

# Concentrations of Metals in the Environment and in Algae: The Bioaccumulation Factor

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**Abstract**—Research on the concentrations of the metals Cu, Cd, Fe, and Mn showed no significant relationships between metal concentrations in water and in brown algae of the Sea of Japan with background concentrations. A significant correlation between metal concentrations in the environment and in the algae was found for zinc; it was the only metal with a wide variation in concentrations exceeding background levels in the habitat of macrophytes. Correspondingly, the only significant correlation between the bioaccumulation factor (BAF) of seaweeds from the Sea of Japan and the content of this element in seawater was found for zinc. It was shown for all studied metals that the highest and most variable BAF values for algae were observed within the background range of metal concentrations in the aquatic environment, which allows us to express the background range (the range caused by natural conditions) graphically. Thus, the high variability of the BAF values of aquatic organisms in the background environmental conditions necessitates very cautious interpretation of biomonitoring data.

**Keywords:** trace metal, background concentrations, threshold concentrations, brown algae, bioaccumulation factor

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## INTRODUCTION

The use of aquatic organisms for biomonitoring of environmental pollution is based on the dependence of their chemical composition with the chemical composition of the environment. This dependence for aquatic organisms has been established in toxicological experiments [44, 45] and confirmed by a number of field measurements [21, 24, 30, 32]. It was shown that the relationship between metal concentration in bioindicator algae and in seawater should be linear, which means the constancy of the accumulation coefficient for a particular element in a wide range of its content in the environment [35]. However, the relationship between the chemical composition of water and that of aquatic organisms in their natural habitat is statistically significant and is detected, as a rule, when there is a wide (more than two orders of magnitude) range of element concentration in the environment [24, 25]. Under natural conditions, the chemical composition of aquatic organisms, in addition to the concentration of dissolved metal forms, is also influenced by other factors that were described in the literature mainly at the end of the 20th century: the amount of elements in the suspended matter and in bottom sediments, especially through trophic transfer into hydrobionts [6], as well as hydrodynamic conditions that

provide the speed of water mixing, the presence of organic compounds that are capable of binding chemical elements in the composition of exo- and endometabolites, and the physiological peculiarities of hydrobionts themselves [2, 3, 17, 39, 43]. The difference in the time scales of biogeochemical processes in organisms and in the environment is an important issue [45].

Many researchers, based on the existence of a linear relationship between the concentration of elements in water and in organisms, have calculated bioaccumulation or bioconcentration factors [26, 45]. The bioaccumulation factor (BAF) is the ratio of the element concentration in hydrobiont tissues ( $\mu\text{g/g d.w.}$ ) versus its concentration in dissolved form in ambient waters ( $\mu\text{g/mL}$ ); the ratio is calculated on the basis of data obtained in field studies. The numerator is the concentration that integrates all natural sources of the element, which are available to the aquatic organism, including dissolved and suspended forms, as well as those obtained with food [25, 38]; the denominator is the concentration of the dissolved metal in the ambient waters. The bioconcentration factor (BCF) is expressed as the ratio of the element concentration in an organism ( $\mu\text{g/g d.w.}$ ) to the concentration of this element in the dissolved form in ambient water ( $\mu\text{g/mL}$ ), which is calculated based on data obtained in short-term experiments with the exposure of organ-

isms in water with the known metal concentration. It was proposed to use the BAF and BCF to recalculate the concentrations of the metal in the environment through their concentration in organisms, and vice versa [45, 46].

Another important task of biogeochemical monitoring is determination of the ecological status of aquatic systems based on the determination of the maximum allowable concentrations of metals in indicator organisms of various systematic groups. In addition to the toxicological approach, several other methods are currently being applied in biomonitoring research [23, 40, 42, 46] including the use of the BAF [29]. However, in order to use this factor to recalculate the content of the element in the body to the concentration of the element in the medium, the rate of accumulation and extraction of the element concentration must be constant and the relationship between the BAF (BCF) of indicator organisms and the metal content in water should give a straight line graph parallel to the abscissa axis. Such a relationship was shown by Fehrmann and Pohl in their study of the adsorption of cadmium by dry algal tissues [27]. However, experiments on living algae show that the rate of accumulation and the BCF decrease with an increase in the metal concentration in the medium [20, 45]. However, the experiments use a deliberately increased concentration of metals, which is practically unattainable in the natural environment. Thus, the BCF value calculated in the experiments should be very carefully used for recalculation of the concentration of the element in organisms and in the natural environment [45]. At the same time, a negative (logarithmic) relationship was found between the concentrations of trace elements in water and BAF values for many aquatic organisms (invertebrates, fish, and algae) under natural conditions [25, 38]. Such a connection imposes restrictions on biomonitoring with respect to the possibility of recalculating the concentrations of metals in the indicator organism on the content of elements in water using the BAF values obtained in the natural environment.

The aims of this work were: (1) to calculate the BAF values for macroalgae based on published and own data for the western part of the Sea of Japan; (2) to consider changes in the BAF values with dependence on the concentration of dissolved metals forms in the ambient waters; and (3) to evaluate the possibility of using the BAF in order to clarify the background concentrations of metals in the environment and in macroalgae.

## MATERIALS AND METHODS

To calculate the BAF values, we used our own data obtained in 1987 on the contents of Fe, Mn, Zn, Cu, Cd, and Ni in water and in algae from the western Sea of Japan (Fig. 1), as well as the literature data on metal contents in macrophytes (brown, red, and green algae)

and in water in their habitats (Table 1). To determine the metal concentration, algae and water were collected in the summer from a depth of 1–2 m. The algae were thoroughly washed with water from the sampling site and placed in plastic containers and then packed in plastic bags and delivered to the laboratory. The algae were dried at a temperature of 85°C in a drying cabinet between sheets of filter paper to avoid contact with metal parts, thoroughly cleaned of fouling, and packed in clean paper bags for storage. Subsequently, algae, homogenized in an agate mortar (a combined sample of three to five specimens from one sampling site), in three replications were mineralized with concentrated HNO<sub>3</sub> (ultra high purity).

Simultaneously with sampling of algae, water samples were taken in a plastic canister; the canister was packed in polyethylene and delivered to the vessel. On the day of sampling, water samples were filtered using a vacuum pump through a Millipore Durapore® Membrane Filter, 0.45 µm pore size. The filtrates were stored in a refrigerator in plastic containers with the addition of HNO<sub>3</sub> of ultra high purity grade up to pH 1–2. Trace elements were concentrated 100 times by liquid extraction in a diethyldithiocarbamate-Na-chloroform system, determined on a Nippon Jarrel Ash AA-780 atomic absorption spectrophotometer in the flame variant without background correction. The degree of extraction of dissolved ionic forms of metals after concentration (85–95%) was repeatedly verified experimentally by the “introduced and found” method.

The content of metals (Fe, Mn, Zn, Cu, and Cd) in algae was determined by the atomic absorption method on a Nippon Jarrel Ash AA-780 instrument in acetylene flame. The correctness of determination of the metal concentrations in the samples was monitored by blank experiments, the method of additives, and the analysis of the standard sample of bottom sediments SDO-1. The measurement error was 7–10%.

The BAF was calculated by dividing the metal concentration in the alga (µg/g d.w.) by the concentration of the dissolved metal in water (µg/mL). The Excel and Statistica 6 programs were used to construct the figures and to calculate the regression equations, the BAF, and the correlation coefficients.

## RESULTS

The BAF values for all macroalgal species, calculated on the basis of our own and the literature data, were characterized by high variability depending on the content of dissolved metals in the medium (Fig. 2). Thus, the dispersion of the BAF values for zinc in algae of the World Ocean varied in the range of four orders of magnitude, that is, from  $2 \times 10^2$  to  $1.4 \times 10^5$ , while the maximum dispersion of values corresponded to Zn concentrations in water up to 2.5 µg/L (Fig. 2). At the western coast of the Sea of Japan, the maximum and

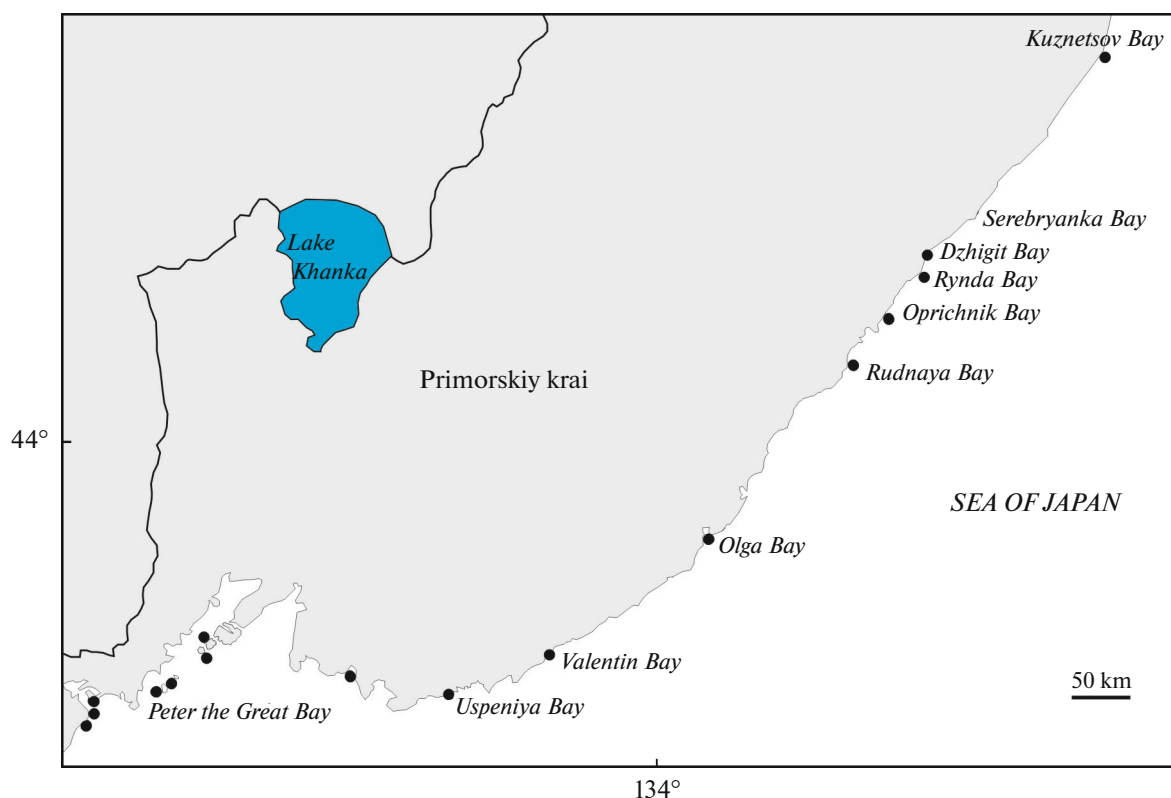


Fig. 1. Sampling stations along the western coast of the Sea of Japan.

most variable BAF values for Zn ( $2.8 \times 10^4$ – $1.4 \times 10^5$ ; coefficient of variation 52%) were determined for *Silvetia babingtonii* (Harvey) that grows in an environment with a concentration of dissolved zinc of 0.2–0.8  $\mu\text{g/L}$  (Table 2). The BAF values for copper in algae of the World Ocean varied from  $5.95 \times 10^2$  to  $5.23 \times 10^4$ . The maximum and most variable BAF values were obtained when the Cu content in the environment was up to 1.3  $\mu\text{g/L}$  (Fig. 2). In the *Fucus* algae of the Sea of Japan, all BAF values ( $1.9 \times 10^3$ – $5.2 \times 10^4$ ) were recorded in water with a concentration of the dissolved element up to 0.7  $\mu\text{g/L}$  (Table 2). The BAF for lead varied between  $1 \times 10^{-1}$  and  $6.9 \times 10^5$  in the algae of the World Ocean. The maximum and most variable BAF values for Pb were in the range of 0.02–0.03  $\mu\text{g/L}$  of the element dissolved in water (Table 2; Fig. 2). The BAF values for Fe and Mn in algae of the World Ocean varied from  $4.4 \times 10^2$  to  $6.6 \times 10^5$  and from  $2.1 \times 10^2$  to  $8.8 \times 10^5$ , respectively (Fig. 2). In an environment where the concentrations of the dissolved forms of Fe and Mn did not exceed 10  $\mu\text{g/L}$  (Table 2) the BAF values for these elements in algae were the highest and most variable. The highest and most variable BAF values for Fe and Mn in the algae of the western coast of the Sea of Japan were recorded in seawater with a content of dissolved metals of 0.2–2.5 and 0.2–8.0  $\mu\text{g/L}$ , respectively (Table 2). The BAF Cd values in the algae of the World Ocean varied from 50 to  $8.3 \times 10^4$ . The

algae from waters with a Cd content up to 0.4  $\mu\text{g/L}$  had the highest and most variable BAF values (Fig. 2) for this metal. In the Sea of Japan, all BAF values ( $4.1 \times 10^3$ – $2.9 \times 10^4$ , the coefficient of variation 45%) were recorded in algae from waters with a cadmium content of 0.08–0.3  $\mu\text{g/L}$  (Table 2).

## DISCUSSION

It was previously shown that marine and freshwater invertebrates (bivalve and gastropod mollusks, polychaetes, and crustaceans) have a significant negative linear relationship between the logarithms of the BAF and the content of metals, such as Zn, Cu, Hg, Cr, Cd, Pb, and As, in ambient water [25, 38]. This relationship appeared to be insignificant only for selenium in marine invertebrates, as well as for arsenic and cadmium in freshwater organisms. A significant negative correlation between the BAF logarithm for the algae and the element concentration in water was previously confirmed for Cd, Zn, Ni, and Cu, but not for Pb [39]. On the basis of the literature and our own data (Table 1), a significant negative relationship was found between the BAF logarithms for the macroalgae and the content of dissolved metals for Fe, Cr, Mn, Zn, Pb, Ni, and Hg in seawater (Table 3). For cadmium, the negative relationship was insignificant. At the same time, when using only our own data on the metal contents in

**Table 1.** Algal species used in calculations of the bioaccumulation factor (BAF)

Species	Metals	Reference
<i>Cystoseira</i> sp., <i>Ulva</i> sp., <i>Enteromorpha</i> sp., <i>Padina pavonica</i> , <i>Caulerpa racemosa</i> , <i>Codium fragile</i> , <i>Gracilaria gracilis</i>	Cd, Pb, Cr, Cu, Zn, Fe	[17]
<i>Caulerpa sertularioides</i> , <i>Dictyota dichotoma</i> , <i>Halimeda opuntia</i> , <i>Galaxaura obtusata</i> , <i>Cystoseira myrica</i> , <i>Hypnea musciformis</i> , <i>Penicillus</i> sp., <i>Chaetomorpha crassa</i> , <i>Rhizocephalus phoenix</i> , <i>Dictyosphaeria cavernosa</i> , <i>Laurencia poiteaui</i> , <i>Plenosporium</i> sp.	Cd, Pb, Cu	[34]
<i>Enteromorpha</i> sp.	Cd, Pb, Cr, Cu, Zn, Mn, Ni	[48]
<i>Ulva</i> sp., <i>Fucus vesiculosus</i> , <i>Polysiphonia lanosa</i> , <i>Ascophyllum nodosum</i>	Cd, Pb, Cr, Cu, Zn, Mn, Ni	[42]
<i>Acatofora specifiara</i> , <i>Enteromorpha</i> sp., <i>E. compressa</i> , <i>Hypnea</i> sp., <i>Ulva lactuca</i> , <i>Lola capillaries</i> , <i>Caulerpa racemosa</i> , <i>Padina gymnospora</i> , <i>Acatofora delilei</i> , <i>Dyctiota bartairesiana</i> , <i>Fucus</i> spp., <i>Sargassum polycystum</i> , <i>Gracilaria verrucosa</i> , <i>Lola</i> sp., <i>Caulerpa scalpeliformis</i> , <i>Dyctiota dichotoma</i>	Cd, Pb, Cr, Cu, Zn, Mn, Ni, Fe	[25]
<i>Enteromorpha</i> sp., <i>Ulva rigida</i>	Cr, Ni	[31]
<i>U. rigida</i>	Cd, Pb, Cu, Zn	[32]
<i>U. rigida</i>	Cd, Pb, Cr, Cu, Zn, Mn, Ni, Fe	[38]
<i>Padina pavonica</i>	Cd, Pb, Cr, Cu, Zn	[23]
<i>Sargassum polycystum</i> , <i>S. swartzii</i> , <i>S. mcclurei</i>	Cd, Cu, Zn, Mn, Fe	[10]
<i>Enteromorpha</i> sp., <i>Porphyra</i> sp.	Hg, Cd, Cu, Pb	[37]
<i>Sargassum pallidum</i> , <i>S. miyabei</i> , <i>Stephanocystis crassipes</i> , <i>Fucus evanescens</i> , <i>Pelvetia wrightii</i> , <i>Ulva fenestrata</i>	Cd, Cu, Zn, Fe, Mn, Ni, Pb	This work

**Table 2.** The concentrations of dissolved metals ( $\mu\text{g/L}$ ): (1) background levels for the coastal waters of the Sea of Japan [14, 15]; (2) concentrations corresponding to the most variable BAF values in algae of the Sea of Japan; (3) concentrations corresponding to the most variable values of BAF in algae of the World Ocean

Characteristics	Metal					
	Zn	Cu	Cd	Pb	Fe	Mn
1	To 0.5–0.8	0.3–1.2	0.005–0.04	0.05–0.1	1–10	2.6–20
2	0.2–0.8	Up to 0.7	Up to 0.3	–	0.2–2.5	0.2–8.0
3	Up to 2.5	Up to 1.3	Up to 0.4	Up to 0.03	Up to 10	Up to 10

*Silvetia babingtonii*, *Stephanocystis crassipes* (Mertens ex Turner), and *Saccharina japonica* (J.E. Areschoug) from the Sea of Japan, growing in a narrower range of metal concentrations in waters, a significant correlation was found only for Zn (Table 4).

High and variable BAF values for algae at low metal concentrations in the environment (Fig. 2) can be explained by several issues. In particular, in the range of low values, the error in determination of the metal content in the natural environment and in hydrobionts is higher. In addition, many data on the content of heavy metals in natural waters obtained before the 1990s were recognized as overestimated because of

imperfect sampling and determination errors [8, 14, 18]. Inflated data on the content of elements in water underestimate the BAF values. However, the results we obtained in 1987 for Fe, Mn, Cu, Zn, and Cd are consistent with more recent data (Table 1; Fig. 2).

High values of natural BAF values at low concentrations of metals in the medium were experimentally confirmed [34, 45]. Thus, the BCF values and the rate constants of metal absorption obtained for the green alga *Ulva lactuca* L. were higher in waters with low concentrations of metals (Cd 0.5–2  $\mu\text{g/g}$ , Zn 1–5  $\mu\text{g/g}$ ) than in waters with high concentrations of these elements (Cd 10–50  $\mu\text{g/L}$ , Zn 20–100  $\mu\text{g/L}$ ). However, even low

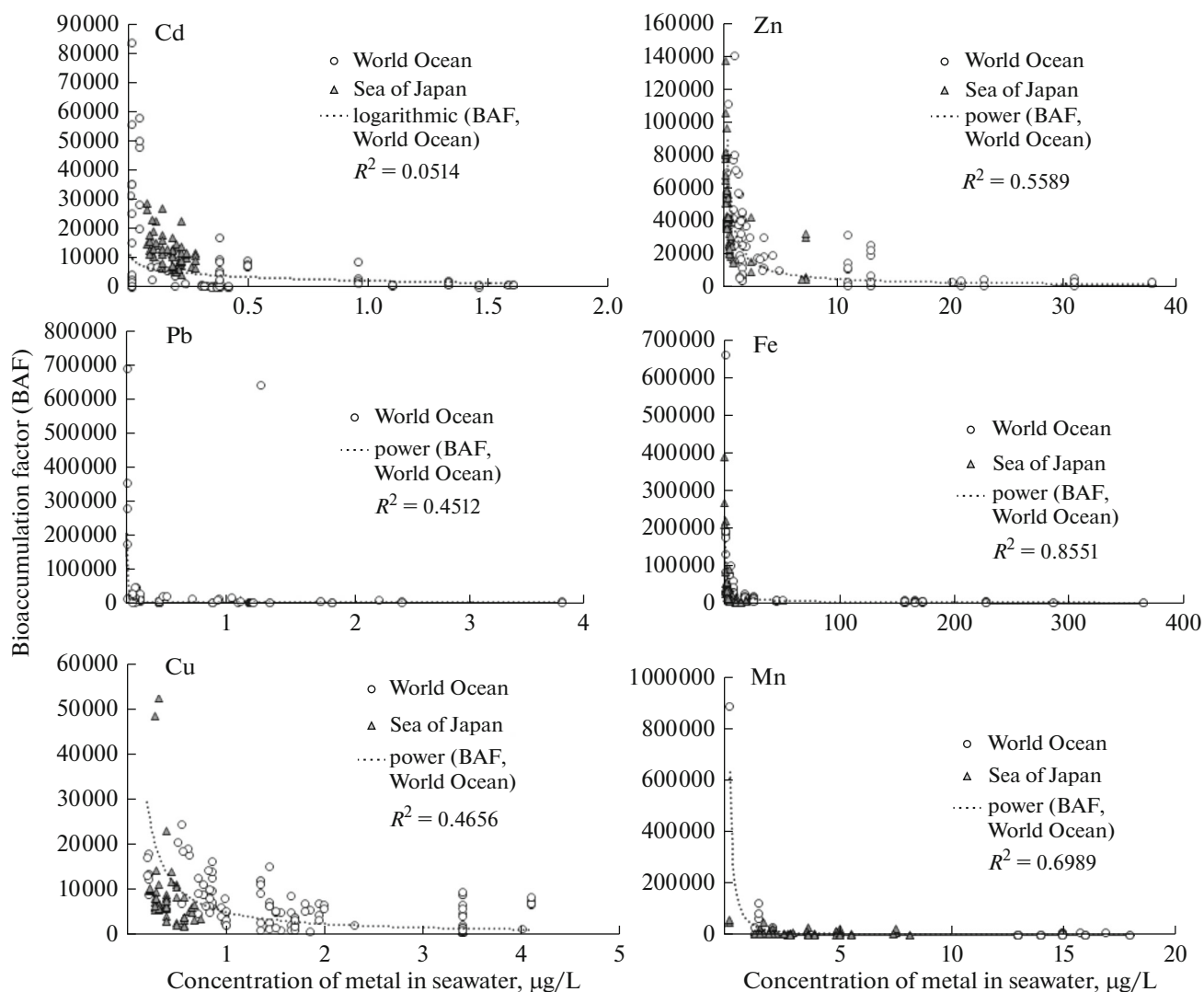


Fig. 2. The bioaccumulation factor (BAF) values of algae of the World Ocean and the Sea of Japan, with the dependence on the concentration of the dissolved metal in seawater. The dashed line is a curve (logarithmic or power) that most accurately describes the relationship between the parameters;  $R^2$  is the coefficient of approximation.

concentrations of metals in the experiment were 2–25 times higher than in natural waters [45]. A decrease in BCF values was also found for *U. lactuca* kept in water contaminated with one of the five elements, Cd, Cu, Pb, Zn, and Ni, at a concentration from 10 to 100 µg/L [34]. Thus, the experimental data on the calculation of the values of BCF and BAF confirm that

with increasing concentrations of metals in the medium, the values of these factors and the intensity of accumulation of elements in aquatic biota decrease. Since the highest and most variable BAF values are observed with a low concentration of metals in water, it is necessary to estimate how these concentrations in the ambient waters correspond to the background level.

Table 3. Linear correlation coefficients ( $r$ ) between Ln BAF (algae of the World Ocean) and Ln C (C is the metal concentration in water, µg/L)

Coefficient	Hg	Cd	Pb	Cr	Cu	Zn	Fe	Mn	Ni
$r$	-0.71*	-0.18	-0.57*	-0.79*	-0.45*	-0.74*	-0.92*	-0.84*	-0.66*
$n$	31	137	130	69	137	74	59	40	46

\* The differences are significant at  $p = 0.01$ . Ln is the natural logarithm;  $n$  is the sample size.

**Table 4.** Parameters of significant ( $p < 0.05$ ) linear relationship equations ( $Y = aX + b$ ): concentrations of dissolved metals in water of the Sea of Japan (X), concentrations of metals in algae (Y); concentration of dissolved metals in water (X), BAF (Y)

Species	X	Y	$a$	$b$	$R^2/r$	$n$
<i>Stephanocystis crassipes</i>	Ln Cd	Ln Cd	0.36	1.53	0.27/0.51	19
	Ln Cu	Ln BAF Cu	-0.82	7.81	0.31/-0.56	19
	Ln Fe	Ln Fe	0.18	3.82	0.24/0.49	19
	Zn	Zn	2.67	16.28	0.61/0.78	19
	Ln Zn	Ln BAF Zn	-0.74	9.93	0.93/-0.96	19
<i>Silvetia babingtonii</i>	Ln Cu	Ln BAF Cu	-0.54	8.21	0.45/-0.67	12
	Zn	Zn	36.99	8.14	0.89/0.95	12
	Ln Zn	Ln BAF Zn	-0.43	10.60	0.4/-0.64	12
<i>Saccharina japonica</i>	Ln Fe	BAF Fe	-2059.3	13174.1	0.27/-0.52	15
	Zn	Zn	1.21	17.71	0.29/0.53	15
	Zn	Ln BAF Zn	-0.37	10.73	0.76/-0.87	15

Ln is the natural logarithm;  $R^2/r$  is the approximation coefficient/linear correlation coefficient;  $a$ ,  $b$ , coefficients of linear equations;  $n$  is the number of pairs of values.

It was suggested that the following concentrations of dissolved metals can be considered as the background levels for the coastal areas of the northwestern part of the Sea of Japan: Zn, 0.5–0.8; Cu, 0.3–1.2; Pb, 0.05–0.1; and Cd, 0.04–0.05  $\mu\text{g/L}$  [14, 15]. The background concentrations of Fe and Mn in the coastal waters of this region are very variable, depend on the season, and presumably are 1–10 and 2.6–20  $\mu\text{g/L}$  [14] (Table 2).

The correlation of BAF values for algae with the corresponding concentration range of dissolved Cu, Fe, Zn, Mn, Cd, and Pb in the coastal waters of the northwestern part of the Sea of Japan (Table 2; Fig. 2) shows that the highest and most variable BAF values were actually obtained for the background range of concentrations of these elements in the environment. Thus, using the curve of BAF variability of metal contents in the algae we can fairly accurately identify the natural range of concentrations of elements in the aquatic environment graphically. Zn and Cd, with their BAF values being the most variable among algae of the World Ocean, were the exceptions; these were recorded for specimens from waters within the range of concentrations exceeding the background level for the Sea of Japan by 3 and 6 times (Table 2; Fig. 2). This indicates the existence of water areas with higher background concentrations of these elements than in the Sea of Japan. In particular, the average concentration of dissolved Zn in the White Sea is approximately 2.9  $\mu\text{g/L}$  [9], which corresponds to the borderline concentration of the element in water with maximum BAF values (Table 2). It is possible that these borderline concentrations of the elements correspond to the maximum value of the natural concentration in which

macrophytes are able to exist without additional energy consumption for mobilizing the defense systems of the organism. Higher background concentrations of cadmium might also be recorded in the open waters of the western part of the Sea of Japan, where the algal samples are collected, compared with the background concentrations determined for the waters of the coastal closed sea areas [14, 15]. This is due to the fact that the concentration of dissolved Cd forms in river waters (0.002–0.01  $\mu\text{g/L}$ ) is often lower than in sea waters (0.05–0.08  $\mu\text{g/L}$ ) [19]. It was previously shown that the Cd content in bioindicator organisms, including algae, is higher in the open sea waters than in closed coastal waters [4, 5, 12].

The high variability of BAF values in organisms from an environment with low concentrations of trace elements confirms that in waters with background concentrations of metals the metal content in living organisms is controlled not as much by the amount of the element in the environment, as by other external and internal factors. The most significant among these are the species peculiarities, the physiological need for elements, and accumulation of other chemical analogues together with the elements, as well as an increased filtration activity of hydrobionts at a low availability of food [1, 44].

The background (the median) and threshold (the median + double median of absolute deviations from the median) concentrations of elements were determined for some mass species of algae and seaweeds of the Sea of Japan [11–13]. It is assumed that organisms with a metal concentration below the threshold values inhabit water areas with the background environmental conditions. In the Sea of Japan, in the range of the

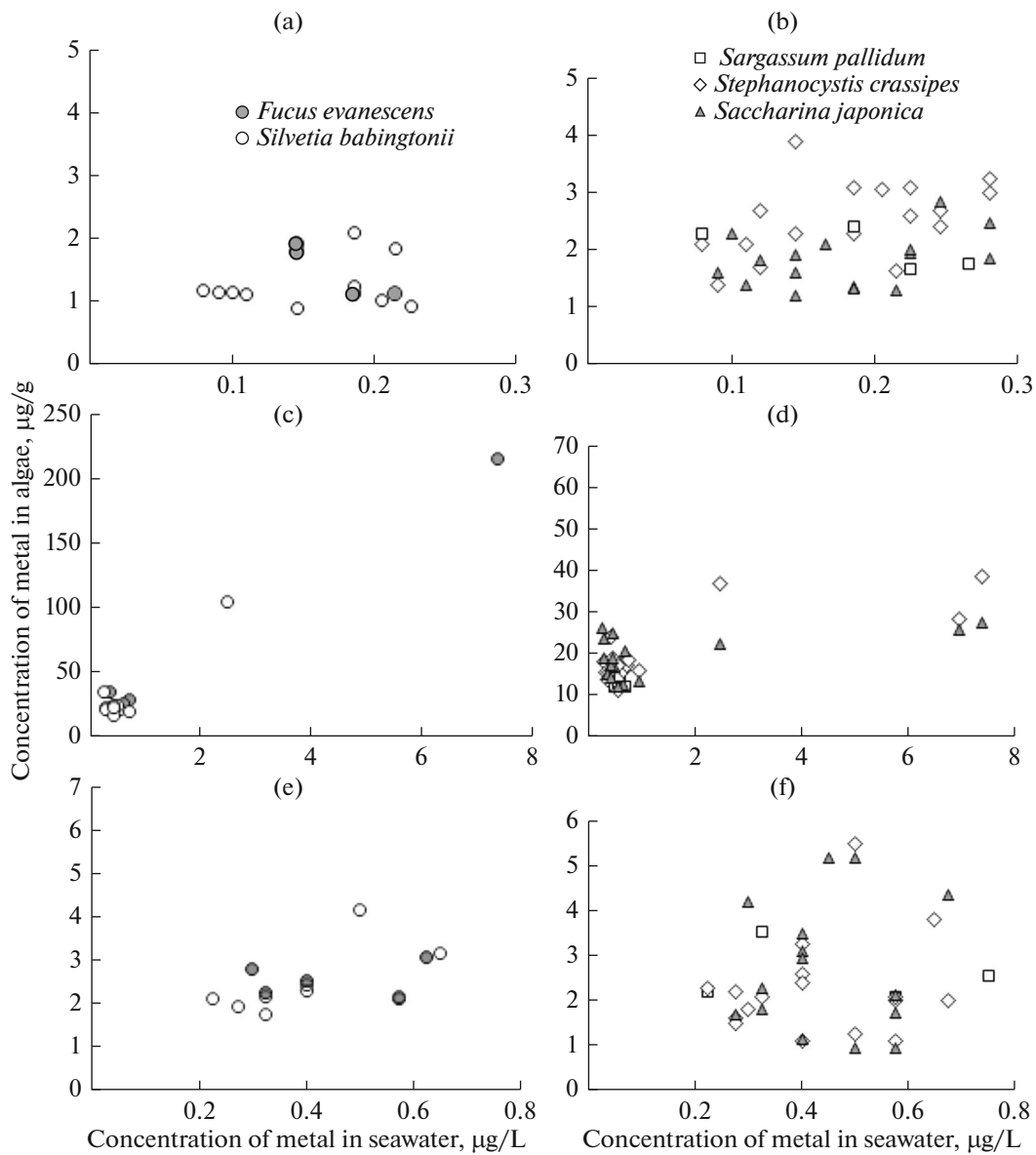
**Table 5.** The maximum concentration of metals in algae ( $\mu\text{g/g}$  d.w.) from the water areas of the Sea of Japan with background levels of dissolved metals

Species	Zn	Cd	Cu	Fe	Mn
<i>Fucus evanescens</i>	35.6 (80)	n.d. (3.1)	3.1 (4.1)	372 (100)	129 (169)
<i>Silvetia babingtonii</i>	34.3 (39)	1.2 (1.6)	5.5 (3.5)	120 (54)	16 (33)
<i>Sargassum pallidum</i>	14.3 (24)	2.3 (1.7)	3.5 (3.9)	130 (672)	183 (455)
<i>Stephanocystis crassipes</i>	23.9 (43)	2.1 (3.2)	3.3 (3.6)	142 (81)	47 (12)
<i>Saccharina japonica</i>	26.3 (43)	1.5 (2.8)	5.2 (3.9)	108 (82)	7 (8)

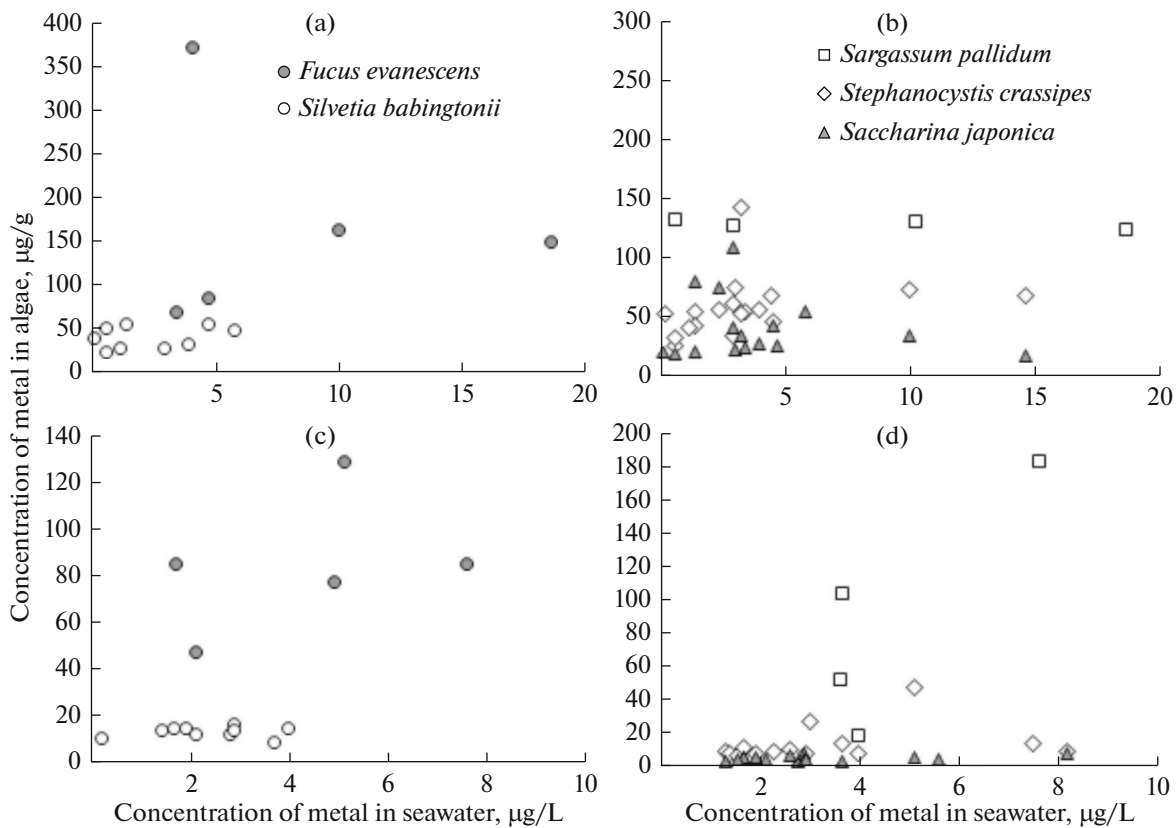
In brackets, the threshold metal concentration in algae [12]; n.d., no data.

background concentrations of dissolved Zn, the content of this element in *Fucus evanescens* (C. Agardh), *Stephanocystis crassipes*, and *Sargassum pallidum* (Turner) C. Agardh did not exceed the threshold val-

ues for these species (Table 5; Fig. 3). In algae grown in waters with concentrations of dissolved cadmium of 0.08–0.3  $\mu\text{g/L}$ , the Cd concentration did not exceed the threshold values (3.1–3.2  $\mu\text{g/g}$  in *Fucus* and



**Fig. 3.** The concentrations of Cd (a, b), Zn (c, d) and Cu (e, f) in some algal species from the western part of the Sea of Japan, with the dependence on the concentration of dissolved metal in water.



**Fig. 4.** The concentrations of Fe (a, b) and Mn (c, d) in some algal species from the western part of the Sea of Japan, with the dependence on the concentration of dissolved metal in water.

*Stephanocystis*, 1.6–1.7  $\mu\text{g/g}$  in *Silvetia* and *Sargassum*), despite the fact that the values were higher than the background (up to 0.05  $\mu\text{g/L}$ ) concentration of the element in the environment (Table 5; Fig. 3). In waters used for fishing, the maximum allowable concentration (MAC) for cadmium is 1  $\mu\text{g/L}$  [7]. Macrophytes are probably able to survive at higher Cd concentrations than the background value found for the coastal waters of the Sea of Japan, since the BAF values for algae are higher and more variable in a wider range of values for dissolved Cd in nature (up to 0.4  $\mu\text{g/L}$ ). As well, the concentration of manganese in algae did not generally exceed the threshold values in the background range of the concentration of this metal in the environment (Table 5; Fig. 4).

In the range of background concentrations of Cu in water (up to 1.2  $\mu\text{g/L}$ ), the concentration of this element in algae from the western part of the Sea of Japan reached 5.5  $\mu\text{g/g}$ , which is slightly higher than the calculated threshold concentrations, that is, from 3.5 to 4.1  $\mu\text{g/g}$  in different species of seaweeds in the Sea of Japan (Table 5; Figs. 3e, 3f). A similar situation was also observed for iron: in the background range of the concentration of this metal in the waters of the Sea of Japan (Table 5; Fig. 4) its concentration in algae exceeded the threshold level. This is probably due to

the fact that iron in seawater mainly has a suspended form, while the suspension, which sticks to thalli, can contribute to an increase in the concentration of this element in macrophytes [6, 28].

In the background range of metal concentrations in waters of the Sea of Japan, the concentrations of Cd, Zn, and Mn in algae did not exceed the threshold values for the area, while the concentrations of Fe and Cu in algae were sometimes higher than the threshold levels. For iron, this is probably due to the presence of readily available suspended forms that algae are able to accumulate. Further research is required with respect to accumulation of copper in algae.

The regression analysis of data for the Sea of Japan showed that the highest and most significant coefficients of correlation and determination ( $p < 0.05$ ) were found between the zinc concentration in water and in macrophytes, in water, and in the BAF of algae (Table 4). The absence of a significant correlation between the concentrations of Fe, Mn, Cu, and Cd in water and their concentration in algae, as well as in water, and the BAF of algae suggests that organisms live in the environment with concentrations of these elements that are physiologically determined for them (namely, background levels). The presence of a significant cor-



relation only in the range of Zn concentrations in the environment that significantly exceed the background level, that is, 0.3–7.4 µg/L (Fig. 4) confirms the hypothesis that the relationship between the element concentration in the environment and in aquatic biota is detectable only when the concentration levels in the environment and in the organic tissues differ by at least two orders of magnitude [25].

Thus, algae of the Sea of Japan, in which the metal concentrations did not exceed the threshold values, live, as a rule, in an environment with the background concentration of dissolved elements (except Cd). The lack of correlation between the contents of Cd, Fe, Cu, and Mn in the algae and in ambient water, as well as the presence of this correlation for Zn, indicates that this relationship depends on the range of concentration of the element in the environment. The highest variability and BAF values of metals in algae were recorded within the background range of metal concentrations in the environment; this allows the creation of a distinct graphical representation of the background ranges of concentrations in organisms and natural concentration ranges in their habitats. The high variability of the BAF of hydrobionts in the background environmental conditions suggests that biomonitoring data should be interpreted very carefully.

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#### COMPLIANCE WITH ETHICAL STANDARDS

The authors declare that they have no conflict of interest. This article does not contain any studies involving animals or human participants performed by any of the authors.

#### REFERENCES

1. Alimov, A.F., *Funktsional'naya ekologiya presnovodnykh dvustvorchatykh mollyuskov* (Functional Ecology of Freshwater Bivalve Mollusks), Leningrad: Nauka, 1981.
2. Burdin, K.S. and Zolotukhina, E.Yu., *Tyazhelye metally v vodnykh rasteniyakh (akkumulyatsiya i toksichnost')* (Heavy Metals in Aquatic Plants (Accumulation and Toxicity)), Moscow: Dialog MGU, 1989.
3. Burdin, K.S., Krupina, M.V., and Saveliev, I.B., Physiological mechanisms for regulating the content of heavy metals in algae, *Vestn. Mosk. Univ., Ser. 16: Biol.*, 1990, no. 2, pp. 35–42.
4. Kavun, V.Ya., Khristoforova, N.K., and Shulkin, V.M., The trace element composition of edible mussel tissues from the coastal waters of Kamchatka and the northern Kuril Islands, *Ekologiya*, 1989, no. 3, pp. 53–58.
5. Kozhenkova, S.I., Chernova, E.N., and Shulkin, V.M., Microelement composition of the green alga *Ulva fenestrata* from Peter the Great Bay of the Sea of Japan, *Russ. J. Mar. Biol.*, 2006, vol. 32, no. 5, pp. 289–296.
6. Patin, S.A. and Morozov, N.P., *Mikroelementy v morskikh organizmakh i ekosistemakh* (Trace Elements in Marine Organisms and Ecosystems), Moscow: Legkaya i Pishchevaya Promyshlennost', 1981.
7. *SanPiN 2.1.5.980-00. Prikaz Ministerstva sel'skogo khozyaistva RF ot 13 dekabrya 2016 goda no. 552 "Ob utverzhdenii normativov kachestva vody i vodnykh ob'ektov rybokhozyaistvennogo znacheniya, v tom chisle normativov predel'no dopustimyykh kontsentratsii vrednykh veshchestv v vodakh vodnykh ob'ektov rybokhozyaistvennogo znacheniya"* (Sanitary Rules and Norms 2.1.5.980-00. Order of the RF Ministry of Agriculture of December 13, 2016, no. 552 "On approval of water quality standards for water bodies of fisheries significance, including standards for maximum permissible concentrations of harmful substances in waters of water bodies of fisheries value"). Published January 16, 2017. <http://publication.pravo.gov.ru/Document/View/0001201701160006?index=12&rangeSize=1>
8. Savenko, V.S., *Khimicheskii sostav vzyeshennykh nanosov rek mira* (Chemical Composition of Suspended Matter in World Rivers), Moscow: GEOS, 2006.
9. *Sistema Belogo morya. T. II. Vodnaya tolshcha i vzaimodeystvuyushchie s nei atmosfera, kriosfera, rechnoi stok i biosfera* (The White Sea System, vol. 2: Water Column and Interacting Atmosphere, Cryosphere, River Run-Off, and Biosphere), Moscow: Nauchnyi Mir, 2012.
10. Khristoforova, N.K., Nguen Hiu Dinh, Shul'kin, V.M., Bogdanova, N.N., and Maslova, L.M., Comparison of mineral composition of *Sargassum* algae from the Sea of Japan and the South China Sea, *Sov. J. Mar. Biol.*, 1983, vol. 9, no. 3, pp. 158–163.
11. Chernova, E.N., *Zostera marina* seagrass as an indicator of environmental pollution by metals: background concentrations and ecological assessment of Peter the Great Bay, in *Sovremennoe ekologicheskoe sostoyanie zaliva Petra Velikogo Yaponskogo morya* (Current Ecological Status of Peter the Great Bay, Sea of Japan), Vladivostok: Izd. Dom Dal'nevost. Fed. Univ., 2012, pp. 382–396.
12. 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 (Engl. Transl.)*, 2016, vol. 56, no. 3, pp. 363–371.

13. Chernova, E.N. and Kozhenkova, S.I., Background metal concentrations in the green alga *Ulva lactuca* from the north-western Sea of Japan, in *Geosistemy v Severo-Vostochnoi Azii: territorial'naya organizatsiya i dinamika* (Geosystems in Northeast Asia: Territorial Organization and Dynamics), Vladivostok: Dal'nauka, 2017, pp. 522–526.
14. Shulkin, V.M., *Metally v ekosistemakh morskikh melkovodii* (Metals in Marine Shallow Ecosystems), Vladivostok: Dal'nauka, 2004.
15. Shulkin, V.M., Orlova, T.Yu., Shevchenko, O.G., and Stonik, I.V., The effect of river runoff and phytoplankton production on the seasonal variation of the chemical composition of coastal waters of the Amursky Bay, Sea of Japan, *Russ. J. Mar. Biol.*, 2013, vol. 39, no. 3, pp. 197–207.
16. Akcali, I. and Kucuksezgin, F., A biomonitoring study: heavy metals in macroalgae from eastern Aegean coastal areas, *Mar. Pollut. Bull.*, 2011, vol. 62, pp. 637–645.
17. Baumann, H.A., Morrison, L., and Stengel, D.B., Metal accumulation and toxicity measured by PAM-chlorophyll fluorescence in seven species of marine macroalgae, *Ecotoxicol. Environ. Saf.*, 2009, vol. 72, pp. 1063–1075.
18. Benoit, G., Hunter, K.S., and Rozan, T.F., Sources of trace metal contamination artifacts during collection, handling, and analysis of freshwaters, *Anal. Chem.*, 1997, vol. 69, no. 6, pp. 1006–1011.
19. Biller, D.V. and Bruland, K.W., Sources and distributions of Mn, Fe, Co, Ni, Cu, Zn, and Cd relative to macronutrients along the central California coast during the spring and summer upwelling season, *Mar. Chem.*, 2013, vol. 155, pp. 50–70.
20. Bryan, G.W., The absorption of zinc and other metals by the brown seaweed *Laminaria digitata*, *J. Mar. Biol. Assoc. U. K.*, 1969, vol. 49, pp. 225–243.
21. Bryan, G.W. and Hummerstone, L.G., Brown seaweed as an indicator of heavy metals in estuaries in South-West England, *J. Mar. Biol. Assoc. U. K.*, 1973, vol. 53, pp. 705–720.
22. Campanella, L., Conti, M.E., Cubadda, F., and Suca-pane, C., Trace metals in seagrass, algae and molluscs from an uncontaminated area in the Mediterranean, *Environ. Pollut.*, 2001, vol. 111, pp. 117–126.
23. Cantillo, A.Y., Comparison of results of Mussel Watch Programs of the United States and France with worldwide Mussel Watch studies, *Mar. Pollut. Bull.*, 1998, vol. 36, no. 2, pp. 712–717.
24. Chakraborty, S., Bhattacharya, T., Singh, G., and Maity, J.P., Benthic macroalgae as biological indicators of heavy metal pollution in the marine environments: a biomonitoring approach for pollution assessment, *Ecotoxicol. Environ. Saf.*, 2014, vol. 100, pp. 61–68.
25. DeForest, D.K., Brix, K.V., and Adams, W.J., Assessing metal bioaccumulation in aquatic environments: the inverse relationship between bioaccumulation factors, trophic transfer factors and exposure concentration, *Aquat. Toxicol.*, 2007, vol. 84, pp. 236–246.
26. Farias, D.R., Hurd, C.L., Eriksen, R.S., and Macleod, C.K., Macrophytes as bioindicators of heavy metal pollution in estuarine and coastal environments, *Mar. Pollut. Bull.*, 2018, vol. 128, pp. 175–184.
27. Fehrmann, C. and Pohl, P., Cadmium adsorption by the non-living biomass of microalgae grown in axenic mass culture, *J. Appl. Phycol.*, 1993, vol. 5, pp. 555–562.
28. García-Seoane, R., Fernández, J.A., Villares, R., and Aboal, J.R., Use of macroalgae to biomonitor pollutants in coastal waters optimization of the methodology, *Ecol. Indic.*, 2018, vol. 84, pp. 710–726.
29. *Handbook of Parameter Values for the Prediction of Radionuclide Transfer to Wildlife*, Technical Report Series, no. 479, Vienna: IAEA, 2014.
30. Haritonidis, S. and Malea, P., Seasonal and local variation of Cr, Ni and Co concentrations in *Ulva rigida* C. Agardh and *Enteromorpha linza* (Linnaeus) from Thermaikos Gulf, Greece, *Environ. Pollut.*, 1995, vol. 89, pp. 319–327.
31. Haritonidis, S. and Malea, P., Bioaccumulation of metals by the green alga *Ulva rigida* from Thermaikos Gulf, Greece, *Environ. Pollut.*, 1999, vol. 104, pp. 365–372.
32. Ho, Y.B., Metals in *Ulva lactuca* in Hong Kong intertidal waters, *Bull. Mar. Sci.*, 1990, vol. 47, pp. 79–85.
33. Horta-Puga, G., Chásaro-Olvera, S., Winfield, I., et al., Cadmium, copper and lead in macroalgae from the Veracruz Reef System, Gulf from Mexico: Spatial distribution and rainy season variability, *Mar. Pollut. Bull.*, 2013, vol. 68, pp. 127–133.
34. Jarvis, T.A. and Bielmyer-Fraser, G.K., Accumulation and effects of metal mixtures in two seaweed species, *Comp. Biochem. Physiol., Part C: Pharmacol., Toxicol. Endocrinol.*, 2015, vol. 171, pp. 28–33.
35. Jayasekera, R. and Rossbach, M., Use of seaweeds for monitoring trace elements in coastal waters, *Environ. Geochem. Health*, 1996, vol. 18, pp. 63–68.
36. Leal, F.M.C., Vasconcelos, M.T., Sousa-Pinto, I., and Cabral, J.P.S., Biomonitoring with benthic macroalgae and direct assay of heavy metals in seawater of the Oporto Coast (Northwest Portugal), *Mar. Pollut. Bull.*, 1997, vol. 34, no. 12, pp. 1006–1015.
37. Malea, P. and Haritonidis, S., Use of the green alga *Ulva rigida* C. Agardh as an indicator species to reassess metal pollution in the Thermaikos Gulf, Greece, after 13 years, *J. Appl. Phycol.*, 2000, vol. 12, pp. 169–176.
38. McGeer, J.C., Brix, K.V., Skeaff, J.M., et al., Inverse relationship between bioconcentration factor and exposure concentration for metals implication for hazard assessment of metals in the aquatic environment, *Environ. Toxicol. Chem.*, 2003, vol. 22, no. 5, pp. 1017–1037.
39. Phillips, D.J.H., Use of macroalgae and invertebrates as monitors of metal levels in estuarine and coastal waters, in *Heavy Metals in the Marine Environment*, Boca Raton, Fla.: CRC Press, 1990, pp. 81–99.
40. Reinmann, C., Filzmoser, P., and Garrett, R.G., Background and threshold critical comparison of methods of determination, *Sci. Total Environ.*, 2005, vol. 346, pp. 1–16.

41. Ryan, S., McLoughlin, P., and O'Donovan, O., A comprehensive study of metal distribution in three main classes of seaweed, *Environ. Pollut.*, 2012, vol. 167, pp. 171–177.
42. Sánchez-Quiles, D., Marbà, N., and Tovar-Sánchez, A., Trace metal accumulation in marine macrophytes: Hotspots of coastal contamination worldwide, *Sci. Total Environ.*, 2017, vol. 576, pp. 520–527.
43. Sanders, J.G. and Riedel, G.F., Trace element transformation during the development of an estuarine algal bloom, *Estuaries*, 1993, vol. 16, pp. 521–532.
44. Wang, W.-X., Fisher, N.S., and Luoma, S.N., Kinetic determinations of trace element bioaccumulation in mussel *Mytilus edulis*, *Mar. Ecol.: Prog. Ser.*, 1996, vol. 140, pp. 91–113.
45. Wang, W.-X. and Dei, R.C.H., Kinetic measurements of metal accumulation in two marine macroalgae, *Mar. Biol.*, 1999, vol. 135, pp. 11–23.
46. Zalewska, T. and Danowska, B., Marine environment status assessment based on macrophytobenthic plants as bio-indicators of heavy metals pollution, *Mar. Pollut. Bull.*, 2017, vol. 118, pp. 281–288.
47. Zbikowski, R., Szefer, P., and Latala, A., Distribution and relationships between selected chemical elements in green alga *Enteromorpha* sp. from the southern Baltic, *Environ. Pollut.*, 2006, vol. 143, pp. 435–448.

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