Vol. 24(4):325-329 | Ocean and Polar Research | December 2002

Article

The Use of the Brown Algae *Sargassum* spp. in Heavy Metal Monitoring of the Marine Environment near Vladivostok, Russia

N.K. Khristoforova*[1] and S.I. Kozhenkova[2]

[1]*Far Eastern State University, 8 Sukhanova str. Vladivostok 690600, Russia*
[2]*Pacific Geographical Institute, 7 Radio str. Vladivostok 690041, Russia*

Abstract : Concentrations of Fe, Mn, Zn, Cu, Pb and Cd in two seaweed species (*Sargassum miyabei* and *S. pallidum*) from different areas in Amursky Bay near Vladivostok were determined. An assessment of heavy metal pollution in this bay was made and the results were compared with those from some localities in the world ocean.

Key words : brown seaweed, heavy metal pollution, *Sargassum*, Amursky Bay, East Sea (Japan Sea), Russia.

1. Introduction

The use of brown seaweeds in monitoring of marine pollution by heavy metals began in Europe and Great Britain in the 1970s. The rules and approaches in their use as indicators of water quality were established in the early 1980s (Phillips 1977, 1980; Bryan 1980). Brown seaweeds belong to indicator organisms that concentrate trace elements proportionally to their concentration in sea water. Species of the genus *Fucus*, inhabiting arctic and boreal waters are widely used to evaluate pollution of shallow waters. In tropical and subtropical latitudes, the *Sargassum* spp. substitute fucoids as indicators (Ishii *et al.* 1978; Khristoforova *et al.* 1983 a, b; Mesmar 1988; Ganesan *et al.* 1991; Jayasekera and Rossbach 1996; Khristoforova and Przhemenetskaya 1999).

Seven species of the genus *Sargassum* inhabit the Far Eastern seas of Russia (Petrov 1968). Two of them, *S. pallidum* and *S. miyabei*, are widespread along the coast of southern Primorye in Peter the Great Bay (the East Sea/ Japan Sea). The ability of brown seaweeds to concentrate heavy metals and their use to assess the environmental quality have been studied in detail and described earlier for the northwestern East Sea (Japan Sea) (Khristoforova *et al.* 1983 a; Khristoforova and Przhemenetskaya 1999). This paper discusses the trace element concentrations in seaweeds from Amursky Bay (the largest Russian Far East city of Vladivostok is situated on the eastern shore of this bay).

Large volumes of industrial effluent and urban runoff are discharged into Amursky Bay. According to official data, the discharge into the bay is more than 120×10^6 m^3 of sewage annually (including 118×10^6 m^3 of urban runoff and 3.127×10^6 m^3 of agricultural effluents). More than half of the sewage (65%) is untreated, one fifth is insufficiently treated, and only 8% of waste water is treated properly (Elyakov 1993). 19.4 *tons* of copper, 14.6 *tons* of zinc, 8.6 *tons* of lead, 7.3 *tons* of cadmium flow into the bay annually (Anikiev and Perepelitsa 1995).

Some researchers studied heavy metal pollution of Amusky Bay using bottom sediments or soft tissues of bivalves (Shulkin and Kavun 1995; Tkalin *et al.* 1998). Brown seaweeds have a longer period of half-life of biologically bound metals than mollusks and, moreover, they are not capable of isolating themselves from unfavorable conditions, as it is typically for mollusks. Therefore, brown seaweeds reflect situation in the environment quite adequate and they can be used, as

*Corresponding author. E-mail : nadezhda@tig.dvo.ru

mollusks, in monitoring of sea water pollution by heavy metals. Heavy metal concentrations in brown seaweeds correspond to the quantity of bioavailable forms of metals in sea water during the period of algal vegetation. Hence, brown seaweeds have proven to be more useful in environmental monitoring than bottom sediments, where metals occur in available and unavailable forms to biota and are accumulated more long time and less fixed period. The aim of the present study was to characterize the quality of coastal areas of Amursky Bay by determining heavy metal concentrations in the thalli of *S. pallidum* and *S. miyabei*.

2. Materials and method

Samples of *S. pallidum* and *S. miyabei* were collected in the summer of 1995 and 1996 at 20 stations in Amursky Bay (Fig. 1). Five individuals of each species were sampled from each location. Seaweed thalli were cleaned and washed thoroughly to remove suspended particles of materials, dried at 85°C, homogenized and mineralized with concentrated nitric acid by heating. The Fe, Mn, Cu, Zn, Pb and Cd concentrations were determined by atomic-absorption spectrophotometry using a Hitachi-180-70 spectrophotometer. Accuracy and precision were checked by regular measurements of blanks, duplicates and certified reference materials SRM 1566a (Table 1).

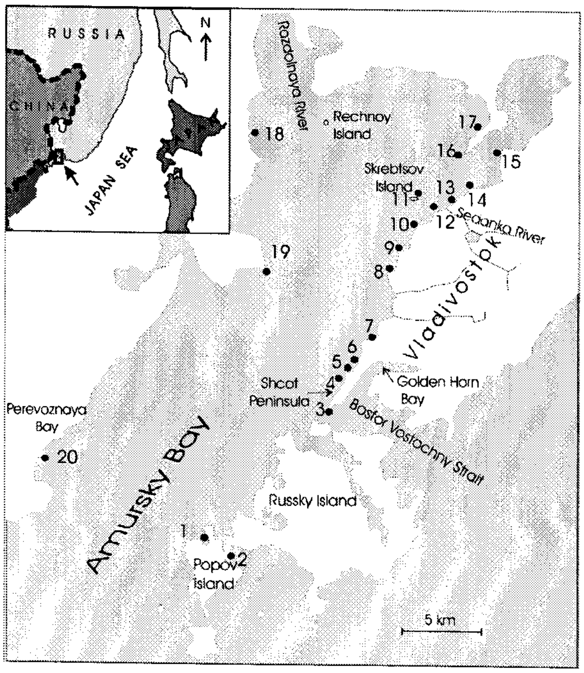

Fig. 1. Sampling sites in Amursky Bay.

Table 1. Certified and analytical ($n = 5$) concentrations of heavy metals ($\mu g \cdot g^{-1}$ dry weight) in standard reference material SRM 1566a (mean ± standard deviation).

Element	Certified data	Analytical data
Fe	539±15	528±11
Mn	12.3±1.5	12.4±0.2
Cu	66.3±4.3	68±1.1
Zn	830±57	965±14
Pb	0.371±0.014	0.3±0.1
Cd	4.15±0.38	4.6±0.1

The results were presented in $\mu g \cdot g^{-1}$ dry weight. Differences between the concentrations of metals in algae sampled in different sites were tested for significance by means of Student's *t*-test.

3. Results and discussion

The results of the summer 1995 and 1996 survey are presented in Table 2 and Table 3. Fe and Mn enter into the sea mainly via river runoff and by the process of transition into solution from sediments in shallow waters (depth about 2-3 m) by resuspension (Khristoforova *et al.* 1994). Therefore, high concentrations of Fe and Mn should be expected in macrophytes growing in areas adjacent to river mouth. As is evident, the effect of the Razdolnaya River runoff is the greatest at stations 16 and 17 located on the De-Friz Peninsula. Here, the mean Fe concentrations in *S. miyabei* are 593 and 548 $\mu g \cdot g^{-1}$ dry weight, respectively; and Mn contents are 487 and 722 $\mu g \cdot g^{-1}$. We noticed that *S. miyabei* at station 18 (Klykov Cape) had lower concentrations of iron than at stations 16 and 17 ($p < 0.01$). Despite that, this sampling site is closer to the river mouth. This may be due to the main mass of river water that moves along the northern towards the eastern shore according to the anti-cyclone rotation (Elyakov 1993). The Sedanka River runoff enriches marine environment with Fe as shown in macrophytes. Considerably high Fe concentrations were found in seaweeds taken from Fedorova Bay (stations 5 and 6) and from Tokarevsky Cape (station 3). The Shcot Peninsula with mentioned stations has no large water flows. Sand beach at Fedorova Bay in the city center makes this place attractive for citizens, while input of untreated wastes from hotels and neighboring houses, and industrial effluents leads to heavy pollution of coastal waters. A dumping place situated between stations 3 and 4 is probably the source of the metal accumulated in *S. pallidum* here. Besides, Tokarevsky Cape is the entrance to Golden Horn Bay where a great

Table 2. Heavy metal concentrations ($\mu g \cdot g^{-1}$ dry weight) in *Sargassum miyabei* in Amursky Bay (mean ± standard deviation), $n = 5$.

	Station	Year	Fe	Mn	Cu	Zn	Pb	Cd
2	Strait of Stark	1995	282±19	604±53	2.6±0.1	24.3±1.0	5.0±0.1	3.3±0.3
3	Tokarevsky Cape	1995	842±31	975±4	10.6±0.4	26.9±0.4	7.7±1.9	4.2±0.1
7	Pervaya River Bay	1995	180±30	165±13	22.3±0.3	17.9±1.1	-	3.0±0.1
8	Vtoraya River Bay	1995	400±30	1921±115	6.3±0.4	32.7±2.4	6.2±0.5	3.4±0.2
9	Grozny Cape	1996	319±56	327±59	1.9±1.6	28.8±24.4	9.2±1.8	3.0±0.4
10	Krasny Cape	1995	498±80	229±16	3.1±0.4	22.9±1.3	10.0±0.1	3.6±0.7
	- " -	1996	634±24	71±1	3.9±0.4	20.2±2.7	9.1±1.8	3.0±0.1
11	Skrebtsova Island	1995	211±28	295±69	2.0±0.2	11.5±0.4	4.9±0.1	3.2±0.4
12	Tupoy Cape	1995	542±171	1700±327	3.6±0.1	21.4±0.8	4.9±0.1	3.0±0.2
13	Sedanka River	1996	1126±37	162±5	3.9±0.4	27.1±8.2	7.4±1.5	2.9±0.2
14	Dalny Cape	1996	408±108	116±25	1.9±0.3	11.8±3.0	4.5±2.1	2.0±0.5
15	Markovsky Cape	1996	324±26	296±15	2.5±0.1	15.5±0.3	7.0±0.1	3.4±0.3
16	Tikhy Cape	1996	593±86	487±29	3.1±0.1	25.1±1.8	9.7±1.5	3.8±0.2
17	De-Friz Peninsula	1996	548±64	722±36	2.6±0.5	20.5±1.7	9.7±3.1	4.9±0.6
18	Klykov Cape	1996	323±56	456±31	2.5±0.9	17.1±1.2	7.4±1.5	3.1±0.4
20	Perevoznaya Bay	1995	492±36	364±40	2.3±0.1	14.0±1.4	4.9±0.1	3.4±0.3

Table 3. Heavy metal concentrations ($\mu g \cdot g^{-1}$ dry weight) in *Sargassum pallidum* in Amursky Bay (mean±standard deviation), $n = 5$.

	Station	Year	Fe	Mn	Cu	Zn	Pb	Cd
1	Alekseeva Bay	1995	1783±135	1450±124	5.1±0.8	16.8±0.4	2.5±0.1	3.6±0.1
3	Tokarevsky Cape	1995	977±10	1752±87	5.8±1.1	35.9±4.7	10.0±0.1	2.7±0.1
4	Kupera Cape	1995	347±13	1311±90	3.5±0.1	23.1±2.6	5.0±0.1	3.1±0.2
5	Fedorova Bay, south	1995	1832±266	856±12	5.8±0.2	46.3±1.5	13.2±0.2	3.8±0.1
6	Fedorova Bay, north	1995	2815±562	564±50	5.6±1.2	30.4±0.5	9.9±0.2	4.6±0.5
12	Tupoy Cape	1996	353±37	368±54	2.6±0.2	18.9±8.4	8.8±1.5	3.0±0.5
14	Dalny Cape	1995	386±36	160±9	2.3±0.2	16.0±0.6	4.8±0.6	3.5±0.2
19	Peschany Cape	1995	307±13	414±32	2.6±0.1	16.2±0.1	4.9±0.1	3.8±0.1
20	Perevoznaya Bay	1995	83±3	19±2	1.2±0.1	5.9±0.1	1.5±0.1	1.2±0.1

number of ships, metal piers and shipyards are located. Steel corrosion increases Fe levels in both marine environment and organisms.

Both *Sargassum* species collected near Tokarevsky Cape (St. 3) contain high amount of copper and zinc. This indicates a heavy anthropogenic pressure in this part of the coast. A similar situation is also found at stations 5 and 6 (Fedorova Bay), 8 and 9. The main pollution sources here are sewage as well as bottom sediments (Tkalin 1992; Tkalin *et al.* 1998). Thus it was reported that the Zn and Cu concentrations in bottom sediments of the southern coastal part of Vladivostok were 300 and 50 $\mu g \cdot g^{-1}$ dry weight, respectively (Anikiev *et al.* 1993). This is ten times higher than background levels. Relatively high levels of copper and zinc in seaweeds were noticed at Krasny Cape and near the Sedanka River mouth, suggesting the influence of local waste waters. As expected, the lowest metal concentrations in macrophytes were found at sites located far from the coast (station 11 - Skrebtsova Island) and from direct sources of pollution (station 14 - Dalny Cape, station 20 - Perevoznaya Bay) as well. It is interesting that the zinc concentrations in the bottom sediments around Skrebtsova Island and at Tokarevsky Cape are approximately equal, 81 and 75 $\mu g \cdot g^{-1}$ dry weight, respectively (Tkalin *et al.* 1998). In contrast, significant difference in concentrations of Zn was found in *S. miyabei* ($p<0.01$), suggesting increased contents of bioavailable forms of Zn in sea water around the Shcot Peninsula as a result of waste water discharge.

High concentrations of Pb in *S. pallidum* occurred in Fedorova Bay and at Tokarevsky Cape. This suggests input of Pb from an industrial source to the environment. High concentrations of Pb in *S. miyabei* at Krasny Cape could be explained by the influence of effluents that are transported by the flows from the heavily industrialized area of the Vtoraya River. The marine environment at Tokarevsky Cape is affected adversely by waste waters that flow into Golden Horn Bay and Bosfor Vostochny Strait, as well as by the resuspension of polluted sediments, gas discharged from automobiles and small vessels.

High concentrations of Fe, Mn, Cu and Cd in *S. pallidum* from Alekseeva Bay (Popov Island) are comparable with those in seaweeds sampled at Tokarevsky Cape and from Fedorova Bay. Considerable pollution by heavy metals of this area, was shown previously by mollusks (Chernova *et al.* 1988; Vaschenko *et al.* 1999).

Sargassum miyabei at Krasny Cape was sampled in 1995 and 1996. Concentrations of Zn, Cu, Pb and Cd are very similar, suggesting that anthropogenic impact in this area remains unchanged. At the same time, Fe concentrations are different in these years, perhaps due to weather-related change in hydrochemical parameters.

Considering environmental situation in Amursky Bay, we notice that the cleanest sites are Dalny Cape near the Sanatornaya railway station where a suburban recreation zone is located and Perevoznaya Bay situated on the western coast of Amursky Bay that is distant from sources of heavy metals flow into the Sea. The Zn, Pb, Cu and Cd concentrations in brown algae taken from these localities and from Skrebtsova Island are comparable with concentrations of these metals in seaweeds from Marine Reserve islands in the southwestern part of Peter the Great Bay, such as the De-Livrona Island (Khristoforova *et al.* 1983 a; Khristoforova 1989) (Table 4). Thus, the concentrations at the stations 11, 14 and 20 could be considered as control or background for Amursky Bay.

Accumulation of metals in organisms can vary depending on the industrial development of a region and anthropogenic load to marine ecosystems, as well as the intensity of water interaction between neighboring areas, and terrigenous runoff and the chemical composition of rocks.

We compare our results with the data for other localities (for instance, Sri Lanca in the Indian Ocean, northwestern coast of Qatar, Honmia Island in the South China Sea, Raul Island (Kermadek Archipelago) in the southwest Pacific Ocean - Table 4). Concentrations of Zn and Cd reflecting anthropogenic input on the marine environment are higher in the seaweeds of Amursky Bay of the East Sea (Japan Sea) than in some other regions. On the other hand, the zinc concentrations in the most contaminated localities of Amursky Bay, i.e., Tokarevsky Cape as well as Fedorova and Vtoraya River Bays, are one order of magnitude lower than in the Red Sea near Aqaba Port.

In conclusion, *S. pallidum* and *S. miyabei* collected along the shore of Amursky Bay in the summer of 1995 and 1996 were found to be heavily contaminated with Fe, Mn, Zn and Cu especially in the sites where industrial effluents and urban runoff are discharged. The results of this study, thus, indicates that metal pollution in the

Table 4. Trace metal concentrations ($\mu g \cdot g^{-1}$ dry weight) in *Sargassum* spp. in some locations of the World Ocean.

Location	Species	Fe	Mn	Cu	Zn	Pb	Cd
De-Livrona Island, Peter the Great Bay, Russia, Japan Sea (background)[1]	*S. miyabei*	42	5	2.3	13	5.7	3.0
	S. pallidum	30	12.8	1.7	16.2	6.0	1.5
Honmia Island, Vietnam, South-China Sea[1]	*S. policystum*	127.7	31	2.9	8.1	ndl[a]	1.4
	S. swartzii	140.5	7.4	2.7	5.5	ndl	1.0
	S. mcclurei	139.3	125.8	3.9	12.2	ndl	2.9
Raul Island, Kardemak Archipelago, Pacific Ocean (background)[1]	*Sargassum sp.*	82.1	6.9	1.4	6	ndl	ndl
Sri Lanca, Indian ocean (background)[2]	*S. filipendula*	-[b]	-	-	7	-	0.35
Galf of Mannar, India, Indian Ocean[3]	*S. wightii*	507	90	25.5	99	-	-
	S. johnstonii	466	110	28.5	38.5	-	-
Coast of Qatar, Arabian Gulf: a-north-west coast (background), b-Doha-city[4]	*S. binderi (a)*	1.6	5.3	0.8	1.5	0.9	0.2
	S. binderi (b)	43.1	6.2	5.1	11.8	1.9	0.6
	S. heteromorphum (a)	12.8	5.4	4.5	5.4	2.1	0.4
	S. boveanum (a)	ndl	3.9	2.2	ndl	7.3	0.2
Aqaba Port, Jordan, Red Sea[5]	*S. asperifolium*	-	-	-	193±7[c]	9.4±1.7	6.8±0.1
	S. subrepandum	-	-	-	203±10	9.1±0.7	6.9±0.1
	S. neglectum	-	-	-	211±10	7.9±0.6	7.2±0.6

[1]Khristoforova 1989; [2]Jayasekera and Rossbach 1996; [3]Ganesan *et al.* 1991; [4]Kureishy 1991; [5]Mesmar 1988.
[a]non-detectable levels; [b]no data; [c]mean ± standard deviation.

marine environment near Vladivostok City is as serious as in some other harbor-cities of different geographical localities.

Acknowledgements

We thank Alena Kiseleva and Victoria Khazova for assistance with field sampling and Tatiana Primak and Galina Vlasova for chemical analyses of biological materials, and Tatiana Koznova for consulting the English version of the manuscript.

References

Anikiev, V.V. and S.A. Perepelitsa. 1995. Estimation of trace element fluxes in the coastal zone of the Japan Sea. *Geochemistry*, 3, 415-425 (In Russian).

Anikiev, V.V., S.A. Perepelitsa, and E.N. Shumilin. 1993. Estimation of influence of antropogenic and natural sources on spatial distribution of heavy metals in bottom sediments of Peter the Great Bay (Sea of Japan). *Geochemistry*, 9, 1328-1340 (In Russian).

Bryan, G.W. 1980. Recent trends in research on heavy-metal contamination in the sea. *Helgolander Meeresuntersuchungen*, 33, 6-25.

Chernova, E.N., V.Yu. Kavun, and N.K. Khristoforova. 1988. The evaluation of chemico-ecological conditions in the areas of mollusks cultivation by the trace element content of Mytilus edulis. *Russian J. Marine Biol.*, 4, 71-74.

Elyakov, G.B. ed. 1993. *The Long-Term Program of Environment Protection and Rational Use of Natural Resources in the Primorskii Krai until 2005 Year (the Ecological Program)*. Part 2. FEB RAS, Vladivostok, 301 p (In Russian).

Ganesan, M., R. Kannan, K. Rajendran, C. Govindasamy, P. Sampathkumar, and L. Kannan. 1991. Trace metal distribution in seaweeds of the Gulf of Mannar, Bay of Bengal. *Marine Poll. Bull.*, 22, 205-207.

Ishii, T., H. Suzuki, and T. Koyanagi. 1978. Determination of trace elements in marine organisms. I. Factors for variation of trace elements. Nippon Suisan gakkaishi. *Bull. Japanese Soc. Scientific Fisheries*, 44, 155-162.

Jayasekera, R. and M. Rossbach. 1996. Use of seaweeds for monitoring trace elements in coastal waters. *Environmental Geochemistry and Health*, 18, 63-68.

Khristoforova, N.K. 1989. *Bioindication and Monitoring of Sea Water Pollution by Heavy Metals*. Nauka, Leningrad, 192 p (In Russian).

Khristoforova, N.K., N.N. Bogdanova, and L.M. Tolstova. 1983a. Mineral composition of Pasific sargasso weeds with respect to the problem of monitoring of water pollution. *Oceanology*, 23, 270-275 (In Russian).

Khristoforova, N.K., Hiu Dinh Nguyen, V.M. Shulkin, N.N. Bogdanova, and L.M. Maslova. 1983 b. Comparison of mineral composition of sargasso weeds from Japan and South China Seas. *Russian J. Marine Biol.*, 3, 48-54.

Khristoforova, N.K. and V.F. Przhemenetskaya. 1999. Sargassaceae as promoting objects for sanitary mariculture. p. 335-341. In: *Proceedings of the International Symposium "Earth-Water-Humans"*. Kanazawa University, Kanazawa.

Khristoforova, N.K., V.M. Shulkin, V.Yu. Kavun, and E.N. Chernova. 1994. *Heavy Metals in Wild and Cultured Species of Marine Mollusks in Peter the Great Bay*. Dalnauka, Vladivostok, 296 p (In Russian).

Kureishy, T.W. 1991. Heavy metals in algae around the coast of Qatar. *Marine Poll. Bull.*, 22, 414-416.

Mesmar, M.N. 1988. Levels of zinc, cadmium and lead in some marine algae from Aquaba Red Sea. *Acta Biologica Hungarica*, 39, 345-349.

Petrov, Yu. 1968. Genus *Sargassum* in the Far Eastern seas of the USSR. p. 42-48. In: *Novosti Sistematiki Nizshikh Rastenii*. Botanical Institute, Leningrad (In Russian).

Phillips, D.J.H. 1980. *Quantative Aquatic Bioligical Indicators*. Elsevier, London, 488 p.

Phillips, D.J.H. 1977. The use of biological indicator organisms to monitor trace metal pollution in marine and estuarine environments a review. *Environmental Pollution*, 13, 381-417.

Shulkin, V.M. and V.Ya. Kavun. 1995. The use of marine bivalves in heavy metal monitoring near Vladivostok, Russia. *Marine Poll. Bull.*, 31, 330-333.

Tkalin, A.V. 1992. Bottom sediment pollution in some coastal areas of the Japan Sea. *Ocean Res.*, 14, 71-75.

Tkalin, A.V., T.S. Lishavskaya, and V.M. Shulkin. 1998. Radionuclides and trace metals in mussels and bottom sediments around Vladivostok, Russia. *Marine Poll. Bull.*, 36. 551-554.

Vaschenko, M.A., L.N. Luchsheva, P.A. Zhadan, N.N. Belcheva, I.G. Syasina, and A.V. Silina. 1999. Evaluation of ecological situation in Alekseev Bay (Peter the Great Bay, Sea of Japan) by biological and biogeochemical indices. *Russian J. Marine Biol.*, 2, 96-97.

Received Jan. 31, 2002
Accepted Dec. 24, 2002