

Assessment of contamination of marine sediments and their potential toxicity in the Uglovoy Bay, Peter the Great Gulf, Sea of Japan

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Research Article

Keywords: Uglovoy Bay, bottom sediments, heavy metals, toxicity, contamination factor, degree of contamination, index of geoaccumulation, sediment quality guideline quotient.

Posted Date: March 29th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1452427/v1>

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Version of Record: A version of this preprint was published at Environmental Science and Pollution Research on June 2nd, 2023. See the published version at <https://doi.org/10.1007/s11356-023-28021-x>.

Abstract

The content of heavy metals in the bottom sediments of the Uglovoy Bay (Peter the Great Gulf, Sea of Japan) was studied based on the surveys carried out in 2016-2021. The contamination of sediments in the bay was compared to the background concentrations of elements and to common contamination indices. The degree of contamination was calculated using the contamination factor (C_f), modified overall degree of contamination (mC_d), and index of geoaccumulation (I_{geo}). The toxicity of marine sediment samples for each metal was evaluated using the TEL/PEL values and the sediment quality guideline quotient (SQG-Q). The sources of pollutants entering the studied water area were analyzed. It is shown that the contamination of the Uglovoy Bay occurs continuously as a result of economic activities on its coast. The dynamics of contamination of the bay for the period 2016-2021 is presented.

1. Introduction

Sediments are an important component of aquatic ecosystems because they provide nutrients and habitat for aquatic organisms (Benhamed et al. 2016). However, human activities result in accumulation of toxic substances such as heavy metals in marine sediments. Heavy metals are well-known environmental pollutants due to their toxicity, persistence in the environment, and bioaccumulation. Metals affect the ecosystem because they are not removed from water by self-purification, but accumulate in sediments and enter the food chain (Astakhov et al. 2015).

Methodological issues of assessing the level of environmental pollution are undoubtedly topical (Caeiro et al. 2005; Rezaee Ebrahim Saraei et al. 2011; Tsatsakis et al. 2016; Tsatsakis 2017). Sediment contamination studies are of significant interest because sea ground is formed over a long period of time accumulating anthropogenic inclusions in its chemical composition. This characteristic is used to obtain averaged information on pollutant flows over a long period of time. Such assessment provides objective information about water body pollution (Zharikov 2013). Sediment layer is an important link in the biogeochemical cycle of heavy metals and an active source of secondary pollution of seawater. Sediments accumulating pollutants reflect the current anthropogenic impact level, but they also may be a risk factor for organisms connected with this substrate. Heavy metals are toxic, stable and indestructible in natural conditions. Sediment contamination with these elements is a major environmental risk to coastal marine ecosystems having a variety of biological consequences (morbidity of plants and animals, partial or complete extinction of some species, and changes in the biotope) (Diaza et al. 2018; Hamed et al. 2017; Kannan et al. 2011).

For the Russian territorial waters, currently there are no officially established characteristics of the water quality in terms of pollutant concentration levels. The contamination level of bottom sediments can be assessed in several ways: 1) relative to the background (however, there is no explicit definition of background concentrations in regulatory documents); 2) by international standard indicators (for example, the threshold values of pollutants according to the Neue Niederlandische Liste and TEL/PEL); and 3) by using various indices (C_f , mC_d , I_{geo} , SQG-Q, etc.).

Applying several indices and utilizing different approaches is recommended for an adequate assessment of sediment quality. Using these kinds of tools helps to determine if there is pollution and also what decisions

need to be made to protect the ecosystem and human health (Caeiro et al. 2005).

Although the study area (the Uglovoy Bay) is accessible for studies, there are few studies of the content of heavy metals in the bottom sediments of this water area. Most publications about the bay focus on the study of water (Petukhov et al. 2019; Tishchenko et al. 2021) and aquatic organisms (Atlas of bivalve mollusks 2000; Rakov 2010; Savinok and Shishlova 2008; Chernova 2012). The goal of this work is to assess the contamination of sediments in the Uglovoy Bay with heavy metals and their potential toxicity, as well as analyze the dynamics of sediment contamination in 2016–2021.

2. Materials And Methods

The Uglovoy Bay is a shallow secondary bay in the Amur Bay (Peter the Great Gulf, Sea of Japan). It is located in the northeastern part of the Amur Bay and connects to the bayhead through a narrow neck of the De Vries Peninsula (Fig. 1). This shoreline forms the main part of the Uglovoy Bay, its strait, and several smaller bays (Trostnikovaya, Brazhnikova, etc.). The geomorphological structure of the Uglovoy Bay floor can be divided into the shallow northern part (prevailing depth of 1.5–2.0 m) and the neck with a sharp increase in depth (4.0–10.0 m). The two parts of the bay are separated by a natural barrier – two long sandy spits between the Razdelny and Sporny capes, as well as an underwater ledge consisting of several oyster reefs (Rakov 2010).

Bottom sediments of the Uglovoy Bay are composed of clayey mud, shell stone, less frequently of sand with pebble and mixed soil. In the area of river mouths, the band of sand and pebble sediments increases. The bed of the bay is laid with dense, sticky clays. The shallow water of the Uglovoy Bay contributes to the occurrence of the zones of disturbance of the bottom sediments in the coastal strip even at moderate sea, while in high winds the disturbance occurs almost throughout the entire water area (Hakanson 1980).

In 2016–2021, bottom sediment samples from the Uglovoy Bay were collected to monitor the content of heavy metals: iron (Fe), manganese (Mn), cadmium (Cd), copper (Cu), nickel (Ni), cobalt (Co), zinc (Zn), arsenic (As), lead (Pb), chromium (Cr), and mercury (Hg).

During the winter (February of 2016 and 2017), the samples were taken from ice by using a tube sampler at three selected stations. In the warm period (September of 2016, May of 2019, and October of 2021) bottom sediment samples were collected by a rubber boat with a benthic bottom sampler. The layout of the sampling stations is shown in Fig. 1.

Bottom sediment samples were analyzed in the ecoanalytical laboratory of the Interdepartmental Center for Analytical Control of the State of the Environment (Vladivostok). Gross metal content was determined by atomic absorption spectrometry on spectrophotometers AA-6800 and AA-6300 with HVG-1 (Shimadzu, Japan) according to the standard procedures (PND F 16.1:2.2:3.17-98 2004; PND F 16.2.2:2.3:3.25-02 2002; RD 52.10.556-95 1996; RD 52.18.685–2006 2007).

To assess the level of sediment contamination in the Uglovoy Bay relative to background concentrations, the contamination factor (C_f) (Hakanson 19980, Rezaee Ebrahim Saraee et al. 2011) and the modified overall degree of contamination (mC_d) (Abrahim and Parker 2008; Rezaee Ebrahim Saraee et al. 2011) were used.

The contamination factor (C_f) was calculated for each pollutant using the Eq. 1:

$$C_f = \frac{C_{sample}}{C_{background}} \quad Eq. 1$$

C_f values were ranked as follows: $Cf < 1$ – low contamination factor, $1 \leq Cf < 3$ – moderate, $3 \leq Cf < 6$ – considerable, and $Cf \geq 6$ – very high contamination factor (Hakanson 1980, Rezaee Ebrahim Saraee et al. 2011).

A modified equation for the generalized approach to calculating the degree of contamination (Abrahim and Parker 2008; Hakanson 1980) is presented below (Eq. 2):

$$mC_d = \frac{\sum_{i=1}^n C_f^i}{n} \quad Eq. 2$$

where, n is the number of elements analyzed, i is the i -th element (or pollutant), and C_f is the contamination factor. Using this generalized formula to calculate mC_d makes it possible to include as many metals as the study can analyze without an upper limit (Abrahim and Parker 2008).

The modified degree of contamination was described according to (Abrahim and Parker 2008; Hakanson 1980): $mC_d < 1.5$ – nil to very low degree of contamination, $1.5 \leq mC_d < 2$ – low degree of contamination, $2 \leq mC_d < 4$ – moderate degree of contamination, $4 \leq mC_d < 8$ – high degree of contamination, $8 \leq mC_d < 16$ – very high degree of contamination, $16 \leq mC_d < 32$ – extremely high degree of contamination, and $mC_d \geq 32$ – ultra high degree of contamination.

Also, the index of geoaccumulation (I_{geo}) (Müller 1969; Rezaee Ebrahim Saraee et al. 2011) was calculated, which is used to assess the pollution of coastal waters under man-induced conditions. I_{geo} was calculated by using the following Eq. 3 (Müller 1969; Rezaee Ebrahim Saraee et al. 2011):

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad Eq. 3$$

where, C_n is the measured concentration of the n -th element in the sediments, and B_n is the background concentration of the n -th element. The factor 1.5 is used to compensate the effect of possible variations in the background values of the studied metal in the environment, as well as under conditions of a very low anthropogenic impact.

The I_{geo} values were interpreted according to the classification proposed by Müller (Müller 1969): ≤ 0 – class 0 uncontaminated sediments; $0-1$ – class 1 uncontaminated to moderately contaminated sediments; $1-2$ – class 2 moderately contaminated sediments; $2-3$ – class 3 moderately to strongly contaminated sediments; $3-4$ – class 4 strongly contaminated sediments; $4-5$ – class 5 strongly to extremely contaminated sediments; and > 5 – class 6 extremely contaminated sediments.

The toxicity of bottom sediment samples was assessed using TEL (threshold effects level) and PEL (probable effects level) values. These two values determine three ranges of chemical concentrations, including those that were rarely, occasionally, or frequently associated with toxic effects. Exceeding PEL values indicates the

toxicity of the sample and a high probability of negative biological effects (Hübner et al. 2009; Macdonald et al. 1996).

The integral estimation of the potential toxicity of the bottom sediments in the Uglovoy Bay was carried out using the sediment quality guideline-quotient (SQG-Q) (Eq. 4). This quotient makes it possible to characterize the toxicity of accumulated pollutants for marine organisms in the abiotic components of the biotope under study. The PEL is used as the main criterion in calculating the SQG-Q:

$$SQG-Q = \frac{\sum_{i=1}^n C^i / PEL}{n}$$

Equation 4

where, n is the number of metals under study, and C^i is mean metal concentration.

The values of SQG-Q quotient were ranked as follows: ≤ 0.1 – not toxic sediments, the lowest probability of negative biological effects; $0.1-1.0$ – moderately toxic sediments, average probability of negative biological effects; and > 1.0 – highly toxic sediments, high probability of negative biological effects (Chernova 2012; Macdonald et al. 1996).

3. Results And Discussion

3.1. Assessment of the contamination level of bottom sediments in the Uglovoy Bay relative to background concentrations and normative values

Average concentrations of heavy metals in bottom sediments of the study area are presented in Table 1. Background values for the Uglovoy Bay (a conditionally clean coastal water area of the Peter the Great Gulf) were taken from published data (Kalinchuk et al. 2010; Shulkin 2004).

As shown in Table 1, during the period from 2016 to 2021, the concentrations of heavy metals at almost all sediment sampling stations exceeded the background values, indicating a significant anthropogenic load on the Uglovoy Bay. The exceptions were several sampling stations in September 2016 (Zn and Pb content), in February 2017 at the exit from the bay near the low water bridge (Pb content), and in 2021 in the central part of the bay (Hg content). For the entire study period, the highest values exceeding the background levels were observed in February 2016. Between 2017 and 2021, the contamination of the bay relative to the background decreased significantly.

Table 1
Average concentrations of heavy metals (mg/kg dry weight) in bottom sediments of the Uglovoy Bay in 2016–2021.

Month/ Year	Fe	Mn	Cd	Cu	Ni	Co	Zn	As	Pb	Cr	Hg
02/2016	30063	417	3.45	353.2	75.3	97.5	293	36.8	47.1	57.3	0.30
09/2016	53985	828	0.57	18.7	34.1	14.6	35	12.5	10.4	77.1	0.09
02/2017	46716	536	0.64	18.7	30.6	24.8	-	-	12.8	-	0.08
05/2019	40338	294	0.91	28.4	28.8	15.8	-	-	24.2	-	0.08
10/2021	38812	370	0.74	25.7	37.2	14.3	46	13.0	27.9	71.5	0.03
back ground	15000	100	0.10	10.0	10.0	8.0	40	1.5	10.0	7.0	0.02
threshold concentrations	-	-	0.80	36.0	35.0	20.0	140	29.0	85.0	100.0	0.30
TEL	-	-	0.68	18.7	15.9	-	124	7.24	30.2	52.3	0.13
PEL	-	-	4.21	108.0	42.8	-	271	41.6	112.0	160.0	0.70

Note: “-” – no data; background concentrations from (Kalinchuk et al. 2010; Shulkin 2004); TEL/PEL (Macdonald et al. 1996); concentrations exceeding threshold values are in bold face (Warmer and van Dokkum 2002).

According to the normative documents, bottom sediments can be compared with international standards, for example, with threshold values in the Neue Niederlandische Liste (Warmer and van Dokkum 2002). The content of heavy metals in bottom sediments of the Uglovoy Bay compared to the threshold values is significantly lower than compared to the background level (Table 1). Maximum values exceeding the threshold values were observed in February 2016 for Cd, Cu, Ni, Co, Zn, As, and Hg. From September 2016 to 2021, the content of heavy metals in the sediments in the major part of the study water area did not exceed the threshold values. The exceptions were bottom sediments at several stations: in September 2016 for Ni (1.05–1.22 threshold), in 2017 for Cd (1 threshold), Ni (1.02 threshold), and Co (1.40–1.46 threshold), in 2019 for Cd (1.09–1.46 threshold), Ni (1.02 threshold), and Co (1.20 threshold), and in 2021 for Cd (1.20 threshold) and Ni (1.05–1.08 threshold).

It should be noted that the Neue Niederlandische Liste were developed based on the background concentrations of pollutants in the Netherlands and the adjoining water area. This is the only document regulating the assessment of marine sediments contamination in Europe. For the studied water area, however, it is more informative to assess the sediments contamination relative to the background concentrations in the Peter the Great Gulf.

To assess the ecological hazard of marine sediments, the obtained concentrations of pollutants can be compared with experimental data on the toxicity of these substances for marine organisms. Quality criteria TEL and PEL developed for marine surface sediments are well known. TEL/PEL are based on the statistical analysis of empirical data on the concentrations of pollutants that trigger various reactions in marine life (Vashchenko et al. 2010; Macdonald et al. 1996). TEL/PEL criteria are closer in their values than other similar

criteria (Hübner et al. 2009). TEL is designed to assess the concentration of a chemical below which adverse effects are rare (i.e., threshold effect level). PEL is designed to estimate the concentration above which side effects occur frequently (i.e., probable effect level) (Macdonald et al. 1996).

According to the results of this study, in February of 2016, the content of pollutants in sediments was above TEL (Table 1). This fact suggests that at these concentrations of heavy metals, marine life occasionally suffer from toxic side effects. In terms of Cu, Ni, and Zn content, marine sediments exceeded PEL threshold (Table 1), which indicates that side effects occur frequently.

In September of 2016, Ni, As, and Cr content in marine sediments exceeded TEL. In 2017, Cd, Cu, and Ni content exceeded TEL. In 2019, Cd, Cu, and Ni content, and in 2021, Cd, Cu, Ni, As, and Cr content exceeded TEL. However, from September 2016 to 2021 concentrations of the analyzed polluting substances did not exceed PEL (Table 1). Therefore, there is a significant improvement of the environmental situation in the studied water area during this period.

3.2. Assessment of the degree of contamination of marine sediments in the Uglovoy Bay and their potential toxicity using various indices

The calculated values of the contamination factor (C_f) vary in a wide range from "low" to "very high". The highest levels of bottom sediments contamination relative to the background ($C_f > 6$, "very high") in decreasing order were obtained for Cu, Cd, As, Hg, Co, Cr, Ni, and Zn in February 2016; for Cr, As, and Mn in September 2016; for Cd in 2017 and 2019; and for Cr, As, and Cd in 2021 (Table 2).

According to the classification by Hakanson (Hakanson 1980), the degree of contamination (mC_d) of marine sediments in the bay was "very high" in February 2016 and "high" in September 2016 and 2021. In 2017–2019, marine sediments in the Uglovoy Bay had the "moderate" degree of contamination (Table 2).

Table 2

Results of calculations of the contamination factor (C_f), the modified overall degree of contamination (mC_d), the index of geoaccumulation (I_{geo}), and the sediment quality guideline quotient (SQG-Q) for the Uglovoy Bay for the period of 2016–2021.

Month/ Year	C_f											mC_d	SQG- Q
	Fe	Mn	Cd	Cu	Ni	Co	Zn	As	Pb	Cr	Hg		
02/2016	2.0	4.2	34.5	35.3	7.5	12.2	7.3	24.6	4.7	8.2	15.0	14.1	1.13
09/2016	3.6	8.3	5.7	1.9	3.4	1.8	0.9	8.4	1.0	11.0	4.7	4.6	0.28
02/2017	3.1	5.4	6.4	1.9	3.1	3.1	-	-	1.3	-	4.0	3.5	0.25
05/2019	2.7	2.9	9.1	2.8	2.9	2.0	-	-	2.4	-	4.0	3.6	0.30
10/2021	2.6	3.7	7.4	2.6	3.7	1.8	1.1	8.7	2.8	10.2	1.4	4.2	0.31
I_{geo}													
02/2016	0.4	1.5	4.5	4.6	2.3	3.0	2.3	4.0	1.7	2.4	3.3	1–5 class	
09/2016	1.3	2.5	1.9	0.3	1.2	0.3	-0.8	2.5	-0.5	2.9	1.6	0–3 class	
02/2017	1.1	1.8	2.1	0.3	1.0	1.1	-	-	-0.2	-	1.4	0–3 class	
05/2019	0.8	1.0	2.6	0.9	0.9	0.4	-	-	0.7	-	1.4	1–3 class	
10/2021	0.8	1.3	2.3	0.8	1.3	0.3	-0.4	2.5	0.9	2.8	-0.1	0–3 class	
Note: “-” – no data; in bold face: $C_f > 6$ (very high), $8 \leq mC_d < 16$ (very high degree of contamination), SQG-Q > 1.0 – (highly toxic sediments), high probability of adverse biological effects and I_{geo} Class 5 (strongly to extremely contaminated sediments).													

Index of geoaccumulation (I_{geo}) in the Uglovoy Bay in February 2016 ranged from class 1 to 5 (from uncontaminated to strongly to extremely contaminated sediments). The maximum I_{geo} values were calculated for Cd and Cu, while the minimum values were for Fe (Table 2). In September of 2016, in 2017 and 2021, I_{geo} ranged from class 0 to 3, while in 2019 from class 1 to 3 (Table 2). Marine sediments were uncontaminated (class 0) with Zn (September 2016 and 2021), Pb (September 2016 and 2017), and Hg (2021) (Table 2).

The toxic effects of heavy metals on aquatic ecosystems range from the extinction of the living organisms to the minimum impact on the reproduction, growth and mortality of aquatic species (Hamed 2017). Heavy metals belong to the priority pollutants of marine ecosystems as they are known for their toxic effects on a variety of organisms. The list of priority pollutants of the marine environment in accordance with the Water Framework Directive of the European Union includes: Cd, Hg, Pb, Ni, as well as various types of hydrocarbon compounds (Warmer and van Dokkum 2002). In addition to direct exposure and toxic effects, Pb, Cd, and Cu bioaccumulate in all living organisms, including humans, animals and plants (Diazza et al. 2018). In addition, As and Cu have significant toxic properties.

The high content of heavy metals in the habitat of bivalve mollusks leads to their accumulation in biological tissues depending on their concentration. Marine flora shows the same response to high concentrations of heavy metals in the habitat (Kovekovdova et al. 2002). Studies for eel grass *Zostera marina L.* collected in the Ugllovoy Bay indicate that the accumulation of Ni, Cu, Zn, Cd, and Mn exceed the concentrations of the range background (Savinok and Shishlova 2008; Chernova 2012). In addition, according to Chernova (2012), the reducing environment in bottom sediments contributes to the accumulation of mobile forms of Mn in the rhizomes of this plant.

Metals with physiological significance (Zn, Mn, and Fe) exhibit the greatest ability to accumulate in biological tissues, carapaces, and skeletons of aquatic organisms (Demina et al. 2009). On the other hand, in conditions of high turbidity, the filtering organisms that are widespread in the Ugllovoy Bay are subject to significant accumulation of heavy metals.

To assess the potential toxic effect of accumulated heavy metals in the sedimentary layer of the bay, the sediment quality guideline-quotient (SQG-Q) was calculated (Table 2). The values of PEL were assumed as the main criteria. Concentrations of pollutants above this index most likely lead to negative biological consequences.

SQG-Q values calculated for February 2016 suggest highly toxic sediments with a high probability of negative biological effects. The cause of this is the high concentration of heavy metals in the sediments of the studied water area. Their content can be represented as a series in decreasing order relative to PEL: Cu > Ni > Zn > As > Cd > Pb > Hg > Cr.

From September 2016 to 2021, the sediment quality guideline-quotient (SQG-Q) values varied between 0.25 and 0.31 representing moderately toxic sediments with an average probability of adverse biological effects. Therefore, the probability of toxic effects decreased significantly.

Regardless of a significant improvement of the environmental situation in terms of heavy metals content in marine sediments during the study period, marine life in the Ugllovoy Bay are still adversely affected by pollution. For example, according to Tishchenko et. al. (2021), underwater photography in 2019 and 2020 showed the absence of eel grass (*Zostera marina L.*) meadows in the Ugllovoy Bay. A comparison of episodic studies of previous years (Rakov 2010; Savinok and Shishlova 2008; Chernova 2012) with the results presented by the authors (Tishchenko et al. 2021) indicates degradation of the bay ecosystem.

3.3. Analysis of the sources of contamination of marine sediments in the Ugllovoy Bay

One of the main sources polluting the studied water area is the runoff of the Aerodromnaya, Peschanka, Ugolnaya and Saperka rivers which contain industrial and household effluents from the Artem and Vladivostok cities. Another source is the advection of water from the northern part of the Amur Bay influenced by the polluted runoff of the Razdolnaya River (Petukhov et al. 2019).

Contamination is also possible as a result of rain-wash from the industrial landscape and other sources. On the bay shore there are industrial buildings of the food industry, warehouses, railway and road infrastructure.

Industrial activity in the coastal zone, as a rule, leads to pollution of the soil which largely determines the chemical composition of marine sediments in coastal waters.

In addition, bottom sediments in the Uglovoy Bay were greatly affected by the construction of the De-Friz-Sedanka low-water bridge between 2009 and 2012. A new four-lane highway now connects the De-Friz Peninsula and the Muravyov-Amursky Peninsula. Typically, hydrotechnical construction in the coastal zone is accompanied by a significant increase in turbidity and contamination with pollutants. The volume of suspended solids entering the sea can be compared with dumping and the annual runoff of large rivers (Mishukov et al. 2009). Further operation of the low-water bridge is also a source of heavy metals (Pb, Cu, Zn) entering the water area.

Before 2012, all untreated wastewater went into the sea. After the reconstruction of the treatment facilities in the Northern planning district in 2012, the volume of untreated wastewater decreased significantly. Despite this, pollutants were accumulated in bottom sediments for a long time. Together with their new inflow with river water and due to the operation of the low-water bridge, pollutants remained to have a negative impact on the water area of the Uglovoy Bay. As a result, according to data from February 2016, there was a significant contamination of marine sediments in the study area.

The main reason for the variation in the annual flow of rivers into the Uglovoy Bay is the monsoon climate. The annual arrival of tropical typhoons into the watershed of the Peter the Great Gulf is the main feature of the coastal climate in the Primorsky Krai. It is accompanied by a period of heavy rains, hurricane winds, and storms with the formation of surging waves, floods and high waters on the rivers (Astakhov et al. 2015). A typhoon in the shelf zone is accompanied by the removal of terrigenous sediments, as well as changes in the sedimentation regime. In September 2016, just before the sampling, Typhoon Lionrock hit southern Primorsky Krai. In 22 days, Vladivostok city received a total of 187 mm of rainfall that led to extreme river floods. Apparently, this caused removal of the surface layer of sediments from the shallow Uglovoy Bay and resulted in a significant decrease in the content of pollutants in the upper layer of marine sediments in the water area.

Figure 2 shows the spatial distribution of heavy metals in marine sediments of the Uglovoy Bay with the data for September 2016 as an example.

As shown in Fig. 2, sampling station 1 located in the strait of the Uglovoy Bay can be described as a sedimentation trap due to its hydrodynamic conditions. This fact determined the accumulation of heavy metals in marine sediments in this part of the water area. Clusters of oyster shells were found in the central part of the bay (station 18) during winter sampling in 2016. This area can also be considered as a predominant sedimentation zone due to vital activity of oysters inhabiting the bay.

The inflow of heavy metals into the bottom sediments of the bay near the low-water bridge (stations 4 and 5) is associated with the erosion of its dam. The results of our studies of the low-water bridge land fill in 2014 and 2016 support this conclusion. The average metal content in the samples of the bridge fill was: Fe 45800 mg/kg, Mn 2141.6 mg/kg, Cu 1323.8 mg/kg, Cr 943.6 mg/kg, Co 641.4 mg/kg, Zn 311.2 mg/kg, Pb 222.0 mg/kg, Ni 204.05 mg/kg, As 115.05 mg/kg, and Cd 6.5 mg/kg.

Sampling stations 7, 8, and 12 are affected by river and mainland runoff. Elevated concentrations of heavy metals here are most likely associated with the arrival of pollutants after heavy rains with rain-wash and river water.

4. Conclusions

The contamination of marine sediments in the Uglovoy Bay with heavy metals occurs continuously as a result of economic activities on its coast. Pollutants mainly enter the bay as part of the river runoff, as a result of planar washout from the urbanized landscape and operation of the low-water bridge.

The concentrations of heavy metals in bottom sediments in 2016–2021 exceeded background values at almost all sampling stations, indicating a significant anthropogenic load on the bay. The content of pollutants in marine sediments of the Uglovoy Bay compared to the threshold values is significantly lower than compared to the background level. Therefore, it is more informative to assess the pollution of the bay in terms of the background concentrations.

The overall total degree of contamination (mC_d) of marine sediments in the Uglovoy Bay was “very high” in February 2016 and “high” in September 2016 and 2021. In 2017–2019, marine sediments in bay had the “moderate” degree of contamination. Index of geoaccumulation (I_{geo}) during the study period varied from class 0 to 5. The maximum I_{geo} values were also observed in February 2016. SQG-Q values in February 2016 suggested a high risk of negative biological effects. According to follow-up studies, SQG-Q values corresponded to moderately toxic sediments.

According to all criteria used in this study, the maximum contamination of marine sediments was observed in February 2016. In September of the same year, after the Typhoon Lionrok, there was a significant decrease in the content of pollutants in the sediments, which remained until 2019. This fact is associated with the influence of extreme flooding during the typhoon in the southern Primorsky Krai. The extreme high-water period is accompanied by a renewal of water masses in the bay, and it also has an effect on the surface layer of the sediments. According to the data from 2021, there is an insignificant increase in the contamination of marine sediments in the bay.

Regardless of a significant improvement of the environmental situation in terms of heavy metals content in marine sediments during the study period, marine life in the Uglovoy Bay are still adversely affected by pollution. A comparison of episodic studies of *Zostera marina L.* in previous years with underwater photography in 2019 and 2020 suggests degradation of the bay ecosystem.

Declarations

Ethical Approval

This study did not involve human or animal subjects.

Consent to Participate

This study did not involve human or animal subjects.

Consent to Publish

This study did not involve human or animal subjects.

Authors Contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Valeriy Petukhov, Evgeniya Petrova, Alexey Kiryanov, Evgeniy Zheldak and Aleksei Kholodov. The first draft of the manuscript was written by Evgeniya Petrova and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

Funding

The authors declare that no funds, grants, or other support were received during the preparation of this manuscript.

Competing Interests

The authors have no competing interests to declare that are relevant to the content of this article.

Availability of data and materials

Data used in this study is provided within the manuscript.

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Figures

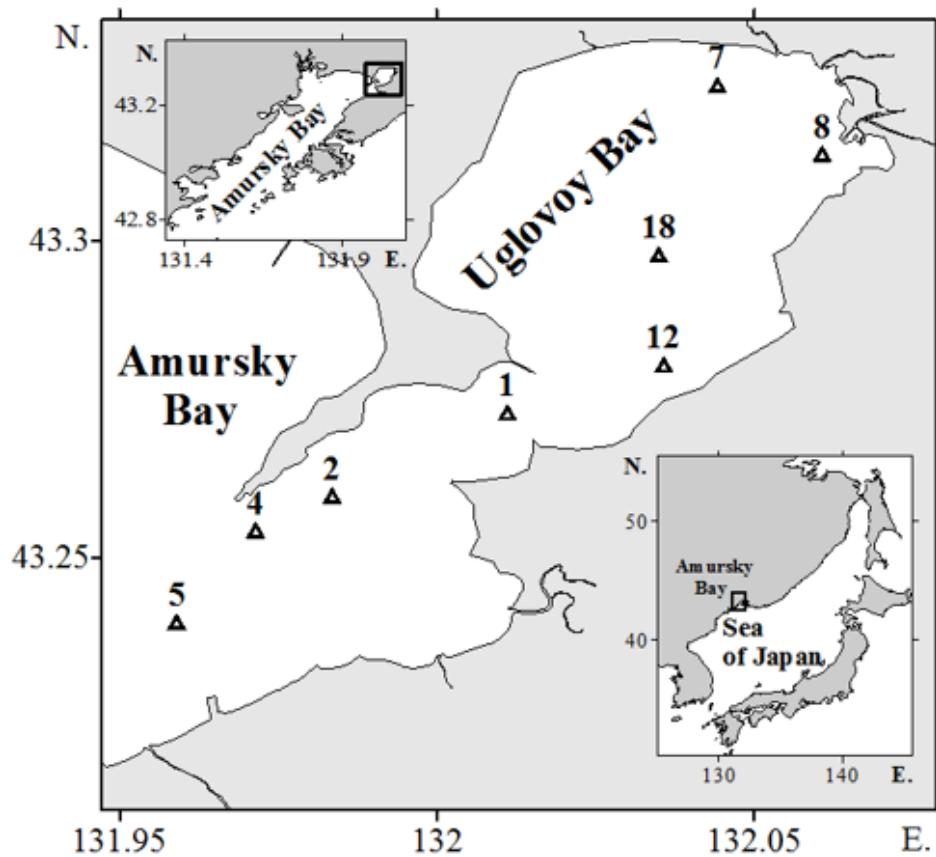


Figure 1

The schematic map with the location of bottom sediment sampling stations in the Uglovoy Bay

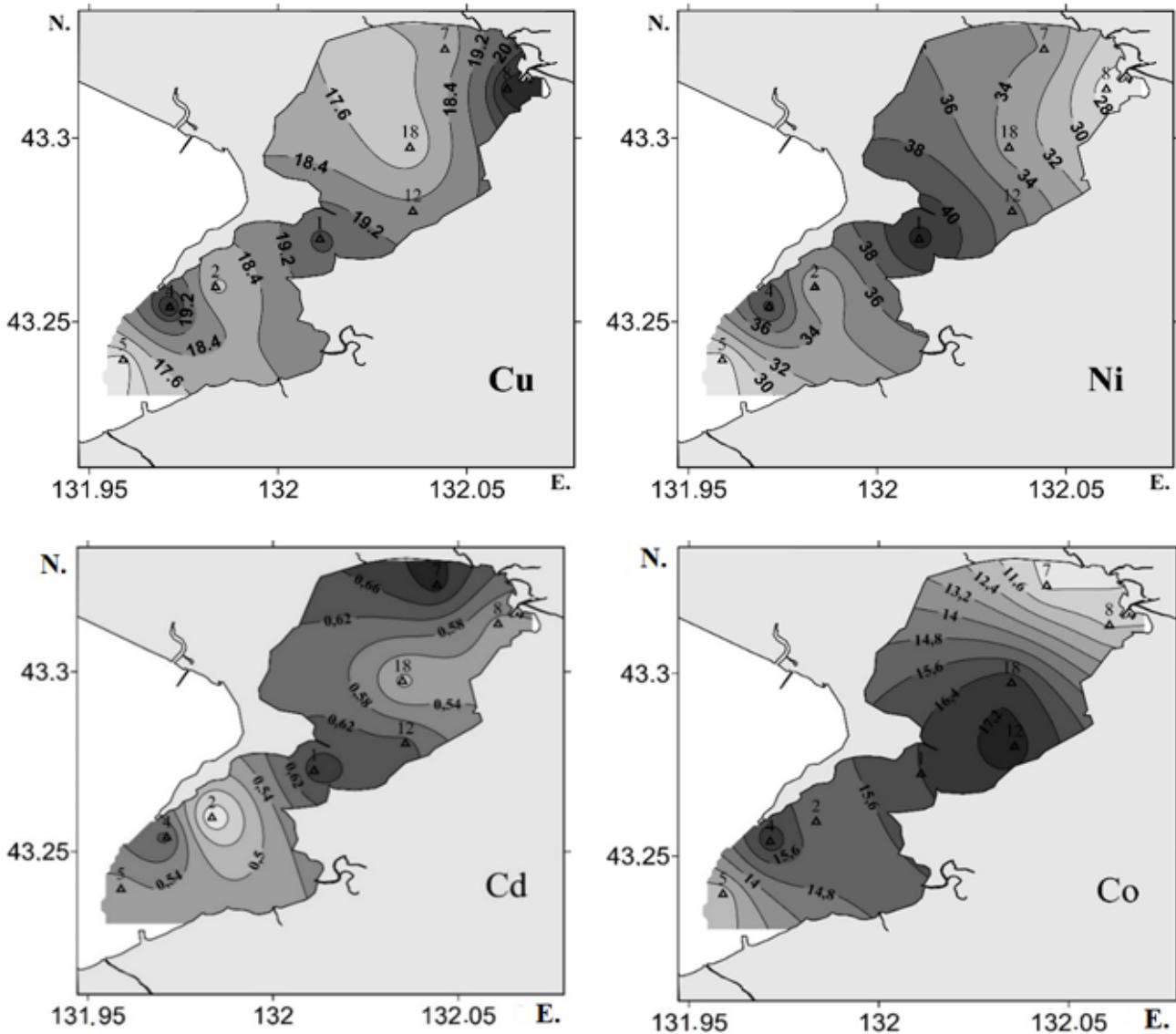


Figure 2

Spatial distribution of heavy metals (mg/kg dry weight) in marine sediments of the Ugllovoy Bay in September 2016.