

Bioindication of Heavy-Metal Pollution in the Coastal Marine Waters of Russky Island (Peter the Great Bay, Sea of Japan)

N. K. Khristoforova^{a, b, *}, A. A. Emelyanov^a, and A. V. Efimov^a

^aFar Eastern Federal University, Vladivostok, 690091 Russia

^bPacific Geographical Institute, Far East Branch, Russian Academy of Sciences, Vladivostok, 690041 Russia

*e-mail: marineecology@rambler.ru

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Abstract—The first assessment of the condition of coastal waters around Russky Island, Peter the Great Bay, in the vicinity of Vladivostok, has been made based on the data on concentrations of Fe, Zn, Cu, Cd, Pb, and Ni in the brown algae *Sargassum miyabei* and *S. pallidum* collected along the coast of the island in July and August 2016. It has been found that the concentrations of heavy metals in algae from waters off Russky Island mostly exceed their background levels in *Sargassum* algae from the northwestern Sea of Japan. On the south-eastern side of the island, facing Ussuri Bay, which is distinguished by a rocky/bouldery coast and beds of *S. pallidum*, algae are characterized by lower concentrations of trace elements than those on the other sides.

Keywords: Russky Island, Peter the Great Bay, bioindication, pollution, heavy metals, *Sargassum miyabei*, *S. pallidum*

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INTRODUCTION

The development of the economy and urbanization of territories cause changes in the ecological situation not only in some particular regions, but over the entire planet. Wastewater discharge and industrial production located near the marine coastal zone lead to significant, and sometimes inevitable, catastrophic consequences. Heavy metals entering the sea in local near-shore areas reach exceptionally high concentrations in the environment and organisms that do not normally occur in nature, which requires continuous monitoring and environmental assessments.

Among the biological methods to control the environmental quality, bioindication based on macrophytic algae has become widely popular since the early 1970s. The use of accumulating bioindicators for monitoring the heavy-metal pollution of the World Ocean is based on their ability to build up 1000- to 100 000-fold higher concentrations of elements, which simplifies the analysis, makes it more rapid, and reduces its cost. They also show the average level of the relative bioavailability of metals in each of the study areas [3, 13–17, 19, etc.]. The choice of *Sargassum* algae as a bioindicator is explained by its high correspondence of their chemical composition to the geochemical conditions of the habitat. Due to having a developed specific surface of contact with the environment, continuously interacting with it, having high levels of alginic content of their tissues, *Sargassum* algae are distinguished by a longer elimination half-

life of metals compared to algae of other phyla and invertebrates. Members of this genus of brown algae have long been recognized as “true reflectors” of habitat conditions and are used in biomonitoring of heavy-metal pollution in warm-water regions [1, 7, 8, 18, etc.].

In spite of its proximity to the city, Russky Island has long remained poorly studied. This was due to its long-term status of being under the control of the navy department and closed to public access. Although there have been publications on the microbial pollution and hydrochemistry of island’s waters in recent years [4–6], no studies of the heavy-metal content of algae growing along its coast have been carried out.

In the current constantly changing conditions there is an urgent need for reliable, complete, economically reasonable, and timely information on the quality of the environment, as well as on the causes and consequences of emerging environmental situations. Measuring the heavy-metal content of brown algae is a reliable way to study pollution of coastal waters. It allows quick determination of the boundaries of geochemical zones formed by the influx of metals from land and associated with the forms of their existence and migration ability. The goal of the present work is to assess the current condition of the coastal waters off Russky Island using data on the heavy-metal content of brown algae of the genus *Sargassum*: *S. miyabei* and *S. pallidum*.

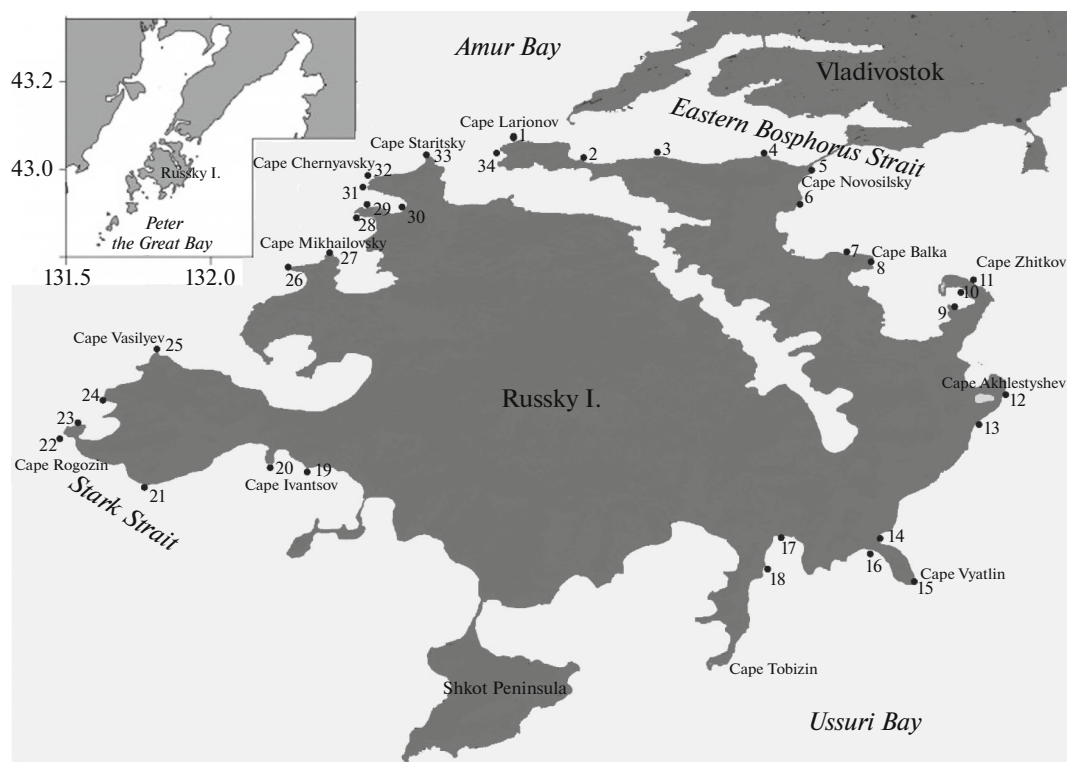


Fig. 1. Russky Island. The points with numerals are sampling stations.

MATERIALS AND METHODS

The macrophytic brown algae *S. miyabei* and *S. pallidum* are warm-water species that are widely distributed in Peter the Great Bay [2]. Algae of both species were collected in July and early August 2016 from the coastal waters off Russky Island (Fig. 1). Sampling was conducted at 34 stations around the island, except for the zone closed for access in the south (Fig. 1). Each sample, including five to seven thalli, was analyzed in triplicate.

Processing of algae, preparation of samples for the analysis, and atomic-absorption determination of the trace-element content were carried out on Shimadzu AA-6800 and Nippon Jarrell Ash AA-85 spectrophotometers at the Geochemical Laboratory of the Pacific Geographical Institute at the Far East Branch of the Russian Academy of Sciences, according to well-known approaches and techniques [3]. The accuracy of determination of metal concentrations was controlled by analyzing the standard specimens (NIES 9.0 “Sargasso”). The determination error did not exceed 15%. The concentration of metals was expressed in terms of micrograms per gram of dry weight. The number of element determinations (together with the blank samples) exceeded 600. Mathematical data processing (calculation of the mean of three parallel samples and the standard deviation) was performed in the

MS Excel software package. The significance of the differences of the mean values for the four compared polygons was evaluated using the Kruskal–Wallis test in the SPSS Statistics package.

Figure 1 shows a map of Russky Island with sampling points along the entire perimeter, which was conditionally divided into four parts (polygons): north–northeast of the island, stations 1–11 (facing the Eastern Bosphorus Strait); east–southeast, stations 12–18 (facing Ussuri Bay); southwest, stations 19–22 (facing the Stark Strait); and west–northwest, stations 23–34 (facing Amur Bay).

RESULTS AND DISCUSSION

This work presents a study of contamination of marine coastal waters around the island by metals such as iron, zinc, copper, cadmium, nickel, and lead. Iron predominantly characterizes the terrigenous runoff; zinc and copper, if they are not associated with extraction and processing of ores, metal smelting, or galvanic processes, indicate impacts of household and municipal activities (both are among the common components of domestic sewage). Cadmium, nickel, and lead are indicators of the technogenic pressure on the environment [3]. Despite the fact that all of them enter the environment when fuel is burned, nickel becomes the most urgent issue due to large volumes of

discharge. As nickel accompanies all oil products, its level in the environment will depend on the influx from ships running on heavy fuel oil, as well as from combined heat and power plants (CHPP) and boilers combusting liquid fuel. The composition of oil includes many heavy metals. Such elements as Fe, Mn, Cr, Co, Ni, V, Mo, Cu, Zn, Pb, Hg, and Sn have been found in oil ash, of which V, Ni, and Zn entered the oil via living organisms in the distant geological past. Moreover, V and Ni in some types of heavy oil reach concentrations that are sufficient for the industrial extraction of these metals [12, 20]. Thus, it can be suggested that nickel concentrations in the environment, including algae, will be directly related to the amount of oil hydrocarbons that are burned. In addition, nickel is easily co-precipitated with iron hydroxide, which suggests that in places with an abundance of iron in the suspended form in water and organisms, the nickel content will also be increased.

The data of analysis of algae samples for level of elements are presented in Table 1.

Iron. According to the data in Table 1, the highest Fe concentrations in algae among all the determinations, exceeding 1000 µg/g, were recorded from four stations: 3 (Bezmyannaya Cove), 24 (Cape Sredny), 30 (Babkin Cove, apex), and 31 (Babkin Cove, cape). At the apex of Babkin Cove, a very high iron concentration was found in *S. miyabei*, more than 5000 µg/g. High concentrations of zinc (23.47 µg/g), copper (3.87 µg/g), and especially nickel (7.65 µg/g) were also detected here. The lead content of algae at this station was low (0.38 µg/g). As was subsequently found, a creek flowing into the apex of the bay, surrounded by waterlogged terrain, drains the surface runoff from the village of Babkino and adjacent territory. All the elements, that is, the indicators of both terrigenous runoff (Fe) and anthropogenic (Zn and Cu) with technogenic (Cd and Ni) impacts, manifested themselves most clearly here. To a greater extent, this was also due to the acid nature of the water in the marsh creek, which not only converts the iron, migrating in fresh waters mainly in a suspended state, into the dissolved form, but also increases the migration activity of other elements that enter the aquatic environment. The only minor element in this area was Pb, indicating the lack of significant sources of its influx into the environment in the adjacent areas.

Low concentrations of iron were observed on the eastern side of the island, at capes Akhlestyshev (stations 12 and 13) and Tobizin (station 18), with the minimum Fe content recorded near the latter, 32 µg/g. This cape was distinguished by low concentrations of all the other metals in algae. Thus, the minimum levels of iron content were found in algae at the capes of the southeastern part of the island facing Ussuri Bay, which is obviously explained by its rocky/bouldery coast and the contact with open waters of the bay. It should be noted that only *S. pallidum* grew along this

side of the island. Due to its having a stronger and thicker stipe and a more powerful holdfast attached to stones than those in *S. miyabei*, it survives more dynamic habitat conditions between boulders. The only other station where the iron concentration in *Sargassum* were also low, 68 µg/g, was on the southwestern side, at Cape Rogozin from the side of Boyarin Cove. Large amounts of this element were detected in algae on the northeastern coast (facing the Eastern Bosphorus Strait), whose shores are characterized by soft soil and an abundance of suspended matter coming with the surface runoff and from bottom sediments.

Zinc and copper are indicators of anthropogenic impact. The highest concentrations of these elements were found in algae from station 9 (in small Zhitkov Cove), which is located opposite to a household sewage discharge site: 98.46 and 9.11 µg/g, respectively. These are very high values among those recorded from the coast of the island. As well, at this station, the maximum Zn content of *S. miyabei* was also at Cape Pospelov, 26.69 µg/g. Meanwhile, station 9 showed the smallest amount of nickel in algae, 4.02 µg/g, which indicates insignificant technogenic impact on this site. Increased values of Zn content of algae, exceeding 20 µg/g, were at stations 1, 2, 3, 4, 7 (all located on the coast of the Eastern Bosphorus Strait) and in the apical part of Babkin Cove (station 30). The lowest concentrations of zinc were found in algae from the coast of Ussuri Bay: 10.61 µg/g at station 12 (the tip of Cape Akhlestyshev); 9.76 µg/g at station 17 (Karpinsky Cove); and 9.39 µg/g at station 18 (Cape Tobizin). High copper concentrations in *Sargassum*, besides the above-noted station 9, were detected at capes Sredny, Balka, and Zhitkov (external side) (5.63, 5.62, and 5.19 µg/g, respectively). The latter two capes are facing the Eastern Bosphorus Strait. The smallest amount of copper in macrophytes was recorded from station 15 (Cape Vyatlin), 1.59 µg/g, which indicates a minimum anthropogenic impact on the environment near this narrow and long cape extending far into the sea, as well as in Bogdanovich and Chernyshev coves (stations 14 and 16) and near capes Tobizin and Mikhailovsky (stations 18 and 27). According to the data on the Zn and Cu content of algae, the northeastern coast of Russky Island is exposed to the strongest anthropogenic pressure.

Cd, Pb, and Ni are evidence of a technogenic impact on the environment and organisms. The Cd content of algae (entering the environment mainly during combustion of diesel fuel, and also from motor vehicles) was distributed more or less evenly all over the stations, varying within the range of 1.21–2.77 µg/g (Table 1). The largest amount of lead in algae was found at stations 11 (Cape Zhitkov) and 7 (Cape Balka), 3.73 and 2.39 µg/g, respectively; an elevated amount was found at stations 10 (Zhitkov Cove, opposite the settlement of builders) and 29 (Cape Ignatyev), 1.71 and 1.81 µg/g, respectively; the lowest

Table 1. The concentrations of heavy metals in *Sargassum* algae from the coastal waters around Russky Island, µg/g DW (m ± σ)

No.	Sampling site	Species	Fe	Zn	Cu	Cd	Pb	Ni
Northeastern part of the island, Eastern Bosphorus Strait								
1	Elena Island	<i>S. miyabei</i>	233 ± 8	21.88 ± 0.12	3.23 ± 0.09	1.95 ± 0.03	<i>0.15 ± 0.09</i>	6.43 ± 0.18
2	Near the canal	<i>S. miyabei</i>	633 ± 11	23.22 ± 0.50	4.83 ± 0.06	2.77 ± 0.09	<i>0.92 ± 0.53</i>	5.93 ± 0.08
3	Bezymyannaya Cove	<i>S. miyabei</i>	1355 ± 53	26.62 ± 1.10	<i>4.53 ± 0.18</i>	1.84 ± 0.01	0.22 ± 0.12	6.54 ± 0.22
4	Cape Pospelov	<i>S. miyabei</i>	652 ± 9	26.69 ± 0.37	<i>4.10 ± 0.20</i>	1.71 ± 0.04	0.29 ± 0.19	5.94 ± 0.21
5	Cape Novosilsky	<i>S. pallidum</i>	563 ± 12	<i>20.32 ± 2.32</i>	<i>2.77 ± 0.11</i>	<i>1.45 ± 0.07</i>	0.40 ± 0.18	5.58 ± 0.26
6	Ayaks Cove	<i>S. miyabei</i>	467 ± 8	15.19 ± 0.72	3.01 ± 0.13	2.41 ± 0.03	0.63 ± 0.09	6.95 ± 0.18
7	Cape Balka (Ayaks Cove)	<i>S. miyabei</i>	197 ± 4	<i>20.49 ± 0.27</i>	5.62 ± 0.08	1.71 ± 0.03	2.39 ± 0.36	6.88 ± 0.07
8	Cape Balka (apex)	<i>S. miyabei</i>	792 ± 17	<i>19.92 ± 0.21</i>	3.34 ± 0.07	1.75 ± 0.01	0.89 ± 0.13	5.82 ± 0.04
9	Zhitkov Cove, opposite sewage discharge	<i>S. miyabei</i>	450 ± 8	98.46 ± 2.73	9.11 ± 1.08	<i>1.21 ± 0.08</i>	0.57 ± 0.09	<i>4.02 ± 0.21</i>
10	Zhitkov Cove, opposite builders' settlement	<i>S. miyabei</i>	464 ± 4	17.11 ± 0.21	<i>2.75 ± 0.02</i>	1.67 ± 0.05	<i>1.71 ± 0.26</i>	<i>4.24 ± 0.09</i>
11	Cape Zhitkov, outer side	<i>S. miyabei</i>	546 ± 18	<i>19.60 ± 1.68</i>	5.19 ± 0.42	1.65 ± 0.04	3.73 ± 0.56	<i>4.37 ± 0.24</i>
Southeastern part of the island, Ussuri Bay								
12	Cape Akhlestyshv (tip)	<i>S. pallidum</i>	63 ± 2	<i>10.61 ± 0.21</i>	2.28 ± 0.37	1.65 ± 0.02	0.41 ± 0.06	<i>4.20 ± 0.08</i>
13	Cape Akhlestyshv (base)	<i>S. pallidum</i>	52 ± 1	13.19 ± 0.46	<i>4.28 ± 0.13</i>	<i>2.12 ± 0.10</i>	0.34 ± 0.05	<i>4.31 ± 0.11</i>
14	Bogdanovich Cove, apex	<i>S. pallidum</i>	77 ± 4	<i>11.65 ± 0.74</i>	<i>1.89 ± 0.07</i>	<i>2.11 ± 0.09</i>	0.19 ± 0.03	<i>4.16 ± 0.25</i>
15	Cape Vyatlin	<i>S. pallidum</i>	88 ± 3	<i>11.24 ± 0.74</i>	<i>1.59 ± 0.08</i>	<i>1.47 ± 0.01</i>	0.27 ± 0.16	4.66 ± 0.10
16	Chernyshev Cove	<i>S. pallidum</i>	476 ± 11	<i>11.63 ± 0.74</i>	<i>1.96 ± 0.12</i>	1.97 ± 0.05	0.17 ± 0.08	6.17 ± 0.37
17	Karpinsky Cove	<i>S. pallidum</i>	193 ± 8	<i>9.76 ± 0.42</i>	2.91 ± 0.25	<i>1.56 ± 0.06</i>	<i>0.11 ± 0.06</i>	<i>4.19 ± 0.07</i>
18	Cape Tobizin	<i>S. pallidum</i>	32 ± 1	<i>9.39 ± 0.42</i>	<i>2.06 ± 0.25</i>	<i>1.57 ± 0.06</i>	<i>0.10 ± 0.06</i>	4.53 ± 0.33
Southwestern part of the island, Stark Strait								
19	Ivantsov Cove	<i>S. miyabei</i>	664 ± 26	<i>16.18 ± 0.45</i>	3.31 ± 0.15	1.68 ± 0.05	0.28 ± 0.16	5.60 ± 0.08
20	Cape Ivantsov	<i>S. pallidum</i>	369 ± 19	<i>19.29 ± 0.70</i>	3.04 ± 0.25	1.68 ± 0.03	0.28 ± 0.16	5.88 ± 0.14
21	Kondratenko Peninsula	<i>S. miyabei</i>	155 ± 9	<i>17.87 ± 0.65</i>	<i>3.78 ± 0.35</i>	2.63 ± 0.05	0.21 ± 0.12	5.72 ± 0.46
22	Cape Rogozin	<i>S. miyabei</i>	609 ± 19	<i>19.22 ± 0.06</i>	3.68 ± 0.06	<i>2.12 ± 0.02</i>	0.22 ± 0.13	5.88 ± 0.14
Northwestern part of the island, Amur Bay								
23	Boyarin Cove, Cape Rogozin	<i>S. miyabei</i>	<i>68.0 ± 1.4</i>	15.11 ± 0.34	3.23 ± 0.02	<i>2.05 ± 0.02</i>	0.24 ± 0.14	4.63 ± 0.32
24	Cape Sredny	<i>S. pallidum</i>	1044 ± 75	16.00 ± 0.60	5.63 ± 0.20	1.80 ± 0.03	0.18 ± 0.10	5.73 ± 0.06
25	Cape Vasilyev	<i>S. miyabei</i>	332 ± 22	16.49 ± 0.49	3.58 ± 0.11	2.02 ± 0.01	1.00 ± 0.15	5.80 ± 0.11
26	Cape Polovtsev	<i>S. pallidum</i>	237 ± 7	14.22 ± 0.02	2.70 ± 0.17	1.98 ± 0.04	0.60 ± 0.09	5.73 ± 0.11
27	Cape Mikhailovsky	<i>S. miyabei</i>	250 ± 11	14.67 ± 0.75	<i>2.03 ± 0.08</i>	<i>2.27 ± 0.07</i>	0.68 ± 0.10	5.80 ± 0.08
28	Cape Ignatyev	<i>S. pallidum</i>	224 ± 10	13.86 ± 0.28	2.88 ± 0.07	2.03 ± 0.02	0.92 ± 0.14	5.27 ± 0.16
29	Cape Ignatyev	<i>S. miyabei</i>	239 ± 7	13.61 ± 0.31	2.08 ± 0.10	<i>2.29 ± 0.04</i>	<i>1.87 ± 0.27</i>	5.72 ± 0.10
30	Babkin Cove, apex	<i>S. miyabei</i>	5283 ± 565	23.47 ± 1.62	<i>3.87 ± 0.10</i>	<i>2.30 ± 0.16</i>	0.38 ± 0.22	7.65 ± 0.20
31	Babkin Cove, cape	<i>S. pallidum</i>	1053 ± 63	16.01 ± 0.56	<i>3.62 ± 0.10</i>	1.83 ± 0.03	0.54 ± 0.08	5.45 ± 0.06
32	Cape Chernyavsky	<i>S. miyabei</i>	608 ± 30	15.86 ± 0.40	3.22 ± 0.20	1.60 ± 0.32	0.22 ± 0.39	5.62 ± 0.20
33	Cape Startitsky	<i>S. pallidum</i>	260 ± 6	15.22 ± 0.15	2.91 ± 0.15	<i>2.21 ± 0.08</i>	0.17 ± 0.09	6.33 ± 0.05
34	Cape Elagin, Elena Island	<i>S. pallidum</i>	423 ± 15	<i>17.82 ± 0.40</i>	3.30 ± 0.14	1.88 ± 0.05	0.35 ± 0.19	5.73 ± 0.17

The high concentrations of elements are highlighted in bold; elevated concentrations, in bold italics; the lowest concentrations, in italics.

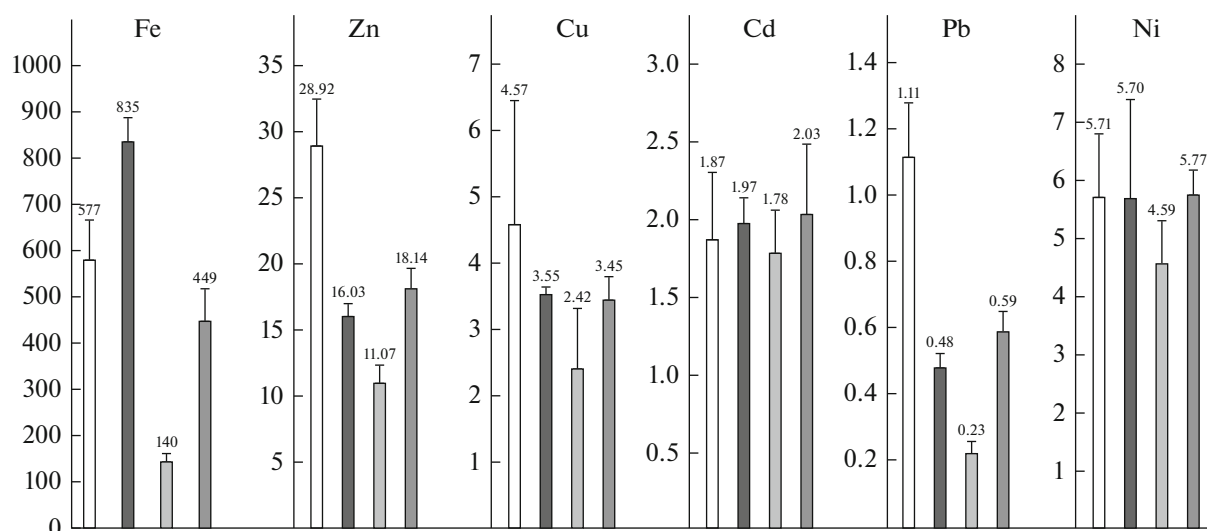


Fig. 2. The mean values of the Fe, Zn, Cu, Cd, Pb, and Ni concentrations in thalli of *Sargassum* algae collected from coastal waters on different sides of Russky Island (the black columns are the northwestern coast; the white columns are the northeastern coast; the light grey columns are the southeastern coast; the dark grey columns are the southwestern coast), $\mu\text{g/g}$ DW.

amount was found at stations 17 (Karpinsky Cove) and 18 (Cape Tobizin), 0.11 and 0.10 $\mu\text{g/g}$, respectively. As can be seen, the range of lead content values reached an order of magnitude. The maximum Pb concentrations in algae were recorded from stations located on the coast of the Eastern Bosphorus Strait. In spite of the ban on using tetraethyl lead as an antiknock additive to fuel and the associated abrupt decrease in the influx of this element into the environment from vehicle exhausts, as well as in spite of the cessation of production of movable typography types, the demand for this metal in a number of industries still remains high and in many of them it does not have alternatives (it is used for protection from various types of dangerous radiation, as an acid-proof lining, a component of printing inks and other dyes, insecticides, bullets for small arms, explosives, white lead, cement, spackling paste, etc.).

At most stations, the nickel concentration in algae was ca. 5 $\mu\text{g/g}$. The highest levels of this element, exceeding 6 $\mu\text{g/g}$, were determined as follows: 6.43 $\mu\text{g/g}$ at station 1 (Elena Island, Eastern Bosphorus Strait); 6.54 at station 3 (Bezmyannaya Cove); 6.59 at station 6 (Ayaks Cove); 6.88 at station 7 (Cape Balka); 6.17 at station 16 (Chernyshev Cove); 6.33 at station 33 (Cape Staritsky); and 7.65 at station 30 (Babkin Cove, apex). The lowest levels were found at both stations in Zhitkov Cove (4.02 and 4.24 $\mu\text{g/g}$), as well as at stations 11, 12, 13, 14, and 17, i.e., at most stations in the east–southeast of the island (from 4.16 to 4.37 $\mu\text{g/g}$). In general, the range of values of nickel concentration in algae was insignificant, from 4.0 to 7.65 $\mu\text{g/g}$.

Thus, the lowest concentrations of all the elements occurred in macrophytes that were collected along the coast facing Ussuri Bay. In algae growing in the northwest and northeast of the island, i.e., on the sides facing Amur Bay and the Eastern Bosphorus Strait, we observed increased concentrations of all the studied elements, except for Cd, which was distributed more or less evenly. Stations 30 (Babkin Cove), 2 (canal), 3 (Bezmyannaya Cove), 7 (Cape Balka), and 9 (Zhitkov Cove, household sewage from the Aquarium), which are subject to strong anthropogenic impact, were especially distinguished by high levels of these elements in algae.

The results presented in Table 1 make it possible to consider each of the sampling stations, highlighting the coves and capes with the largest and lowest concentrations of elements in algae along the coastline. The integral pattern of levels in the metals in *Sargassum* on different sides of the island coast is provided in Fig. 2. As noted, the southeastern side was distinguished by absolute growth of *S. pallidum*, whereas the northeastern coast was almost completely (except for Cape Novosilsky) overgrown by *S. miyabei*. In the southwest, *S. miyabei* dominated; in the northwest, both species colonized the coast to equal extents. Therefore, in order to characterize the geochemical conditions on different coasts of the island, we compared the mean concentrations of the elements in *Sargassum* algae without taking the species into account (Fig. 2).

The highest Fe concentrations are typical for the northwest of the island (Amur Bay coast), although a very high variability in concentration of this element was noted for macrophytes from this side. The pres-

Table 2. The ranges of heavy-metal contents in thalli for *S. miyabei* and *S. pallidum* from the coastal waters around Russky Island compared to the ranges of background concentrations for these species from the northwestern Sea of Japan, µg/g DW

Species	Fe	Zn	Cu	Cd	Ni	Pb
<i>S. miyabei</i>	68–1457	13.6–26.7	2.0–6.5	1.2–2.8	4.0–7.6	0.4–3.7
<i>S. pallidum</i>	32–1053	8.8–19.3	1.6–7.6	1.5–2.3	4.2–6.5	0.2–0.9
<i>S. miyabei</i> *	79–746	8.9–23.9	1.3–4.7	0.7–2.9	0.8–3.6	0–3.8
<i>S. pallidum</i> *	61–672	6.2–23.8	0.9–3.9	0.5–1.7	0.4–3.8	0–5.5

*Ranges of background concentration according to [9].

ence of soft sediments on the side facing the Eastern Bosphorus Strait also explains the large number of stations with a high iron content of algae in this sector of the coast. The smallest amounts of iron were found in *Sargassum* on the rocky southeastern coast. The differences in mean values are significant for each side of the island (Kruskal–Wallis test for Fe = 0.013).

In terms of anthropogenic impact, the parts of the island coastline are clearly different. Despite the fact that there is a high variability of Zn concentrations in algae from the northeastern side of the island, the significance of the differences for the other three sides is obvious (the Kruskal–Wallis test for Zn is 0.001). In terms of the copper content, the inhabitants of different sides of the coast also differ markedly: the highest mean level of this metal was found in *Sargassum* from the coast of the Eastern Bosphorus Strait; the lowest was found from the Ussuri Bay coast. The mean copper concentrations almost did not differ between inhabitants of the northwestern and southwestern coasts.

No significant differences between the sides of the island were observed both in the cadmium and in the nickel contents of algae, although a major part of the stations with the lowest Ni concentrations in algae are located in the southeast. The highest concentrations of Pb, like those of Zn, were recorded from the northeast of the island (the coast of the Eastern Bosphorus Strait); however, this side is characterized by a very high variability in the concentration of the element in macrophytes (the same as for Zn concentrations) caused by strong and diverse impacts on the coast. As well, despite the fact that the lowest lead concentrations were found mainly in algae from the southeast, the differences between the mean values for this side and for the northwest are insignificant, with their ranges overlapping.

Based on this understanding of the distribution of the levels of the elements over macrophytes at certain stations around the island and the general biogeochemical pattern on its different sides contacting with

different water masses, we can now proceed to assessment of the ecological situation in near-shore waters. This is based on comparing the determined quantitative values with the known data on the background ranges of heavy-metal concentrations in *Sargassum* algae from the northwestern Sea of Japan (Table 2). The values of the element concentrations in algae detected in extreme cases, that is, at the apex of Babkin Cove and opposite the household sewage discharge site in Zhitkov Cove, were 5283.0 µg/g for Fe, 98.46 for Zn, and 9.10 for Cu.

A comparison of the ranges of the element concentrations in the algae *S. pallidum* and *S. miyabei* from the coastal waters off Russky Island with the background ranges of their levels in *Sargassum* algae from the northwestern Sea of Japan showed that the minimum iron concentrations in algae of the island are lower than the lower values of the background ranges. At the same time, the maximum amounts of this element in macrophytes from the coastal waters around the island are higher than the upper boundaries of the background ranges. As a typical terrigenous element, Fe enters the marine environment mainly due to surface runoff, river drainage, mobilization to solution from bottom sediments in shallow waters, and stirring and bioturbation of bottom sediments [3, 11]. The algae collected at the rocky Cape Tobizin in the southeast of the island are least exposed to the impact of terrigenous runoff, which is quite explainable, as there are almost no sources of it here.

The lowest values of zinc concentrations in algae from the near-shore waters are higher than the lower values of the background ranges, whereas the highest concentration of this element in *S. pallidum* is slightly below the background maximum. The levels of copper, both lower and upper, in algae of the island are higher than the boundary background values of this element. Thus, the island is within the zone of substantial anthropogenic impact.

The lower boundaries of the range of cadmium levels in algae of the island are higher than the back-

ground ones; the maximum Cd concentration in *S. pallidum* is higher than the upper boundary of the background range; for *S. miyabei*, the highest level almost coincided with the upper boundary of the background range. This is also true for lead. For macrophytes of the island, the minimum values of the lead concentration range are above the background minimum, while the maximum values are below the background maximum, which is apparently due to a lower technogenic pressure on the island than that exerted on the background areas (or due to the use of the data on the background maximum of lead in algae obtained before 2003, when the ban on tetraethyl lead additive to gasoline fuel was introduced). For nickel, both the maximum and minimum concentrations in algae from the coastal waters of the island are higher than the background ones, which indicates more significant pollution of the surrounding waters; this is not surprising.

The detected concentrations of the elements in algae from the coastal waters off the island that were sometimes lower than the minimum values of the background range are obviously explained the fact that the lower boundary of the background range was estimated once and is rather arbitrary [9].

CONCLUSIONS

Russky Island is located within the outer roadstead zone of the port of Vladivostok; therefore, the increased concentrations of Ni in algae from the waters on all the sides of the island, compared to the background levels of Ni content of *Sargassum* algae from the northwestern Sea of Japan, are undoubtedly caused by the traffic of ships running on hydrocarbon oil-derived fuel. The higher concentrations of Zn and, especially, Cu in macrophytes, compared to the background range of these elements, indicate an anthropogenic impact on the waters surrounding the island. The difference in the levels of elements in algae that grow on different sides of the island, facing the water masses of the Eastern Bosphorus and Stark straits, Amur and Ussuri bays, is related both to the different levels of pollution of the surrounding waters and with the difference in geomorphology of the shores. The lowest concentrations of elements in algae growing along the rocky and stony southeastern coast that faces the open and offshore part of Ussuri Bay, compared to other sides of the island, indicate that the lowest heavy-metal contamination of the waters occur near this shore of Russky Island.

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REFERENCES

1. Kobzar, A.D. and Khristoforova, N.K., Monitoring heavy-metal pollution of the coastal waters of Amur Bay (Sea of Japan) using the brown alga *Sargassum miyabei* Yendo, 1907, *Russ. J. Mar. Biol.*, 2015, vol. 41, no. 5, pp. 384–388.
2. Perestenko, L.P., *Vodorosli zaliva Petra Velikogo* (Seaweeds of Peter the Great Bay), Leningrad: Nauka, 1980.
3. Khristoforova, N.K., *Bioindikatsiya i monitoring zagryazneniya morskikh vod tyazhelymi metallami* (Bioindication and Monitoring of Sea Waters Pollution by Heavy Metals), Leningrad: Nauka, 1989.
4. Khristoforova, N.K., Boichenko, T.V., Emelyanov, A.A., and Popova, A.V., Microbiological control of the water condition in the Novik Bay (Peter the Great Bay, Sea of Japan), *Izv. Tikhookean. Nauchno-Issled. Inst. Rybn. Khoz. Okeanogr.*, 2017, vol. 189, pp. 121–130.
5. Khristoforova, N.K., Gamayunova, O.A., and Afanasyev, A.P., State of the Kozmin and Wrangel Bays (Peter the Great Bay, Sea of Japan): dynamics of pollution by heavy metals, *Izv. Tikhookean. Nauchno-Issled. Inst. Rybn. Khoz. Okeanogr.*, 2015, vol. 180, pp. 179–186.
6. Khristoforova, N.K., Emelyanov, A.A., Berdasova, K.S., and Degteva, Yu.E., Ecological characteristic of water in the Eastern Bosphorus Strait by oxygen parameters, *Izv. Tikhookean. Nauchno-Issled. Inst. Rybn. Khoz. Okeanogr.*, 2015, vol. 181, pp. 161–168.
7. Khristoforova, N.K. and Kobzar, A.D., Brown algae as indicators of water pollution by heavy metals in the Rudnaya Bay (Sea of Japan), *Izv. Tikhookean. Nauchno-Issled. Inst. Rybn. Khoz. Okeanogr.*, 2012, vol. 168, pp. 220–231.
8. Khristoforova, N.K. and Chernova, E.N., Comparison of the content of heavy metals in brown algae and seagrasses, *Dokl. Biol. Sci.*, 2005, vol. 400, nos. 1–6, pp. 61–63.
9. Chernova, E.N. and Kozhenkova, S.I., Determination of threshold concentrations of metals in indicator algae of coastal waters in the northwest Sea of Japan, *Oceanology (Moscow, Russ. Fed.)*, 2016, vol. 56, no. 3, pp. 363–371. doi 10.7868/S0030157416030023
10. Chernova, E.N., Khristoforova, N.K., and Vyshkvartsev, D.I., Heavy metals in seagrasses and algae of Pos'et Bay, Sea of Japan, *Russ. J. Mar. Biol.*, 2002, vol. 28, no. 6, pp. 387–392.
11. Shul'kin, V.M., *Metally v ekosistemakh morskikh melkovodii* (Metals in Ecosystems of Marine Shallow Waters), Vladivostok: Dal'nauka, 2004.
12. Yashchenko, I.G., Heavy vanadium-rich oils of Russia, *Izv. Tomsk. Politekh. Univ.*, 2012, vol. 321, no. 1, pp. 105–111.
13. Akcali, I. and Kucuksezgin, F., A biomonitoring study: Heavy metals in macroalgae from eastern Aegean coastal areas, *Mar. Pollut. Bull.*, 2011, vol. 62, no. 3, pp. 637–645. doi 10.1016/j.marpolbul.2010.12.021
14. Brito, G.B., de Souza, T.L., Bressy, F.C., et al., Levels and spatial distribution of trace elements in macroalgae species from the Todos os Santos Bay, Bahia, Brazil, *Mar. Pollut. Bull.*, 2012, vol. 64, no. 10, pp. 2238–2244. doi 10.1016/j.marpolbul.2012.06.022

15. Bryan, G.W., Recent trends in research on heavy-metal contamination in the sea, *Helgol. Meeresunters.*, 1980, vol. 33, pp. 6–25.
16. Fowler, S.W., Use of macroalgae as a reference material for pollutant monitoring and specimen banking, *Monitoring Environmental Materials and Specimen Banking* (Proc. Int. Workshop, Berlin (West), 1978), the Hague: Martinus Nijhoff, 1979, pp. 247–260.
17. Hédouin, L., Bustamante, P., Fichez, R., and Warnau, M., The tropical brown alga *Lobophora variegata* as a bioindicator of mining contamination in the New Caledonia lagoon: a field transplantation study, *Mar. Environ. Res.*, 2008, vol. 66, no. 4, pp. 438–444. doi 10.1016/j.marenvres.2008.07.005
18. Khristoforova, N.K. and Kozhenkova, S.I., The use of the brown algae *Sargassum* spp. in heavy metal monitoring of marine environment near Vladivostok, Russia, *Ocean Polar Res.*, 2002, vol. 24, no. 4, pp. 325–329. doi 10.4217/OPR.2002.24.4.325
19. Strezov, A. and Nonova, T., Monitoring of Fe, Mn, Cu, Pb and Cd levels in two brown macroalgae from the Bulgarian Black Sea coast, *Int. J. Environ. Anal. Chem.*, 2003, vol. 83, no. 12, pp. 1045–1054.
20. Bashkin, V., Galiulin, R., and Galiulina, R., Heavy metals in oil. How to deal with them and where to apply? Neftegaz.Ru. <https://neftegaz.ru/analysis/view/8121-Tyazhelye-metally-v-nefti.-Kak-s-nimi-borotsya-i-gde-primenyat>. Cited November 1, 2017.

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