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Background Concentrations of Heavy Metals in Brown Algae from the Northwest Sea of Japan

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Abstract

Background concentrations of Fe, Mn, Cu, Zn, Pb, Cd, and Ni were calculated for brown algae *Costaria costata* from the northwest Sea of Japan. Also the paper contains refined data on heavy metal concentrations in the widespread distributed brown algae, such as *Stephanocystis crassipes, Sargassum pallidum* and *S. miyabei.* As the upper threshold levels of metal background concentrations, the median values plus double medians of absolute deviations from the medians were used (Me + 2MAD). The lower threshold level of the background concentration equal to the physiological need for an element is the median of 15% minimum values in the sampling minus the double median of absolute deviations from the median (Me_{15} – $2MAD_{15}$). The calculated ranges of the background concentrations of metals in algae were compared with concentrations of elements in macrophytes collected from habitats with background concentrations of metals in water.

Keywords

Heavy Metals, Background Concentrations of Metals, Threshold Level, Algae, *Costaria costata*, Biomonitoring, Northwest Sea of Japan

1. Introduction

Sustainable use of the sea coast and coastal waters implies the comprehensive assessment of this natural-technogenic system. Heavy metals are one of the most toxic groups of contaminants. In order to estimate the heavy metals pollution, both data of direct chemical analysis, data on metal concentration in the bottom sediments and dominant benthic organisms—bivalves and algae—used in the world (Goldberg, Bowen, Farrington, Harvey, Martin, Parker et al., 1978; Rainbow & Phillips, 1993; Jayasekera & Rossbach, 1996, et al.). Biomonitors accumulate metals from the environment with natural characteristics with consideration for their own needs (Chernova & Shulkin, 2019) and, in the presence of the elevated concentrations, in proportion to their content in the environment (Jayasekera & Rossbach, 1996). However, the sanitary and hygienic standards rather than environmental ones of the toxic element concentrations in organisms were set. These sanitary and hygienic standards are designed for provision of safety of foods and raw materials but they are also used as the criteria for evaluation of the hydrobionts life environment state which is wrongful. Another approach to the assessment of metal pollution of the aquatic area using the hydrobionts is based on comparison of the obtained concentrations in the indicator organisms from the study habitat area with the "supposedly-background" concentrations in organisms from the "supposedly-clean" habitats. The drawback of this method is a subjective choice of such habitats.

At present time, some more approaches to determining the background ranges and threshold concentrations of elements in organisms developed for the ecological assessment of the coastal waters. One of the first attempts to set the natural threshold of metal concentrations in marine organisms made by the United States National Oceanic & Atmospheric Administration (NOAA) when performing the international program Mussel Watch along the coast of the Central and South America and the Caribbean (Cantillo, 1998). As the threshold concentration of metals in mussels and oysters, the authors of the program have taken 85 percentile of sampling. Scanes and Roach (1999) have determined the background levels of metal content in the oysters of New South Wales, Australia, using the methods of principal components and cluster analysis. The stations adjacent to the forest and farm lands were included into the group with low concentrations of metals. The authors have calculated the mean and upper 95% confidence limit (UCL) for the background locations. In relation to the mean and UCL, the enrichment factors (EFs) were calculated, and the EFs higher than 1.5 were accepted as reliable. Villares, Puente, & Carballeira (2002) determined the background concentrations for green algae—Ulva and Enteromorpha from the Spanish coast as 95% confidence interval of the mean for the first subpopulation identified by method of modal analysis. The bioaccumulation factor (BAF—ratio of the mean concentration of metal in algae to the mean content of element in water) is proposed for calculation of the threshold metal concentrations in algae by Polish researchers (Zalewska & Danowska, 2017). These threshold concentrations were obtained by multiplying the mean BAF and targets of the metal concentrations in water according to the Directive 39/2013 of the European Parliament (Directive 39/2013—Anon, 2013). Using the microelement composition of soils and freshwater mollusks, it was shown that the calculation of median (Me) plus the double median of absolute deviations from the median (Me + 2MAD) is most likely for determining the threshold background concentration of metals in the ecosystem components (Reinmann, Filzmoser, & Garrett, 2005; Lukashev, 2007). This method can be used both with a normal distribution of sampling and in its absence.

The purpose of this article is to determine the background and threshold concentrations of metals in brown algae *Costaria costata* from the coastal waters of the Russian part of the Sea of Japan and to refined data for other widespread distributed macrophytes.

2. Materials and Methods

2.1. Data

We used data on microelement concentrations in samplings of widespread brown algae species from Laminariaceae (*Costaria costata*) and Sargassaceae (*Sargassum miyabei, Sargassum pallidum, Stephanocystis crassipes*) which are bioindicators of metal compounds in the marine environment. The algae were sampled in July-August of 1987-2017 at 115 stations along the coasts of Primorskii Krai (**Figure 1**). Sargassum samples (*S. miyabei* and *S. pallidum*) were collected in Peter the Great Bay in the south and along the eastern coasts of Primorskii Krai northward to Olga Bay, while *Stephanocystis crassipes* and *Costaria costata* along the entire Primorskii Krai coast line. Three or five specimens of occurring algae species were collected from each site. The thalli were washed clean of particulate matter with seawater, cleared of epiphytes, and dried at

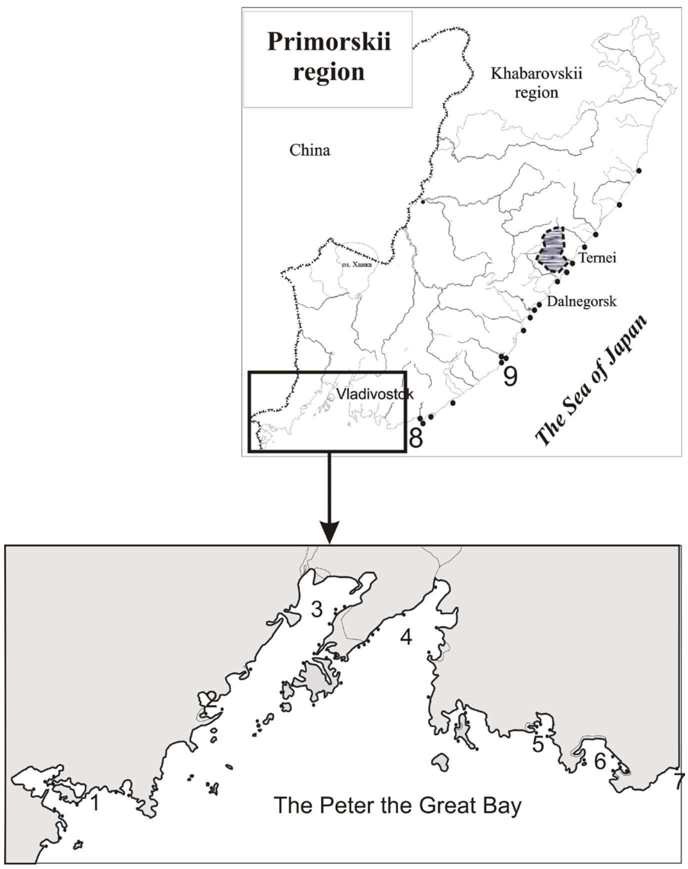

Figure 1. Schematic map of brown algae sampling stations in the northwestern part of the Sea of Japan. 1—Posyet Bay, 2—Slavyanskii Bay, 3—Amurskii Bay, 4—Ussuriiskii Bay, 5—Vostok Bay, 6—Nakhodka Bay, 7 - 8—Kievka Bay, 9—Olga Bay. Points indicate sampling locations.

85˚C. The further sample preparation was performed in accordance with method published earlier (Chernova & Kozhenkova, 2016) in the Pacific Geographical Institute, FEB RAS.

In addition to our own data, we used also published results obtained by other authors using the same procedures and equipment (Khristoforova & Maslova, 1983; Khristoforova, Zin, Shulkin, Bogdanova, & Maslova, 1983; Khristoforova & Przhemenetskaya, 1999; Kobzar & Khristoforova, 2015).

Samplings of *C. costata* from 42 stations, *S. miyabei* from 97 stations, *S. pallidum* from 72 stations, and *S. crassipes* from 46 stations were treated for statistical analysis of metal concentrations in the thalli of brown algae.

2.2. Methods

The descriptive statistics was created with Excel software; the normal distributions of metal concentrations and metal concentration logarithms were verified using the critical coefficients of asymmetry and excess (Lakin, 1990). After discarding the statistic outliers being beyond the range of normal or lognormal distribution, the values of Me ± 2MAD were calculated for residual sample. The value of Me + 2MAD was considered as the upper threshold concentration. To distinguish the lower background threshold of an element concentration in algae (considered as the minimum physiological level), the values of $Me_{15} - 2MAD_{15}$ were calculated for 15% of the least values in a sampling. The range of $Me_{15} \pm 2MAD_{15}$ was taken as the physiologically needed amount of an element in algae, comparable to the natural background range as such under minimum anthropogenic impact compared to the background range calculated using Me ± 2MAD values, which does not exclude the anthropogenic component (Chernova, 2012).

The calculated ranges of the background concentrations of metals in algae were compared with concentrations of elements in macrophytes collected from habitats with background concentrations of metals in water (Shulkin, 2004; Shulkin, Orlova, Shevchenko, & Stonik, 2013).

3. Results and Discussion

The background is the microscale stable level of the environment state on which the local natural and anthropogenic impact features are placed. In the geochemistry, the arithmetic mean value (under conditions of normal distribution) or geometric mean (for other types of concentration distribution) in samples is taken as the background value of the chemical element concentration in the natural object (Reinmann, Filzmoser, & Garrett, 2005; Lukashev, 2007). The background concentration of an element in living organisms is the sum of the physiologically needed amount of the element and some nontoxic excess accumulated from the environment with the regional background level of microelement to which the organisms are adapted (Chernova & Khristoforova, 2008; Chernova, Khristoforova, & Gonokhov, 2009). Even specimens of the same species collected from the same ecotope may have different microelement concentrations. This is caused by the genetic heterogeneity of a population and the presence of several hypo- and hyper-concentrators of chemical elements (Lobel & Wright, 1983). The lower limit of concentrations should conform to the minimum physiological amount for essential elements (Cu, Zn, Ni, Fe, and Mn) and zero concentration of nonessential ones (Pb and Cd). In view of this, the background concentration of a microelement in organisms must fall in a definite range of values. The upper limit of background values should conform to a limiting value of the element concentration in organism to which the species is adapted to the geochemical conditions (Ermakov & Tyutikov, 2008).

The method of calculation of the threshold value as median plus double median of absolute deviations from the median (Med + 2MAD) and background (median) was used in the samples of algae (Chernova, 2012; Chernova & Kozhenkova, 2016). In this work, the threshold concentrations of metals in *Costaria costata* were calculated, and those in *Stephanocystis crassipes* were refined. The background concentrations of Pb in Sargassum species were refined also (**Table 1**). $Me_{15} \pm 2MAD_{15}$, a median of microelement concentrations from 15% of the least values of the sampling (**Table 2**) was calculated to distinguish the properly natural background concentrations of microelements in the macrophytes. A value of $Me_{15} - 2MAD_{15}$ is the lower threshold level of the background concentrations (Chernova, 2012) because it is close to the minimum concentration of microelement in the hydrobionts under geochemical and hydrological conditions of this region (**Table 2**).

Comparison of these values with the empirically obtained background concentrations of elements in algae (Fe, Mn, Cu, Zn, Ni) (Kozhenkova, 2000) has shown that they are similar. The assessed values of the "natural background" for Cd and Pb appeared to be lower than those empirically obtained using the data of the 20th century, which is possibly related to the difficulties of their determination in previous years. The lower threshold levels of background concentrations

Table 1. Median (Med)/threshold (Med + 2MAO) and P_{85} (in brackets) of metal concentrations in brown algae of the northwest Sea of Japan (μg/g of dry weight).

Species (n)	Cu	Mn	Fe	Zn	Pb	Cd	Ni
C. costata (42)	2.5/6.3 (3.7)	11.3/22.3 (29)	129/205 (365)	21.2/55.4 (31.0)	0.5/0.8 (0.9)	0.5/0.6 (1.0)	3.4/8.4 (4.8)
S. pallidum (72)	2.3/3.9 (4.4)	168/455 (673)	317/672 (799)	14.5/23.8 (24.1)	0.6/1.5 (1.3)	1.1/1.7 (2.0)	2.0/3.8 (3.2)
S. miyabei (97)	2.9/4.7 (4.2)	266/714 (813)	353/746 (838)	16.6/23.9 (22.6)	0.8/1.8 (2.4)	1.6/2.9 (1.8)	2.3/4.2 (3.6)
S.crassipes (45)	2.4/3.6 (4.6)	9/12 (10.7)	87/194 (618)	26.1/42.7 (45.3)	0.6/1.4 (1.4)	2.2/3.2 (3.2)	2.8/4.2 (4.8)
MPC	-	-	-	-	2.5 - 5 (0.5)	5.0 - 10.0 (1.0)	-

MPC—Maximal permissible concentrations of the metals in food raw material of alga (Gigienicheskie…, 2001) (in brackets—μg/g of wet weight).

Table 2. Minimum physiologically required amount of metals in algae (Med_{15} ± 2MAD) from the coastal waters of the northwest Sea of Japan.

Species (n)	Cu	Mn	Fe	Zn	Pb	Cd	Ni
C. costata	1.2 ± 0.2	6.7 ± 1.0	55 ± 20	14.2 ± 2.6	0.3 ± 0.1	0.4 ± 0.06	2.2 ± 0.14
S. pallidum	1.1 ± 0.2	21 ± 9.4	92 ± 31	7.1 ± 0.9	0.12 ± 0.08	1.0 ± 0.14	0.6 ± 0.2
S. miyabei	1.5 ± 0.2	16 ± 13	116 ± 37	10.7 ± 1.8	0.22 ± 0.04	0.9 ± 0.22	1.2 ± 0.4
S.crassipes	1.8 ± 0.4	6.7 ± 0.9	43 ± 8	16.1 ± 0.9	0.23 ± 0.1	1.3 ± 0.25	1.9 ± 0.4

constituting the physiologically required amount of metals with minimum level of the geochemical background in different species of algae from the same region are comparable (**Table 2**). At the same time, they can differ in organisms of different sea water areas in connection with different geochemical and hydrological conditions. So, the values of Me_{15} ± $2MAD_{15}$ for brown alga *Fucus distichus* subsp. *evanescens* from the Sea of Japan differ from values for other species and subspecies of Fucus genes from the Sea of Okhotsk and White Sea by the reduced concentration of Mn in connection with the lower contribution of the river discharge (Chernova, 2016). The concentration of manganese in organisms, the same as that of iron, depends on the proximity to the sources of terrigenous runoff. The algae from the Sea of Japan have also distinguished by the greater value of Me_{15} ± $2MAD_{15}$ for Zn and Cd due to the lower biomass in coastal zone of the Sea of Japan (littoral and upper sublittoral). Biomass actively extracts essential zinc and its chemical counterpart cadmium from water for its physiological needs (Chernova, 2016).

According to the directly proportional relationship between the metal content in water and organisms, organisms must accumulate background concentrations of elements under background conditions. For the coastal waters of the northwest Sea of Japan, the following concentrations of the dissolve metals in the sea water were proposed as background concentrations: Zn—0.5 - 0.8; Cu—0.3 - 1.2; Pb—0.05 - 0.1; Cd—0.04 - 0.05; Fe—1 - 10 and Mn—2.6 - 20 μg/l (Shulkin, 2004; Shulkin, Orlova, Shevchenko, & Stonik, 2013). The consistence between concentrations of metals in algae and in sea water was studied (Chernova & Shulkin, 2019) and it was shown that the macrophytes in which the concentrations of metals do not exceed the threshold levels (Med + 2MAD) grow in the habitats with the background metal concentrations in water (**Table 3**). The exception is provided by some data on Fe, which prevails in water mainly in suspended form (Shulkin, 2004) and can be adsorbed onto the thalli surface and to increase the metal concentrations in algae.

The health-based exposure limits of metal concentrations in the algal raw materials occur for the most toxic elements (Pb, Cd, As, Hg) (Gigienicheskiye…, 2001). So, the concentration of Pb in algae should not exceed 0.5 μg/g of wet weight and about 2.5 - 5 μg/g of dry weight basis (approximately 10% - 20% of wet weight). The concentration of Cd should not exceed 1.0 μg/g of wet weight

Table 3. Maximum concentration of metals in algae (μg/g d.w.) from the coastal water of the northwest Sea of Japan with background levels of dissolved metals in seawater (from: Chernova & Shulkin, 2019).

Species	Cu	Mn	Fe	Zn	Cd
Fucus distichus sbsp. evanescens	3.1 (4.1)	129 (169)	372 (100)	35.6 (80)	n.d. (3.1)
Silvetia babingtonii	5.5 (3.5)	16 (33)	120 (54)	34.3 (39)	1.2 (1.6)
Sargassum pallidum	3.5 (3.9)	183 (455)	130 (672)	14.3 (24)	2.3 (1.7)
Stephanocystis crassipes	3.3 (3.6)	47 (12)	142 (194)	23.9 (43)	3.1 (3.2)
Saccharina japonica	5.2 (3.9)	7 (8)	108 (82)	26.3 (43)	1.5 (2.8)

In brackets the threshold metal concentration in algae (Chernova & Kozhenkova, 2016); n.d., no data.

or 5 - 10 μg/g of dry weight. As we can see (**Table 1**), the threshold concentrations of Pb and Cd in *Costaria costata* and other brown algae from the northwest Sea of Japan do not exceed these values.

Therefore, this work contains background concentrations of trace metals for *Costaria costata* from the northwest Sea of Japan and supplements earlier calculated ranges and threshold concentrations of Fe, Mn, Cu, Zn, Cd, Pb, Ni in algae *Stephanocystis crassipes, Sargassum pallidum* and *S. miyabei*. The possibility to use the obtained threshold concentrations of elements in the macrophytes for the ecological assessments of the coastal waters of seas is verified by their accordance with the concentrations of metals in macrophytes from habit areas with background conditions.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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