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ИнБЮМ – IBSS

Морской биологический журнал
Marine Biological Journal
2023, vol. 8, no. 2, pp. 18–41
https://marine-biology.ru

UDC [502.175:504.5](265.54.04)

ORGANIC MATTER IN THE ECOSYSTEM OF THE VLADIMIR BAY (THE SEA OF JAPAN): FOOD RESOURCE AND ENVIRONMENTAL RISK FACTOR

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Received by the Editor 09.12.2021; after reviewing 06.04.2022;
accepted for publication 16.02.2023; published online 31.05.2023.

To understand the accumulation process resulting from the input of toxic substances and elements into water areas, the study of the organic matter content in the aquatic environment and bottom sediments is of great importance. Moreover, such investigation is significant for identifying negative alterations in the ecosystem and potential environmental risks driven by the nature management. We aimed at analyzing the importance of organic matter as a factor of the environmental contamination in the Vladimir Bay (the Sea of Japan) and determining the toxicity of hydrobionts and the environmental risk to both the ecosystem and human health. This complex work was carried out applying chemical, analytical, microbiological, and hydrobiological techniques; it included mathematical and cartographic data processing, as well as calculation of accumulation factor and sediment quality guideline quotient. Seawater, bottom sediments, and macrobenthos sampled in the Vladimir Bay in July 2014 were analyzed. Chemical, ecological, and microbiological parameters of the bay waters were determined; those allowed to estimate the organic matter accumulation in the aquatic environment and bottom sediments and to establish the trophic status of the ecosystem in summer. Mass macrobenthic species and groups were identified; indices of benthic population abundance were determined indicating high levels of biomass. In surface waters, the abundance of heavy metal resistant groups of bacteria was estimated. In bottom sediments, heavy metal content and its spatial distribution were determined. Heavy metal concentrations in the sea urchin gonads were quantified. The results of the microbiological assessment were compared with maximum permissible concentrations (MPC), and a significant pollution of the bay waters (more than 3 MPC) in terms of Cd was revealed. For Ni, Cu, Zn, and Cd, background concentrations were exceeded in the bottom sediments; for Cd and Zn, clarke content was exceeded. The correlation between concentrations of organic matter in the bottom sediments and heavy metal content there was checked, as well as the correlation between heavy metal concentrations in the bottom sediments and in the sea urchin gonads (a statistically significant correlation was revealed for Zn). For the bay bottom sediments, the contamination factor C_f was determined; its values characterize the contamination with zinc as high, and with cadmium and copper – as very high. Also, the degree of contamination C_d was estimated; its values evidence for an average degree of contamination for the bottom sediments in total. The environmental risk quotients were calculated. According to SQG-Q value, the bay bottom sediments are classified as moderately polluted. As established, Cd and Pb content in the sea urchin gonads from the Vladimir Bay does not exceed the permissible values set in Technical Regulation of the Customs Union 021/2011. However, based on ILCR value, it can be concluded that there is a carcinogenic risk arising from consuming the sea urchin gonads.

Keywords: Vladimir Bay, Sea of Japan, organic matter, trophicity, bottom sediments, macrobenthos, heavy metals, accumulation factors, environmental risk, human health risk

High concentrations of organic matter (hereinafter OM) in marine ecosystems often result from natural processes occurring there. Specifically, OM is accumulated in "trap bays": water areas deeply incised into the coast, with a relatively narrow mouth and limited or specific water exchange. Such water areas are accumulators of OM, which is a food resource generally determining the trophic status of the environment in the ecosystem. Marine ecosystems, which have a high trophic status and are characterized by great variety of ecotopes, are key areas for the development of mariculture and the rational use of natural populations. Moreover, those are the areas of natural formation and conservation of biodiversity.

OM accumulation in a marine ecosystem has a pronounced positive effect up to a certain level of values for OM dissolved in water and accumulated in bottom sediments. When exceeding this level, negative consequences arise. In addition to more pronounced and short-term manifested eutrophication, there is a less noticeable and more extended in time accumulation of toxic substances and elements entering a bay or a bight. For bottom sediments, this effect is especially significant. The processes of OM transformation and destruction at the boundary of bottom sediments and a water column and in sediments are the main cause of both the mobilization of heavy metals (hereinafter HM) into pore and bottom waters and the binding of elements [Shulkin, 2004; Zhang et al., 2014]. Entering a water column, HM cause its secondary pollution; then, HM are accumulated in organisms *via* food chains. The analysis of element migration in various ecosystem components is an important direction of toxicological studies; it allows to assess both toxic effects for organisms of different trophic levels [Saroop, Tamchos, 2021; Vashchenko et al., 2010] and risks to human health [Birch, 2011; Donets et al., 2020].

The Vladimir Bay is located on the eastern coast of the Primorsky Krai. This water area is deeply incised into the coast; its mouth is relatively narrow. In central areas of bights, the depth exceeds 20 m; at the bay mouth, the value is 40 m. The currents within the bay are mainly due to wind-wave processes. The effect of the Primorsky Current is insignificant since the bay water area is quite closed. There are no currents formed by a river flow because of the lack of full-flowing rivers entering the bay. This water area is under anthropogenic load since 1907, when the first settlement occurred, Veselyi Yar. Later, because of the deployment of military facilities on the bay coast, new settlements arose: Timofeevka (1932), Nord-Ost, and Rakushka (1934). In 1934–1999, the Vladimir-Olginsk naval base of the Pacific Fleet was located in the bay water area (now, it is disbanded).

A few marine biological studies of the Vladimir Bay cover particular commercial macrobenthic species [Gavrilova et al., 2006; Kulepanov, Ivanova, 2006] and some invasive species [Lutaenko, Kolpakov, 2016]. Macrobenthic composition, abundance, and distribution are described by the authors [Galysheva et al., 2018]. Several scientific works are devoted to the analysis of Neogene deposits [Vashchenkova, Tsoy, 2014] and the prospects for mariculture development [Gavrilova et al., 2019]. There are no published data on hydrochemical and microbiological studies by other researchers. Complex works have not been carried out.

The aim of this work is to analyze the level of organic matter as a possible factor in the formation of environmental toxicity in the Vladimir Bay and to assess the contamination of hydrobionts and the environmental risk to both the ecosystem and human health.

Research objectives are: 1) to analyze OM content in the aquatic environment in terms of chemical and microbiological indicators and to assess the trophic status of the water area; 2) to determine the granulometric composition of the bottom sediments and OM content in them; 3) to assess the composition and abundance of macrobenthic organisms; 4) to assess HM content in environmental components and macrobenthic organisms; and 5) to analyze the relationship between OM and HM accumulation in the bay bottom sediments, as well as to assess the environmental risk for the organisms inhabiting it and the toxicological risk driven by their consumption by humans.

MATERIAL AND METHODS

Sampling. The data of the analysis of seawater, bottom sediments, and macrobenthos sampled in the Vladimir Bay (the Sea of Japan) (Fig. 1) in July 2014 served as the material for the work, as well as the authors' information on other water areas of the Primorsky Krai [Galysheva, 2010]. In total, 17 complex stations were surveyed, covering different bay areas down to a depth of 25 m (the depth limit is associated with diving descents). Seawater, bottom sediments, and macrobenthos were sampled at the entire net of stations. Water for microbiological analysis (due to limited possibility of ensuring the seeding sterility in the field) was sampled at particular stations (sta. 2, 4, 5, 8, and 11–14), which cover all bights of the bay, and at the control station (C) outside the bay. The sea urchin *Strongylocentrotus intermedius* (A. Agassiz, 1864) was chosen to serve as a bioindicator based on the following criteria: its high biomass and frequency of occurrence in the bay; sensitivity to various toxicants, *inter alia* HM, at all stages of the life cycle; and the fact that humans consume gonads [Vaschenko et al., 2005]. Sea urchins were sampled at sta. 2, 7, 10–12, and 14 out of the total quantitative macrobenthic samples. In total, we analyzed 26 samples of surface water (17 for hydrochemical parameters and 9 for microbiological indicators), 17 samples of bottom sediments, 102 quantitative samples of macrobenthos, and 18 samples of the sea urchin gonads. When carrying out chemical, ecological, and microbiological analysis, a triplicate of the measurement of each indicator was observed for each sample (Table 1). There were six macrobenthic samples at each station. Primary analysis was carried out in a field laboratory; final one, in the laboratories of the UNESCO international chair in marine ecology and the chair in soil science of the Institute of the World Ocean (School) of the Far Eastern Federal University (FEFU).

Hydrochemical analysis. Seawater was sampled from the surface 50-cm layer according to [Rukovodstvo po khimicheskomy analizu, 2003]. Oxygen dissolved in water and BOD_5 values were determined in accordance with the Winkler method. Permanganate oxidizability was established by the Skopintsev technique. To determine two forms of phosphorus (organic and mineral), the Morphy–Riley method was applied [Rukovodstvo po khimicheskomy analizu, 2003]. The analysis was carried out on the day of sampling, in triplicate for each indicator.

Microbiological analysis. Water was sampled from the surface layer into sterile plastic containers. The samples were transported to the field laboratory and analyzed on the day of sampling, in compliance with terms of storage and transportation according to international technical standards GOST 31861-2012 and GOST 31942-2012. The abundance of colony-forming heterotrophic microorganisms (hereinafter CHM) in 1 mL of water was determined applying the Koch plate count technique in a medium for marine microorganisms (MMM) with the addition of 1.5% agar [Yoshimizu, Kimura, 1976]. The abundance of metal-resistant forms in a CHM community was established by the plate count technique in the MMM with addition of metal salts at concentrations inhibiting the growth of sensitive forms of bacteria. As additives, metal chlorides (Zn, Cu, Cd, Ni, and Co) and lead nitrate were used [Bezverbnaya et al., 2003]. Resistance testing was carried out for each toxic additive (element by element) for all samples taken (in triplicate).

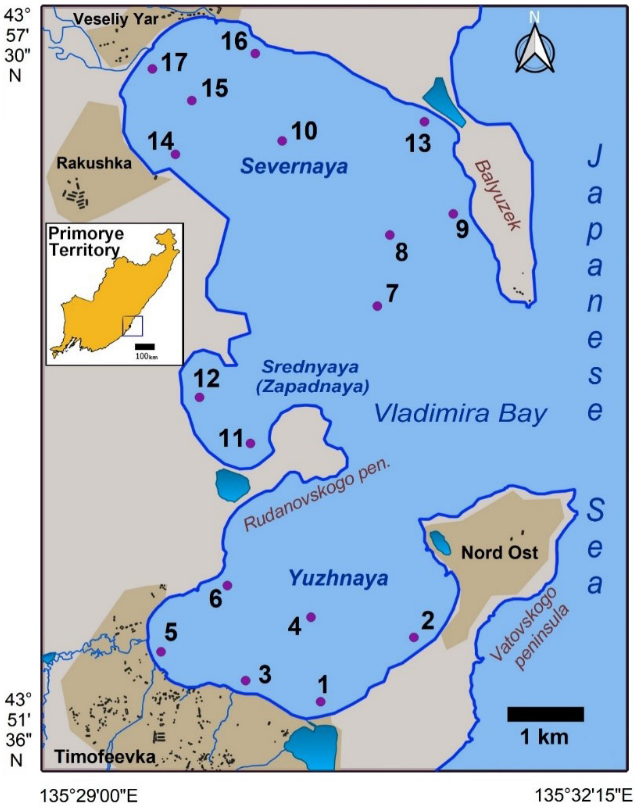

Fig. 1. The map of sampling in the Vladimir Bay

Table 1. Amount of factual material for chemical, ecological, and microbiological assessment

Sample type	Surface water for hydrochemical analysis	Surface water for microbiological analysis	Bottom sediments	Sea urchins
Number of samples	17	9	17	18
Assessment parameters	DO, BOD_5, PO, P_{total}, P_{min}, P_{org} (6 parameters)	CHM, groups of bacteria resistant to heavy metals – Cu, Cd, Ni, Co, Zn, Pb (7 parameters)	Granulometric composition, OM, Cu, Cd, Ni, Zn, Pb, Fe, Cr (9 parameters)	Cu, Cd, Ni, Zn, Pb, Cr (6 parameters)
Number of parameter determinations	306	189	459	324

Note: abbreviations for the parameter names are given below in the text – in the sections describing different types of analysis.

Granulometric analysis of bottom sediments. The particle size of surface bottom sediments was determined mechanically (GOST 12536-79), while the amount of the finest fractions in samples with silt prevalence was established by the pipette method [Kachinsky, 1958]. The sediment type was determined by the dominant fraction.

Analysis of organic matter content in bottom sediments. The total content of organic carbon (C_{org}) was determined by the Tyurin method modified by the Central Research Institute of Agrochemical Services for Agriculture (GOST 26213-91).

Assessment of composition and quantitative indicators of macrobenthos. Sampling was carried out by scuba divers from a motor boat in the horizon of the upper sublittoral (3–27 m). At each station, epibenthos was sampled (using a hydrobiological frame with an area of 1 m^2), as well as infauna (using a diving gear grab with a capture area of 0.025 m^2). Sampling with each tool was carried out in triplicate. In total, there were 102 samples. Primary processing was carried out in the field laboratory. Unidentified animal species were fixed with a 4% formaldehyde solution, and plants were placed in herbarium; to each species, a code was assigned. Further identification was carried out in the laboratories of the FEFU Institute of the World Ocean, and the data of primary processing were supplemented. All indicators are recalculated to 1 m^2.

Analysis of heavy metal content in bottom sediments and hydrobionts. In bottom sediments, the total content of Fe, Cd, Ni, Cr, Cu, Zn, and Pb was determined. Sampled sediments were treated with a mixture of hydrochloric, hydrofluoric, perchloric, and nitric acids. The procedure was followed by determination of the total content of elements by flame atomic absorption spectrometry (AAS) (the regulatory document PND F 16.1:2.2:2.3.36-02) on a Shimadzu AA-6800 atomic absorption spectrophotometer (Japan).

At least three specimens of the sea urchin *S. intermedius* were selected for the analysis at each station from each macrobenthic sample in which this species occurred. A total of 18 specimens were sampled. Gonads were preliminarily dried in an oven at a temperature of +85 °C and grinded. Then, samples of 0.40–0.50 g were dried to a constant weight and subjected to acid decomposition with concentrated high-purity nitric acid. After that, these samples were transferred to a 2% nitric acid solution. HM content (Zn, Cu, Pb, Cr, Cd, and Ni) was determined by AAS on a Shimadzu AA-6800. The accuracy was controlled by analyzing standard samples (NIST 2976). The determination error did not exceed 15%.

Calculation of accumulation factor and sediment quality guideline quotient. Indices of HM contamination of bottom sediments (the contamination factor C_f and the degree of contamination C_d) were determined in accordance with the algorithm proposed by Hakanson [1980] and successfully tested in various water areas [Chakraborty et al., 2014; Liang et al., 2018; Saroop, Tamchos, 2021; Vashchenko et al., 2010; *etc.*]:

$$C_f = C/C_b \,, \tag{1}$$

$$C_d = \sum C_f \,, \tag{2}$$

where C is the mean concentration of a substance in bottom sediments;

C_b is the background concentration of this substance in bottom sediments [Shulkin, 2004].

An integral assessment of potential toxicity of bottom sediments in the Vladimir Bay was carried out applying the sediment quality guideline quotient, SQG-Q [Birch, 2011; MacDonald et al., 1996; Vashchenko et al., 2010; *etc.*]. This index allows characterizing the toxicity of accumulated pollutants for marine hydrobionts in abiotic components of a studied biotope and is determined by the formula:

$$SQG - Q = \sum PEL - Q/n \,, \tag{3}$$

where ∑PEL-Q is the ratio of the mean concentration of a toxicant in bottom sediments to the PEL (probable effect level) for the same toxicant [MacDonald et al., 1996];

6n is the number of toxicants.

To determine individual carcinogenic risk when exposed to non-threshold toxicants, a calculator establishing incremental lifetime cancer risk, ILCR, was used (http://www.popstoolkit.com/tools/HHRA/Carcinogen.aspx). This coefficient is widely applied in Canada and the USA. ILCR index estimates incremental lifetime carcinogenic risk when a product is consumed over a certain period of time.

Cartographic and statistical data processing. Maps of the distribution of OM and HM content in bottom sediments were built by the kriging interpolation in Surfer software package (Golden Software). The final design of the cartographic material was carried out in QGIS program based on the digitization of raster topographic maps of the studied area, the access to which is free.

To determine the strength of the relationship between the analyzed indicators, we used the Pearson correlation coefficient, the assessment of linear approximation trends, and the value of the approximation reliability R^2.

RESULTS

Ecological assessment of the aquatic environment. The well-being of natural waters and OM amount there can be estimated by values of the content of oxygen dissolved in water (hereinafter DO), BOD_5, permanganate oxidizability (hereinafter PO), and P_{org} concentration. DO content depends on two groups of processes: some increase it (release during photosynthesis and adsorption from the atmosphere), while others decrease (consumption for the oxidation of organic substances). According to DO value, conclusions are drawn about the intensity of the self-purification in water bodies and the oxidation of dissolved OM [Khristoforova et al., 2015]. Chemical and environmental control of the Vladimir Bay state showed sufficient DO content in its surface waters and the lack of areas with the values below the summer standard of 6 mg $O_2 \cdot L^{-1}$ [Prikaz Minsel'khoza Rossii no. 552, 2016]. The mean value was 8.79 mg $O_2 \cdot L^{-1}$, and the minimum one was 7.22 mg $O_2 \cdot L^{-1}$ (Table 2).

Table 2. Hydrochemical parameters and trophic status of the Vladimir Bay surface waters (mean ± *SD*)

Sta.	Temperature, °C	DO, mg $O_2 \cdot L^{-1}$	BOD_5, mg $O_2 \cdot L^{-1}$	PO, mg $O \cdot L^{-1}$	P_{min}, μg$\cdot L^{-1}$	P_{org}, μg$\cdot L^{-1}$	P_{total}, mg$\cdot L^{-1}$	Trophic status
1	+21.4	9.06 ± 0.04	1.04 ± 0.05	1.12 ± 0.02	27.78 ± 0.36	256.69 ± 6.72	284.47 ± 1.89	O
2	+20.5	8.42 ± 0.07	1.13 ± 0.05	1.12 ± 0.07	**109.12** ± 8.64	44.34 ± 1.16	153.46 ± 10.03	M
3	+20.7	8.69 ± 0.22	1.46 ± 0.05	1.44 ± 0.28	13.89 ± 1.44	809.57 ± 67.76	823.46 ± 67.76	O
4	+22.2	9.10 ± 0.18	1.80 ± 0.11	1.60 ± 0.07	**75.39** ± 0.19	516.00 ± 32.89	591.39 ± 12.05	M
5	+22.3	8.90 ± 0.07	1.43 ± 0.06	2.08 ± 0.04	**61.50** ± 1.49	230.45 ± 12.81	291.95 ± 16.30	M
6	+22.1	8.54 ± 0.28	0.81 ± 0.29	1.36 ± 0.18	**93.25** ± 3.80	22.13 ± 9.52	115.38 ± 2.50	M
7	+21.2	8.93 ± 0.11	1.37 ± 0.16	1.76 ± 0.09	23.81 ± 6.46	5.09 ± 0.06	28.09 ± 1.09	O
8	+21.0	8.98 ± 0.08	1.51 ± 0.23	3.52 ± 0.22	43.65 ± 6.08	87.36 ± 14.81	131.01 ± 5.95	O

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Sta.	Temperature, °C	DO, mg $O_2 \cdot L^{-1}$	BOD_5, mg $O_2 \cdot L^{-1}$	PO, mg $O \cdot L^{-1}$	P_{min}, $\mu g \cdot L^{-1}$	P_{org}, $\mu g \cdot L^{-1}$	P_{total}, $mg \cdot L^{-1}$	Trophic status
9	+21.4	9.23 ± 0.12	1.27 ± 0.12	1.92 ± 0.10	**53.57** ± 9.94	489.17 ± 21.27	542.74 ± 22.76	M
10	+20.8	8.84 ± 0.14	1.46 ± 0.10	0.16 ± 0.10	**51.58** ± 8.56	71.94 ± 10.24	123.52 ± 10.19	M
11	+19.0	9.19 ± 0.16	2.24 ± 0.11	3.36 ± 0.15	**69.44** ± 13.25	42.85 ± 7.63	112.29 ± 5.62	M
12	+19.0	9.26 ± 0.35	1.38 ± 0.2	1.36 ± 0.14	**71.42** ± 5.53	190.59 ± 12.6	262.01 ± 12.24	M
13	+21.0	8.77 ± 0.40	1.32 ± 0.11	3.60 ± 0.51	39.68 ± 5.01	8.98 ± 0.11	48.66 ± 5.12	O
14	+19.9	7.22 ± 0.26	0.34 ± 0.02	2.24 ± 0.09	41.66 ± 4.01	194.15 ± 13.44	235.81 ± 17.65	O
15	+19.8	8.82 ± 0.15	1.02 ± 0.19	1.28 ± 0.26	**63.49** ± 11.13	45.06 ± 16.96	108.55 ± 23.11	M
16	+20.2	8.48 ± 0.44	2.71 ± 0.20	2.88 ± 0.15	21.82 ± 2.01	15.61 ± 3.18	36.98 ± 4.80	O
17	+19.1	8.50 ± 0.34	3.90 ± 0.43	2.56 ± 0.08	31.74 ± 5.37	192.84 ± 17.95	224.58 ± 14.82	O

Note: M, mesotrophic; O, oligotrophic. The values of the concentration of mineral phosphorus compounds for the stations with mesotrophic status are highlighted in bold.

BOD_5 indicates the presence of easily oxidizable OM in water, most often being waste products of hydrobionts or entering with municipal wastewater. At most stations, BOD_5 levels corresponded to the standard of 2.1 mg $O_2 \cdot L^{-1}$ [Prikaz Minsel'khoza Rossii no. 552, 2016], varying within 0.34–1.80 mg $O_2 \cdot L^{-1}$. Only at three stations (sta. 11, 16, and 17) the values of biochemical oxygen consumption exceeded the standard and amounted to 2.24, 2.71, and 3.90 mg $O_2 \cdot L^{-1}$, respectively.

PO reflects the content of hardly oxidizable substances in water (decomposition products of dead organisms, as well as oil, heavy fuel oil, and other hydrocarbons entering water with surface flushing and runoff). For the purest waters, PO values usually do not exceed 3–5 mg $O \cdot L^{-1}$ and may vary by season [Khristoforova et al., 2015]. The values of PO ranged from 0.16 to 3.60 mg $O \cdot L^{-1}$, reaching a maximum at sta. 13. To date, PO value is not standardized for fishery basins.

Phosphorus is one of the elements determining the productivity of natural waters. The concentration of its organic (P_{org}) and mineral (P_{min}) compounds is an important component of the OM balance in the aquatic environment. During the period of our study, summer values of total concentrations of phosphorus compounds (P_{total}) were high. At 50% of the analyzed stations, those exceeded 200 $\mu g \cdot L^{-1}$. The contribution of organic and mineral forms of phosphorus to its total content was different: at 8 stations, where P_{total} values were higher than 200 $\mu g \cdot L^{-1}$, its organic compounds with concentrations above 100 $\mu g \cdot L^{-1}$ prevailed. A maximum of 809.57 $\mu g \cdot L^{-1}$ was detected in the Yuzhnaya Bay, at sta. 6. In accordance with the water quality standards for fishery basins [Prikaz Minsel'khoza Rossii no. 552, 2016], the trophic status can be judged by the concentration of phosphate ions (P_{min}): up to 50 $\mu g \cdot L^{-1}$ phosphates are characteristic of oligotrophic waters; 50–150 $\mu g \cdot L^{-1}$, of mesotrophic (those are highlighted in bold in Table 2); and more than 200 $\mu g \cdot L^{-1}$, of eutrophic. Eutrophic values were not revealed. The ratio of the stations with oligotrophic and mesotrophic status was approximately 1 : 1 (see Table 2).

CHM can serve as a microbiological indicator of the total OM level in the aquatic environment, describing water quality of the marine ecosystem and allowing both to rank OM level in the environment and to classify pollution. According to a saprobity scale, waters with CHM content of up to 10^3 cells·mL^{-1} are oligosaprobic; up to 10^5, mesosaprobic (subdivided into categories of a lower rank); with abundance of 10^6 cells·mL^{-1} and more, polysaprobic [Obshchaya i sanitarnaya mikrobiologiya, 2004]. The ecological and bacteriological assessment of surface waters revealed a uniform distribution of CHM abundance at a level of 10^3 CFU·mL^{-1} in the surface layer (Table 3). This allows to consider waters as α-mesosaprobic, *i. e.*, enriched with OM. The control station outside the bay was characterized by the same level of heterotrophic bacteria.

Table 3. Abundance of colony-forming heterotrophic microorganisms (CHM) in the Vladimir Bay surface waters

Station	2	4	5	8	11	12	13	14	Control (C)
CHM (× 10^3 CFU·mL^{-1})	1.5	5.3	7.2	1.2	1.5	5.2	3.8	7.3	4.5

Organic matter in bottom sediments. The content of organic carbon (C_{org}) in soft sediments varied from 0.11 to 3.64% *per* 100 g of dry sample weight. The minimum values were recorded in pebbles (fine psephite) and sands (fine-grained psammite) of the shallowest stations (depth of 3–5 m), while the maximum values were registered in silts (siltstones) at depths of 10, 15, 20, and 25 m (Tables 4, 5, Fig. 2).

The spatial distribution of C_{org} values in the surface layer of the bay bottom sediments has a characteristic manifestation and is determined by a combination of factors: remoteness from the coast, bottom topography, intensity of hydrodynamics and sedimentogenesis, and granulometric composition of bottom sediments. The maximums are confined to central areas of the Severnaya and Yuzhnaya bays and to the apex of the Srednyaya Bay, *i. e.*, to zones of accumulation with a prevalence of siltstone fractions and the lowest water dynamics. There, active sedimentation occurs of both small remains of organisms and OM – suspended and dissolved in water.

Table 4. Granulometric composition of the Vladimir Bay bottom sediments (excluding silt fractions)

Sta.	Depth, m	Content of sediment fractions (mm), %								Sediment type
		> 10	10–5	5–2	2–1	1–0.5	0.5–0.25	0.25–0.1	< 0.1	
1	3	0	0.5	0.5	0.3	0.6	21	67.3	8.9	Fine-grained psammite
2	3	0	0	0.7	0.7	0.5	38.3	59.7	0.1	Fine-grained psammite
3	3	0	0	2.1	2.8	3.3	24.1	50.8	16.1	Fine-grained psammite
5	4	0	0	3.7	5.7	5.7	26.5	55.5	2.9	Fine-grained psammite
6	6	0	0	2.5	12.3	17.3	39.5	26.6	1.8	Coarse-grained psammite
8	27	0	0	0.9	0.6	1.3	17.8	75	3.7	Fine-grained psammite
9	5	0	0	0.8	1.2	3	24.7	66.5	3	Fine-grained psammite
10	20	39.8	2.1	4.4	5.9	5.1	14.3	26.1	2.3	Fine psephite
13	5	0	0	1.6	1.8	1.6	4	83.3	6.8	Fine-grained psammite
14	5	68.5	0	4.6	8	6.5	8.1	2.8	1.5	Fine psephite
17	5	0	0	0.6	4.3	8.8	23.8	56.9	4.8	Fine-grained psammite

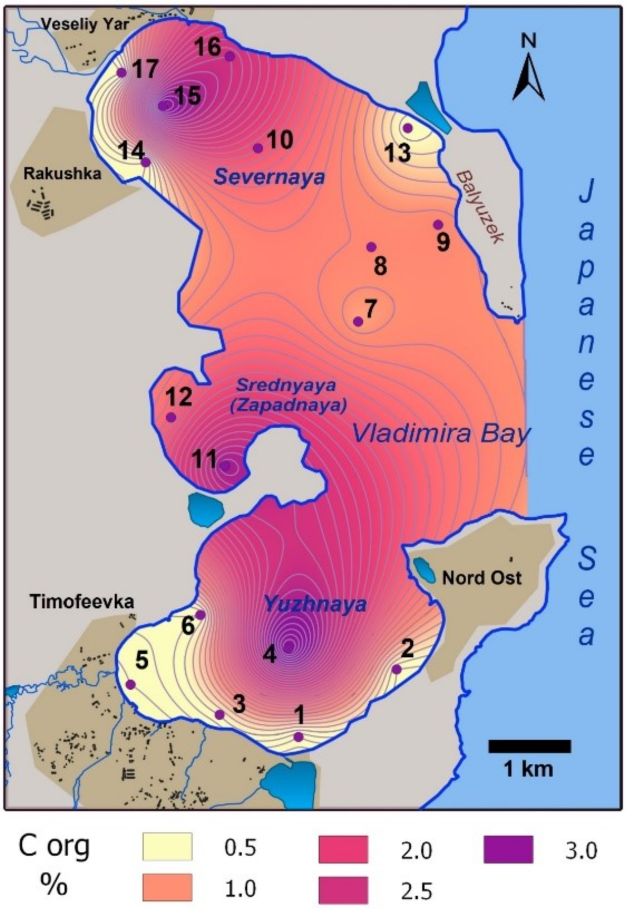

Fig. 2. Map of organic carbon (C_{org}) distribution in the Vladimir Bay bottom sediments

Table 5. Granulometric composition of silt fractions of the Vladimir Bay bottom sediments

Sta.	Depth, m	Content of sediment fractions (mm), %						Sum of particles		Sediment type
		1.00–0.25	0.25–0.05	0.05–0.01	0.01–0.005	0.005–0.001	< 0.001	< 0.01	> 0.01	
4	21	1	36	30	18	4	11	33	67	Pelitic siltstone
7	24	30	43	11	4	7	5	16	84	Fine-grained psammite
11	5	1	12	50	18	10	9	37	63	Psammitic siltstone
12	10	1	66	20	7	2	4	13	87	Psammitic siltstone
15	18	1	15	59	13	7	5	25	75	Pelitic siltstone
16	7	1	28	61	3	2	5	10	90	Psammitic siltstone

Characteristics of macrobenthos. In total, 15 macrobenthic taxa of the highest rank were identified: 11 phyla of marine animals (Porifera, Cnidaria, Nemertea, Annelida, Sipuncula, Arthropoda, Mollusca, Brachiopoda, Bryozoa, Echinodermata, and Chordata) and 4 divisions of plants (Rhodophyta, Ochrophyta, Chlorophyta, and Tracheophyta). The total species richness of the macrobenthos of the Vladimir Bay sublittoral includes at least 63 species: 45 species of invertebrates and 18 species of plants. The highest species richness was recorded in the classes Florideophyceae, Gastropoda, Bivalvia, Malacostraca, Polychaeta, Phaeophyceae, and Asteroidea.

The mean biomass of macrobenthos at stations varied from 40.7 to 2,442.3 g·m^{-2}. The minimum value was registered at sta. 4, in the central Yuzhnaya Bay, where one Bivalvia species and one Polychaeta species were noted. At 30% of stations, the mean biomass reached 500 g·m^{-2}, and the rest were characterized by high values (from 500 g·m^{-2} to maximum ones). Thus, the general background of biomass values can be described as evenly high. The values of mean biomass for the Vladimir Bay are similar to those for the Vostok Bay (Table 6).

Table 6. The values of mean biomass and abundance of macrobenthos in different water areas off the Primorsky Krai marine coast

Area	Mean biomass ± *SD*, g·m^{-2}	Mean settlement density ± *SD*, ind.·m^{-2}
Udobnaya Bight	4,523.9 ± 9,324.2	108.5 ± 90.3
Kievka Bight	1,634.9 ± 954.5	159.1 ± 124.6
Rudnaya Bight	1,173.5 ± 1,268.6	77.0 ± 54.4
Nakhodka Bay (except for Nakhodka Bight)	1014.9 ± 825.2	250.6 ± 365.4
Vostok Bay	864.5 ± 662.0	170.2 ± 762.0
Vladimir Bay	841.2 ± 583.0	57.4 ± 12.3
Trinity Bay	473.7 ± 627.1	93.7 ± 80.4
Zolotoy Rog Bay	204.2 ± 50.1	115.0 ± 4.9

Note: *SD* is standard deviation. The data on all the water areas, except for the Vladimir Bay, are given according to [Galysheva et al., 2018].

The dominant macrozoobenthic species with mean biomass at station of more than 100 g·m^{-2} included species typical for the Sea of Japan: sea urchin *S. intermedius* (frequency of occurrence was 44%); starfish *Asterina pectinifera* (Muller & Troschel, 1842) (36%); bivalves *Mizuhopecten yessoensis* (Jay, 1857) (12%), *Crenomytilus grayanus* (Dunker, 1853) (8%), and *Pododesmus macrochisma* (Deshayes, 1839) (4%); and holothurian *Cucumaria japonica* Semper, 1868 (4%). In macrophytobenthos, the following species prevailed: brown algae *Desmarestia viridis* (O. F. Müller) J. V. Lamouroux, 1813 (frequency of occurrence was 24%), *Costaria costata* (C. Agardh) De A. Saunders, 1895 (16%), and *Saccharina japonica* (Areschoug) C. E. Lane, C. Mayes, L. D. Druehl & G. W. Saunders, 2006 (12%), as well as seagrasses *Zostera marina* Linnaeus, 1753 (16%) and *Phyllospadix iwatensis* Makino, 1931 (12%).

Heavy metals in the environment. The level of HM content in surface waters was determined by the abundance of metal-resistant microorganisms, which, due to their exceptional specificity, allow to assess properly environmental pollution with these elements [Bezverbnaya et al., 2003; Kalitina et al., 2015]. In general, lead-resistant bacteria turned out to be the least common group (those were detected at two stations only). The most common ecological and trophic group occurring at all stations in high concentrations (from 10^2 to 10^3 CFU·mL^{-1}) were cadmium-resistant bacteria (Table 7).

Interestingly, Cu- and Zn-resistant microorganisms were also found at almost all stations and formed a general background with lower cell concentration. However, at the control station outside the bay, the abundance of Zn-resistant bacteria was two orders of magnitude higher. In general, bacteria resistant to several metals were simultaneously registered in microbial communities of the Vladimir Bay surface waters at most stations. The least common were Pb-, Ni-, and Co-resistant bacteria.

Table 7. Distribution of the abundance of heavy metal resistant microorganisms (CFU·mL^{-1}) in the Vladimir Bay surface waters (mean ± *SD*)

Sta.	Ecological and trophic groups of microorganisms					
	Cu	Cd	Ni	Co	Zn	Pb
2	(7.0 ± 0.09) × 10^2	(1.8 ± 0.1) × 10^2	(1.2 ± 0.28) × 10^2	0	(2.0 ± 0.12) × 10	(5.0 ± 0.1) × 10^2
4	(2.4 ± 0.09) × 10^3	(1.8 ± 0.17) × 10^3	(2.0 ± 0.1) × 10^2	0	(5.0 ± 0.2) × 10	(2.0 ± 0.02) × 10
5	(1.02 ± 0.12) × 10^3	(2.08 ± 0.1) × 10^3	0	(8.2 ± 0.06) × 10^2	(2.0 ± 0.02) × 10	0
8	(1.08 ± 0.08) × 10	(1.0 ± 0.03) × 10^2	0	0	0	0
11	(1.0 ± 0.28) × 10^2	(1.7 ± 0.02) × 10^2	(2.3 ± 0.1) × 10^2	(4.0 ± 0.2) × 10^2	(2.0 ± 0.04) × 10	0
12	(1.1 ± 0.1) × 10^2	(9.0 ± 0.1) × 10^2	(2.0 ± 0.1) × 10^2	(1.0 ± 0.31) × 10^3	(1.2 ± 0.05) × 10	0
13	0	(1.0 ± 0.2) × 10^2	(6.0 ± 0.3) × 10	0	(2.0 ± 0.02) × 10	0
14	(3.5 ± 0.3) × 10^2	(1.8 ± 0.12) × 10^3	0	(1.8 ± 0.2) × 10^2	0	0
C	(1.6 ± 0.3) × 10^2	(9.0 ± 0.2) × 10^2	0	(2.0 ± 0.08) × 10	(1.1 ± 0.3) × 10^2	0

When assessing the ecological state of bottom sediments, it is recommended to analyze the total content and the concentration of acid-soluble (conditionally total) and mobile forms of HM. Depending on HM form under determination, pollution is assessed *via* comparison with the clarke content of the element in the Earth's crust, or with maximum permissible concentration (MPC) and approximate permissible concentration established for soils, or with a background. We determined the total concentrations compared with the clarke content of the element in the Earth's crust [Vinogradov, 1962] and background concentrations for Peter the Great Bay [Shulkin, 2004].

The concentrations of the analyzed compounds (Cd, Ni, Pb, Cu, Zn, Fe, and Cr) varied in different ranges. Specifically, the multiplicity of the difference between the maximum and minimum values ranged from 1.9 to 70.3, indicating the most even background of bottom concentrations for Cr and the most varying background for Cu (Table 8). For Pb, Fe, and Zn, the max/min ratio was 3.6, 4.6, and 6.7 times. There was more than 13-fold variation in the range of Ni content in bottom sediments. The highest concentrations of HM compounds in bottom sediments were as follows: Cd, 0.75 µg·g^{-1}; Ni, 33.0; Pb, 10.9; Cu, 21.1; Zn, 115.3; Fe, 17,437; and Cr, 16.26 µg·g^{-1}.

For almost all elements, the total content of HM in bottom sediments was below the clarke value. An exception was Cd: for this element, an excess of clarke values was noted at many stations. Maximum concentrations of Cd occurred at stations with the highest values of C_{org}. For several stations, an excess of the clarke value for Zn was registered. Interestingly, the maximums are associated with increased OM concentrations in bottom sediments and the prevalence of the fine silt fraction as well. Apparently, this contributes to accumulation of these elements from the aquatic environment and concentration in accumulative zones of the bay. For all studied stations, iron and zinc prevail in the range of concentrations, while the content of cadmium is always minimum (compared to that of other metals). The general sequence of decreasing HM concentrations in bottom sediments is as follows: Fe > Zn > Cu > Cr > Pb > Ni > Cd. At several stations, Cr and Pb "switched places" in this sequence, while the rest of the pattern was repeated. When comparing our data with the descending clarke sequence of these elements, Fe > Zn > Cr > Ni > Cu > Pb > Cd [Vinogradov, 1962], it can be seen that positions of iron, zinc, and cadmium coincide in two sequences.

Table 8. Concentrations of heavy metals (μg·g^{-1}) in the Vladimir Bay bottom sediments (mean ± *SD*)

Station	Cd	Ni	Pb	Cu	Zn	Fe	Cr
1	**0.75** ± 0.08	2.5 ± 0.1	3.0 ± 0.2	10.9 ± 0.1	26.7 ± 0.5	4,681 ± 154	7.45 ± 0.11
2	0.00	2.5 ± 0.2	3.4 ± 0.2	10.2 ± 4.0	34.9 ± 1.0	6,893 ± 2,579	7.80 ± 0.04
3	0.45 ± 0.03	3.8 ± 0.2	7.5 ± 0.2	10.3 ± 0.1	74.5 ± 0.4	13,168 ± 151	4.43 ± 0.38
4	0.69 ± 0.03	3.7 ± 0.4	8.3 ± 0.1	9.4 ± 0.1	**115.3** ± 8.7	**17,437** ± 169	**16.26** ± 0.11
5	0.35 ± 0.01	3.8 ± 0.2	7.4 ± 0.1	10.1 ± 0.2	61.6 ± 0.4	14,952 ± 138	2.74 ± 0.67
6	0.19 ± 0.01	3.2 ± 0.1	4.5 ± 0.1	12.7 ± 1.4	45.6 ± 0.8	6,721 ± 19	2.04 ± 0.13
7	0.00	2.9 ± 0.1	4.1 ± 0.1	2.0 ± 0.1	30.3 ± 0.1	10,571 ± 165	12.00 ± 0.27
8	0.42 ± 0.03	**33.0** ± 0.7	9.2 ± 0.1	16.2 ± 0.1	97.4 ± 0.2	14,708 ± 77	9.00 ± 0.44
9	0.26 ± 0.01	2.8 ± 0.1	6.3 ± 0.1	5.8 ± 0.1	35.8 ± 0.2	7,085 ± 34	3.32 ± 0.20
10	0.11 ± 0.01	4.6 ± 0.1	8.5 ± 0.1	1.6 ± 0.1	17.3 ± 0.1	4,289 ± 4	11.19 ± 0.07
11	0.73 ± 0.01	2.6 ± 0.1	3.2 ± 0.1	10.8 ± 0.1	35.7 ± 0.1	5,533 ± 19	5.59 ± 0.11
12	0.72 ± 0.01	2.7 ± 0.2	3.3 ± 0.1	11.2 ± 0.1	36.3 ± 0.1	5,609 ± 3	5.91 ± 0.09
13	0.35 ± 0.01	3.4 ± 0.1	7.1 ± 0.2	**21.1** ± 0.4	28.5 ± 0.1	6,262 ± 8	2.04 ± 0.04
14	0.64 ± 0.01	2.8 ± 0.1	3.4 ± 0.1	10.7 ± 0.1	65.3 ± 0.1	11,622 ± 216	6.63 ± 0.07
15	0.44 ± 0.01	5.0 ± 0.1	**10.9** ± 0.1	18.5 ± 0.1	113.6 ± 0.5	12,378 ± 12	13.46 ± 0.07
16	0.06 ± 0.01	3.2 ± 0.1	3.1 ± 0.2	1.4 ± 0.2	22.5 ± 0.1	3,781 ± 32	0.66 ± 0.07
17	0.19 ± 0.01	3.4 ± 0.1	5.8 ± 0.2	0.3 ± 0.1	39.2 ± 0.1	11,052 ± 43	2.68 ± 0.07
Max/min	13.6	13.2	3.6	70.3	6.7	4.6	24.64
Clarke	0.13	58	16	47	83	46,500	83
BG_{sands}	0.1 ± 0.05	15 ± 3	20 ± 5	8 ± 2	30 ± 7	–	–
$BG_{aleuropelite}$	0.2 ± 0.1	45 ± 5	35 ± 5	2 ± 3	100 ± 10	–	–

Note: clarke content is given according to [Vinogradov, 1962]; background concentrations of metals (BG) are given for the coastal bottom sediments of the northwestern Sea of Japan [Shulkin, 2004]. Maximum concentrations of heavy metal compounds are highlighted in bold.

HM spatial distribution over the surface of the Vladimir Bay bottom is characterized by four types. "Unipolar" is revealed for Ni; it has one area of maximum values: at the Severnaya Bay mouth, at a depth of 25 m (Fig. 3). "Bipolar" distribution has two areas of maximum concentrations; it is registered for Pb, Cr, and Cu. "Tripolar" is typical for the most common metals: Zn and Fe; the maximums of their concentrations are recorded in the zones of the most pronounced sedimentogenesis. "Vector" distribution is noted for Cd; it is characterized by a clear gradient of its concentration decrease in bottom sediments inward from the coast in almost all areas of the bay.

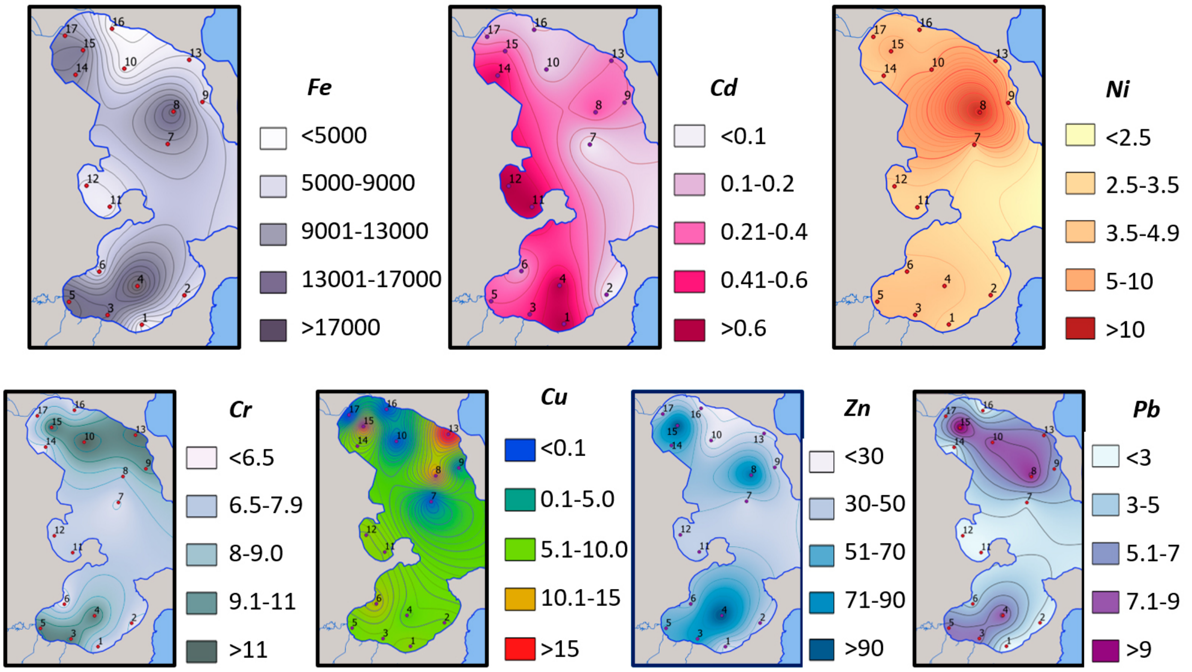

Fig. 3. Maps of the distribution of heavy metal concentrations (μg·g^{-1}) in the Vladimir Bay bottom sediments (the stations are indicated on the maps with numbers)

Heavy metals in the sea urchin gonads. In *S. intermedius* gonads, the concentrations of the same six HM were determined, as in bottom sediments (excluding Fe). The range of concentrations was as follows: Pb, 2.36–13.46 μg·g^{-1} dry weight; Cd, 0.22–0.62; Cu, 3.05–5.12; Cr, 1.34–2.32; Ni, 0.89–4.65; and Zn, 32.51–118.94 μg·g^{-1} dry weight. This range was narrower than that for bottom sediments. The maximum variability (5.70 times) was recorded for Pb content (Table 9). Out of all HM, the highest concentrations are typical for zinc; the lowest ones, for cadmium. Nickel, copper, lead, and chromium occupy an intermediate position, replacing each other in a sequence of descending concentrations at different stations. On average, decreasing concentrations form the following sequence: Zn > Pb > Cu > Ni > Cr > Cd.

Table 9. Heavy metal concentrations in *Strongylocentrotus intermedius* gonads (μg·g^{-1} dry weight) from the Vladimir Bay

Station	Metals					
	Pb	Cd	Cu	Cr	Ni	Zn
2	2.36 ± 0.44	0.36 ± 0.02	3.30 ± 0.77	1.58 ± 0.21	2.65 ± 1.20	70.11 ± 16.58
7	3.89 ± 0.85	**0.62 ± 0.02**	3.21 ± 0.48	**2.32 ± 0.31**	2.58 ± 0.67	101.83 ± 21.37
10	5.89 ± 2.23	0.51 ± 0.08	3.99 ± 0.49	2.16 ± 0.14	2.05 ± 0.58	**118.94 ± 28.67**
11	2.82 ± 0.21	0.28 ± 0.03	3.05 ± 0.37	1.38 ± 0.16	**4.65 ± 2.21**	84.85 ± 15.68
12	3.01 ± 0.21	0.59 ± 0.08	3.58 ± 0.25	1.68 ± 0.11	1.54 ± 0.58	92.41 ± 15.81
14	**13.46 ± 1.19**	0.22 ± 0.03	**5.12 ± 0.06**	1.34 ± 0.47	0.89 ± 0.71	32.51 ± 21.47
Max/min	5.70	2.81	1.68	1.73	5.22	3.66

Note: the mean values based on the results of three replicates and *SD* are given. Maximum values are highlighted in bold.

DISCUSSION

In general, the oxygen regime of the Vladimir Bay (DO and BOD_5) is normal; there are no hypoxia zones. Nevertheless, in the apex of the Srednyaya Bay and in the apex of the Severnaya Bay, areas with a high level of BOD_5 were recorded, which determines intensive DO consumption for the oxidation of easy-to-decompose OM. When analyzing the trace of hard-to-decompose OM (*inter alia* household wastewater from villages, containing synthetic surfactants and other compounds), it can be concluded that this trace is not significant in terms of PO values.

The values of the content of phosphorus in organic forms are quite high and reach a maximum, 809.57 $\mu g \cdot L^{-1}$, in the Yuzhnaya Bay, near the village of Timofeevka. However, the concentrations of mineral phosphorus compounds (P_{min}), according to which the trophic status is classified, generally characterize the Vladimir Bay waters in summer as mesotrophic. An even CHM distribution in surface waters at the level of 10^3 $CFU \cdot mL^{-1}$ (including the control station outside the bay) indicates α-mesosaprobic level of OM [Obshchaya i sanitarnaya mikrobiologiya, 2004]. Comparison of microbiological data with a trophicity scale shows oligomesotrophic level, and this coincides with our direct chemical assessment. Thus, the water mass of the bay in summer has mesotrophic level of OM, which is sufficient to maintain the abundance of organisms in biocenoses formed there. Moreover, the water mass successfully "utilizes" incoming OM of both natural and household origin. In general, villages and the coastal strip insignificantly affect the formation of eutrophication conditions.

The content of organic carbon in soft sediments reached 3.64% of dry sample weight. In the series of maximum C_{org} values obtained for different water areas of the Primorsky Krai marine coast [Galysheva, 2010], the Vladimir Bay is between the Nakhodka Bay (except for Nakhodka Bight) and the Amur Bay (Fig. 4).

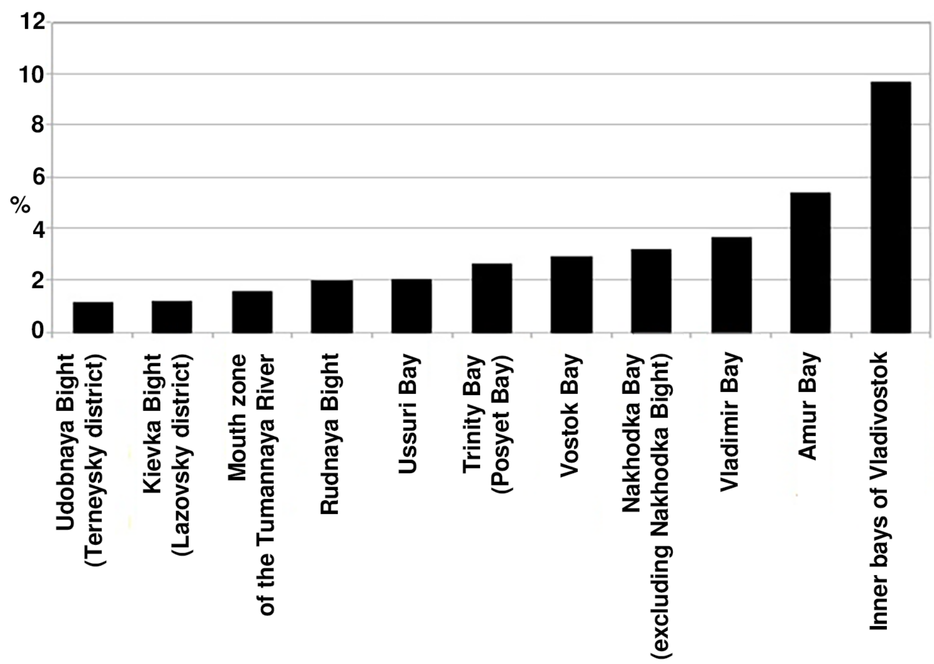

Fig. 4. Range of the maximum values of organic carbon (C_{org}) content (% *per* 100 g of dry sample weight) recorded in the bottom sediments off the Primorsky Krai marine coast

Accordingly, the Vladimir Bay can be attributed to marine areas with a relatively high OM content in soft sediments. This indicates the severity of the processes of OM accumulation in the bay ecosystem even under conditions of oligomesotrophic level of seawater. The reasons for the formation of conditions for OM accumulation in the environment of the bay are natural, since the anthropogenic load there is weak (compared to the load on the Nakhodka and Amur bays).

Metal-resistant microorganisms, a part of heterotrophs, can help in assessing the level and nature of the technogenic pressure on the bay surface waters. The abundance of Cd-, Pb-, Co-, and Ni-resistant forms of bacteria reflects mainly the technogenic load on the environment from which those are sown, while the abundance of Cu- and Zn-resistant forms serves as an indicator of biological natural or anthropogenic load [Khristoforova et al., 2018]. Copper and zinc are part of the molecules of living organisms; Cu and Zn enter the environment during the decomposition of waste products or the death of the organisms themselves. Municipal wastewater with faecal effluent also contains these microelements at high concentrations. In general, the microbial association of the Vladimir Bay was mostly characterized as Cd-resistant. When checking ecological and physiological properties of colonies grown on a Cd-enriched substrate, more than half of cultivated heterotrophic bacteria showed a high degree of resistance to this HM.

To transit from microbiological data to an ecological assessment of the degree of pollution for the marine area, a scale is used that shows correlations between the microbial index (the proportion of a particular metal-resistant group as a percentage of CHM) and MPC of heavy metals for fishery basins [Bezverbnaya et al., 2003]. When recalculating the absolute abundance of metal-resistant groups in the format of the microbial index and comparing it with a scale for assessing the degree of contamination, we can conclude as follows. A relatively even background of Cd-resistant bacteria indicates a significant degree (> 3 MPC) of cadmium contamination in the Vladimir Bay waters (Table 10). "Vector" distribution of Cd concentrations in bottom sediments shows the gradient of its content decrease from the coast towards the central area of the bay, and this gives grounds to assume the presence of a coastal source of cadmium.

Table 10. Assessment of the ecological state of the Vladimir Bay surface waters on a scale of correlation of the microbial index with the maximum permissible concentration (MPC) for heavy metals in fishery basins

Station	Cd	Cu	Zn	Pb	Ni	Co
2	▲	Δ	*	*	*	○
4	▲	*	*	○	*	○
5	▲	*	*	○	○	*
8	Δ	○	○	○	○	○
11	▲	○	*	○	Δ	Δ
12	Δ	○	*	○	*	*
13	Δ	○	*	○	*	○
14	▲	○	○	○	○	*
C	Δ	○	*	○	○	○

Note: C denotes the control station outside the bay. The symbols indicate the degree of pollution: ○, background (< MPC); *, insignificant (≈ 1 MPC); Δ, tangible (1–3 MPC); ▲, significant (> 3 MPC).

The correlation analysis of the relationship between OM in the bay bottom sediments and HM concentrations, grain-size characteristics, and sediment depth confirmed known dependences of an increase in OM content with a rise in proportion of the finest fractions and stabilization of hydrodynamic conditions associated with depth (Fig. 5) [Romankevich et al., 2009]. A positive correlation between an increase in HM content due to a rise in C_{org} concentration in bottom sediments (at low values of the Pearson coefficient) was revealed for four elements: Zn, Cd, Cr, and Pb. The data on Cu, Fe, and Ni content do not show a correlation with the values of OM content. Thus, only in relation to four out of the seven microelements, one can assume the effect of the accumulated OM concentration as a possible factor of the binding and deposition in the composition of bottom sediment.

The values of the contamination factor C_f (Table 11) are ranked as follows (in terms of pollution levels): $C_f < 1$, low; $1 \leq C_f < 3$, moderate; $3 \leq C_f < 6$, high; and $C_f \geq 6$, very high [Hakanson, 1980; Vashchenko et al., 2010]. The Vladimir Bay bottom sediments are characterized by a low level of Pb and Ni contamination (only one value at sta. 8 for nickel is > 1). Interestingly, this location has a high level of Zn pollution as well, while other studied spots are characterized by moderate (10 stations) and low (6 stations) pollution with this compound. Bottom sediments are the most polluted with Cd and Cu: high and very high Cd and Cu pollution was recorded for sta. 9 and 4, respectively. It is worth noting as follows. Sta. 4, 12, and 15, which are located in the central areas of the Severnaya and Yuzhnaya bays and in the apex of the Srednyaya Bay (there, OM is actively accumulated), are also characterized by high levels of Cd and Cu pollution. For Zn and Ni, such a relationship was not revealed.

Table 11. Assessment of the ecological state of the Vladimir Bay bottom sediments by the values of the contamination factor, the degree of contamination, and the sediment quality guideline quotient

Station	C_f					C_d	SQG-Q
	Cd	Ni	Pb	Cu	Zn		
1	7.47	0.17	0.15	1.36	0.89	10.04	0.29
2	0.00	0.17	0.17	1.28	1.16	2.78	0.24
3	4.52	0.25	0.38	1.29	2.48	8.92	0.31
4	3.47	0.08	0.24	4.70	1.15	9.64	0.33
5	3.52	0.25	0.37	1.26	2.05	7.46	0.29
6	1.86	0.21	0.23	1.59	1.52	5.41	0.31
7	0.00	0.19	0.21	0.25	1.01	1.66	0.08
8	4.16	2.20	0.46	2.03	3.25	12.09	0.53
9	2.56	0.19	0.32	0.73	1.19	4.98	0.17
10	1.13	0.31	0.43	0.20	0.58	2.64	0.08
11	3.67	0.06	0.09	5.40	0.36	9.58	0.29
12	3.61	0.06	0.09	5.60	0.36	9.73	0.30
13	3.46	0.23	0.36	2.64	0.95	7.63	0.48
14	6.43	0.19	0.17	1.34	2.18	10.30	0.31
15	2.22	0.11	0.31	9.25	1.14	13.02	0.51
16	0.28	0.07	0.09	0.70	0.23	1.36	0.06
17	1.91	0.23	0.29	0.04	1.31	3.77	0.06

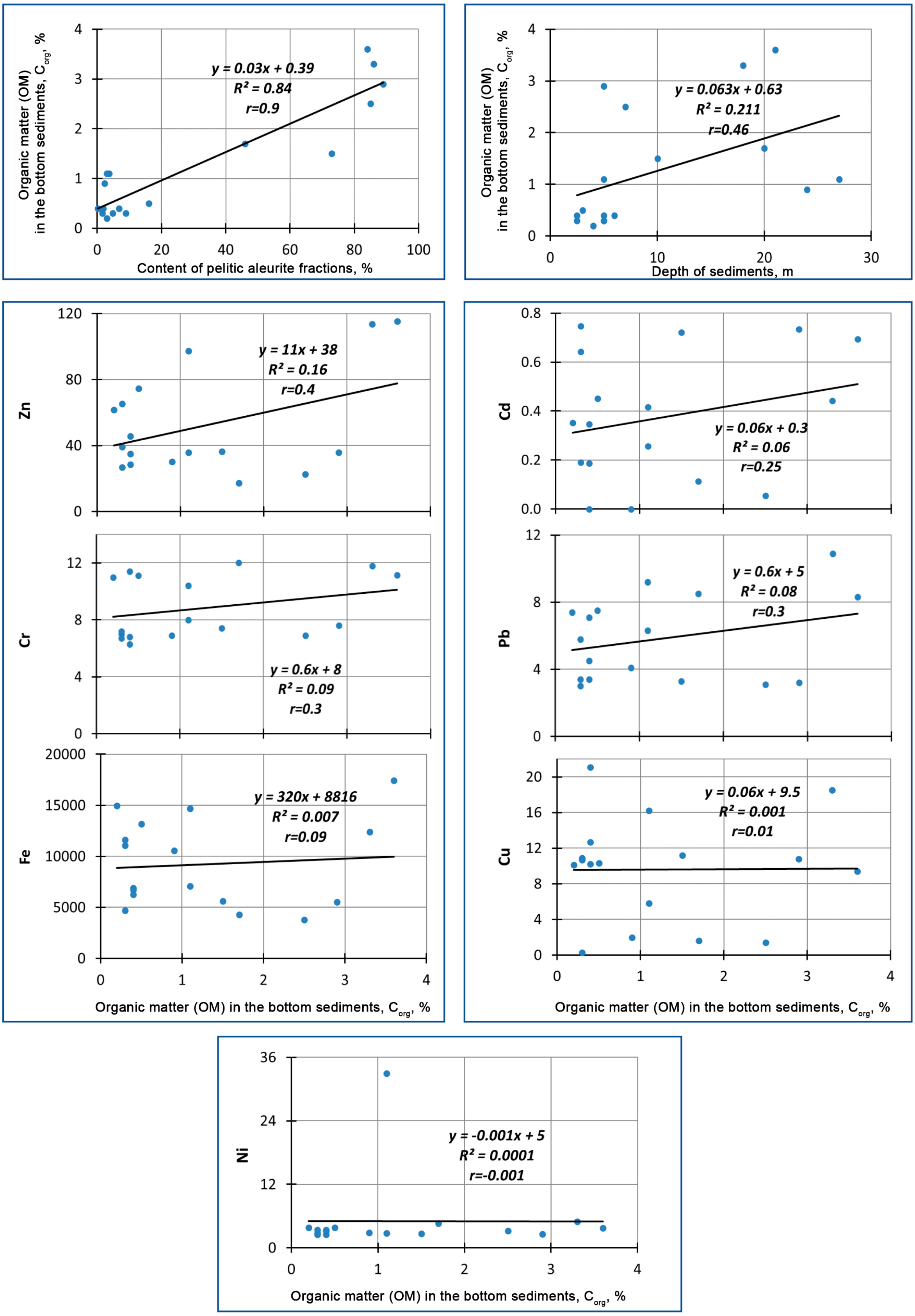

Fig. 5. Correlation analysis of the relationship of organic matter (OM) in the Vladimir Bay bottom sediments with heavy metal concentrations, grain-size characteristics, and depth of sediments (R^2, the coefficient of determination; r, the Pearson correlation coefficient)

Increased OM concentration in sediments, which is characteristic of finely dispersed fractions, determines a decrease in the content of inorganic carbon and in pH value and, accordingly, a change in the redox potential of bottom sediments. A drop in pH values enhances the migration ability of elements included in the composition of sediments; moreover, it is a risk factor for secondary pollution during accumulation of toxic elements and their compounds in sediments. Thus, based on the values of the microbial index and C_f, it can also be concluded that Cd enters the bay water from coastal sources and is deposited in bottom sediments. However, C_{org} accumulation in sediments can contribute to HM binding and then release HM into a water column later (with a change in the redox potential of sediments themselves and a decrease in pH values) [Shulkin, 2004].

The values of the degree of contamination C_d for sediments (see Table 11) are ranked in accordance with the total value of C_f for the background area, which is equal to 6 [Vashchenko et al., 2010], as follows: $C_d < 6$, low degree of HM contamination; $6 \leq C_d < 12$, moderate; $12 \leq C_d < 24$, high; and $C_d > 24$, very high. Most of the stations (8 out of 17) are characterized by a moderate degree of contamination of bottom sediments. High contamination is recorded for sta. 8 and 15.

SQG-Q values (Table 11) are ranked as follows [MacDonald et al., 1996; Vashchenko et al., 2010]: SQG-Q ≤ 0.1, non-toxic sediments, the lowest probability of observing negative biological effects; 0.1 < SQG-Q < 1, moderately toxic sediments, average probability of observing negative biological effects; and SQG-Q > 1, highly toxic sediments, high probability of observing negative biological effects. Despite the fact that the Vladimir Bay bottom sediments are HM-contaminated, in general those can be characterized as moderately toxic. The highest potential toxicity was registered at sta. 8.

In the sea urchin gonads, Zn was accumulated at maximum concentrations. In the bottom sediments, Zn content was high as well (and even exceeded the clarke values at three stations). However, when analyzing the correlation of pairs of values (Zn in sediments – Zn in *S. intermedius* gonads) obtained for each station, a clear inverse relationship was revealed, with the Pearson correlation coefficient $r = -0.96$ (Fig. 6). In other words, the higher Zn concentration in gonads, the lower observed Zn content in bottom sediments.

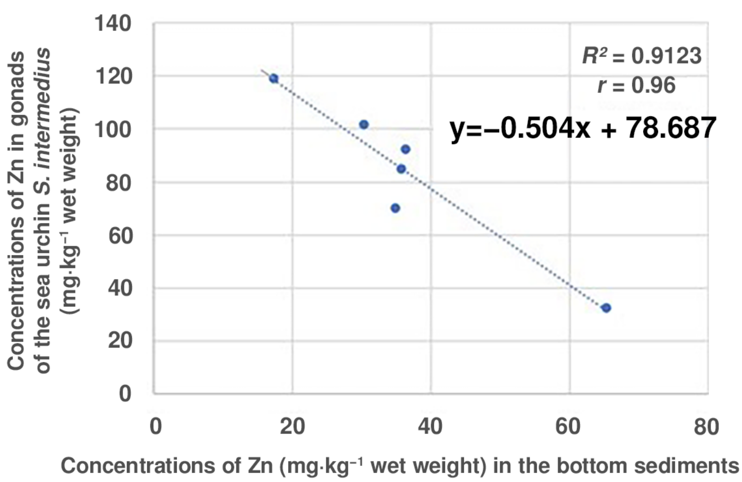

Fig. 6. Correlation analysis of the relationship of Zn concentration values in the bottom sediments and in gonads of the sea urchin *Strongylocentrotus intermedius*

Out of all forms of metals in the environment, living organisms are capable of absorbing and assimilating only biologically available ones, wherein marine invertebrates can regulate the intake of zinc into their bodies [Shulkin, 2004]. Apparently, despite high Zn concentrations in bottom sediments, the content of its bioavailable form for hydrobionts in water and marine sediments is low. Accordingly, subsequent alimentary absorption by sea urchins also determines its low concentrations in gonads. A similar pattern was noted earlier for mytilids from the Muravyov-Amursky Peninsula coast [Shulkin, 2004]. The absorption of Zn in a bioavailable form by sea urchins is likely to occur from bottom waters during continuous passage of water through body cavities (the same as for all hydrobionts).

Sea urchin roe is not only a valuable food product, but also a highly effective therapeutic and prophylactic supplement. Given this fact, one of the tasks for ecologists is to determine whether roe quality complies with existing standards and to assess the health hazard when consuming it as food. Technical Regulation of the Customs Union *On Food Safety* (TR TS 021/2011) determines permissible levels of certain toxic HM; the values are given in mg·kg^{-1} wet weight. The recalculation of the values obtained by us in terms of wet weight and comparison of these results (Table 12) with the established permissible levels showed as follows. Cd and Pb content in the sea urchin gonads at any sampling station in the Vladimir Bay does not exceed the determined permissible values.

Table 12. Pb and Cd concentrations (mg·kg^{-1} wet weight) in gonads of the sea urchin *Strongylocentrotus intermedius* from the Vladimir Bay (mean ± *SD*)

Station	Pb	Cd
2	0.52 ± 0.09	0.08 ± 0.00
7	0.86 ± 0.19	0.14 ± 0.00
10	1.31 ± 0.49	0.11 ± 0.02
11	0.63 ± 0.05	0.06 ± 0.01
12	0.67 ± 0.05	0.13 ± 0.02
14	2.99 ± 0.26	0.05 ± 0.01
PL	10.00	2.00

Note: PL denotes a permissible level (Technical Regulation of the Customs Union 021/2011).

However, we assessed the overall health risk from continuous consumption of the sea urchin roe from the Vladimir Bay during the summer season applying the ILCR calculator. It indicated the existence of carcinogenic risk. ILCR value, if taking into account actual Cd and Pb concentrations in gonads, was $5.27 \cdot 10^{-5}$. The permissible value, which is a criterion for the safety of a marine product, is 10^{-5}.

Conclusions:

1. The Vladimir Bay ecosystem with a relatively high level of organic matter in summer successfully "utilizes" organic matter of both natural and household origin. The effect of villages and the coastal strip on the formation of eutrophication conditions is insignificant. Chemical and environmental indexes indicate mesotrophic status of surface waters. Ecological and microbiological assessment in terms of the abundance of colony-forming heterotrophic microorganisms showed α-mesosaprobic level of the water quality. The conversion of microbiological data into chemical data in accordance with a comparison scale indicates the oligomesotrophic status of the studied water horizon.

2. According to the maximum C_{org} value in the Vladimir Bay, it belongs to marine areas with high content of organic matter in bottom sediments. Maximum concentrations were recorded in central and apex areas of its bights.
3. Mass macrozoobenthic species are *Strongylocentrotus intermedius*, *Asterina pectinifera*, *Mizuhopecten yessoensis*, *Crenomytilus grayanus*, *Pododesmus macrochisma*, and *Cucumaria japonica*. Mass species of macrophytobenthos are *Desmarestia viridis*, *Costaria costata*, *Saccharina japonica*, *Zostera marina*, and *Phyllospadix iwatensis*. Mean biomass of benthos is (841 ± 583) $g \cdot m^{-2}$, and this indicates high levels of bioresources in the bay. In macrozoobenthos, echinoderms prevail, primarily sea urchins.
4. In general, microbial communities of the Vladimir Bay surface waters are characterized by simultaneous presence of ecological and trophic groups resistant to various metals. Comparison of the results of the microbiological assessment with the MPC scale indicates a significant contamination of the bay surface waters with Cd (> 3 MPC). The general background with a lower cell abundance is formed by Cu- and Zn-resistant microorganisms.
5. For most heavy metals (HM), the total content in bottom sediments was below the clarke values. For several HM, background concentrations were exceeded. The sequence of decreasing concentrations of the studied HM in sediments is as follows: Fe > Zn > Cu > Cr > Pb > Ni > Cd. Horizontal spatial distribution of HM concentrations in bottom sediments is characterized by four types: "unipolar," "bipolar," "tripolar," and "vector." In the sea urchin gonads, HM content varied less than in the bottom sediments. On average, decreasing concentrations form the following sequence: Zn > Pb > Cu > Ni > Cr > Cd.
6. The correlation analysis confirmed the dependence of an increase in the concentration of organic matter in bottom sediments on an increase in the proportion of the finest fractions and depth. A positive correlation was registered for C_{org} and four elements (Zn, Cd, Cr, and Pb), in relation to which the effect of the accumulated organic matter concentration is assumed as a possible factor of the binding and deposition in the composition of bottom sediment. An analysis of the relationship between HM concentrations in sediments and the sea urchin gonads showed a high negative correlation for Zn. Apparently, the inverse relationship is due to biologically unavaliable form of zinc compounds in bottom sediments.
7. C_f characterizes the contamination of the bay bottom sediments with zinc as high, and with cadmium and copper, as very high. C_d value indicates a moderate degree of HM contamination for bottom sediment in general. According to SQG-Q, the bay sediments are classified as moderately toxic.
8. The risk to human health, determined by total presence of Cd and Pb in the sea urchin gonads, showed compliance with the permissible values specified in Technical Regulation of the Customs Union *On Food Safety*. Meanwhile, according to ILCR value, it is possible to predict the existence of carcinogenic risk driven by long-term consumption of gonads of the sea urchin *S. intermedius* from the Vladimir Bay.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (project FZNS-2023-0011).

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ОРГАНИЧЕСКОЕ ВЕЩЕСТВО В ЭКОСИСТЕМЕ ЗАЛИВА ВЛАДИМИРА (ЯПОНСКОЕ МОРЕ): РЕСУРС ПИТАНИЯ И ВОЗМОЖНЫЙ ФАКТОР ЭКОЛОГИЧЕСКОГО РИСКА

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Исследование содержания органического вещества в водной среде и донных отложениях крайне важно для понимания аккумуляционного процесса в отношении поступающих в среду акватории токсических веществ и элементов, а также выявления негативных изменений в экосистеме и потенциальных экологических рисков при осуществлении природопользования. Цель работы — проанализировать значение органического вещества как фактора контаминации среды залива Владимира (Японское море) и оценить токсичность гидробионтов и экологический риск для экосистемы и здоровья человека. Комплексная работа выполнена с применением химико-аналитических, микробиологических и гидробиологических методов; она включает математическую и картографическую обработку данных и расчёт коэффициентов загрязнения и экологического риска. Проведён анализ проб морской воды, донных отложений и макробентоса, отобранных в заливе Владимира в июле 2014 г. Определены химико-экологические и микробиологические параметры вод залива, позволяющие оценить процессы накопления органического вещества в водной среде и донных отложениях и установить трофический статус экосистемы в летний период. Выявлены массовые виды и группы макробентоса, определены показатели обилия донного населения, свидетельствующие о высоких уровнях биомассы. Установлена численность металлрезистентных групп бактерий в поверхностных водах. Оценено содержание и пространственное распределение тяжёлых металлов (ТМ) в донных отложениях. Установлены концентрации ТМ в гонадах морских ежей. Результаты микробиологической оценки соотнесены с ПДК; они выявляют значительное загрязнение вод залива (более 3 ПДК) в отношении Cd. Для Ni, Cu, Zn и Cd в донных отложениях обнаружено превышение фоновых концентраций, для Cd и Zn — превышение кларковых значений. Проверена корреляционная связь концентраций органического вещества в донных отложениях с содержанием в них ТМ, а также связь концентраций ТМ в грунтах и гонадах морских ежей (значимая корреляция выявлена в отношении Zn). Для донных отложений определены фактор загрязнения C_f, характеризующий их загрязнение в заливе цинком как высокое, а кадмием и медью — как очень высокое, а также степень загрязнения C_d, свидетельствующая о среднем уровне загрязнения донных осадков в целом. Проведён расчёт индексов экологического риска. По величине SQG-Q грунты залива отнесены к категории умеренно токсичных. Установлено: согласно нормативам Технического регламента Таможенного союза «О безопасности пищевой продукции» 021/2011, содержание Cd и Pb в гонадах морских ежей из залива Владимира не превышает допустимых уровней, однако по значению ILCR (индекс нарастающего пожизненного риска) можно сделать прогноз об опасности возникновения онкологических заболеваний при употреблении гонад в пищу.

Ключевые слова: залив Владимира, Японское море, органическое вещество, трофность, донные отложения, макробентос, тяжёлые металлы, коэффициенты накопления, экологический риск, риск здоровью человека