 pp 96–106
[15] Neue Niederlandische Liste, Altlasten Spektrum 3/95 PTS Limits and Levels of Concern in Environment, Food and Human Tissues
[16] Saet J 1990 Geochemistry of Environment (Moscow: Nedra) p 336
[17] 2014 About Approval of Methodical Instructions for Implementation of State Monitoring of Water Bodies in Terms of Organization and Observation of the Content of Pollutants in Bottom Sediments of Water Bodies: Order of the MNR 112 The Bulletin of Normative Acts of Federal Bodies of Additional Power
[18] Hayter E 2006 Evaluation of the State-of-the-Art Contaminated Sediment Transport and Fate Modeling System U.S. Environmental Protection Agency Office of Research and Development Washington DC p 128
[19] Lepland A 2010 Sedimentation and Chronology of Heavy Metal Pollution in Oslo Harbor, Norway Marine Pollution Bulletin 60 p 1512–22
[20] Patin C 1997 Ecological Problems of Oil and Gas Resources of Sea Shelf (Moscow: VNIRO) p 349