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SHORT COMMUNICATIONS

Long-Term Monitoring of Sea Water Pollution by Heavy Metals in Northern Primorye with the Use of Brown Algae

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Macrophytic brown algae are used as indicator organisms for estimating and controlling the level of heavy metal pollution of sea and estuarine waters. The main factor making them suitable for permanent monitoring of environmental quality is that the concentration of microelements in their tissues does not undergo short-term fluctuations which occur in sea water and serves as an average integral parameter characterizing the relative biological accessibility of metals under certain conditions.

In northern Primorye, brown algae have been used for monitoring ecological conditions in coastal sea waters since 1976 (Khristoforova *et al.*, 1981). The part of the coast adjoining the Dal'negorskii mining region is characterized by very high contents of some heavy metals in the environment and organisms. As lead and zinc ores are mined and processed there, the main pollutants brought by the Rudnaya River and by air are zinc, lead, and accompanying elements: copper, cadmium, and others. The contribution of this region to the total water pollution in Primorye is 64.6% by lead and 77.7% by zinc (*Doklad* ..., 1995).

Because of recession, the amount of pollutants released to the environment decreased by 1993 both in the entire Primorye area and the Dal'negorskii region. As the mining and processing of ores at industrial enterprises decreased by a factor of 1.5–2.0, a lower level of sea water pollution in the coastal zone could be expected. However, the relationship between environmental changes and the level of industrial activity is not linear. Hence, the purpose of our investigation was to determine the existing level of heavy metal pollution of coastal waters using brown algae as indicators and to estimate its dynamics in the last years.

The algae were collected on the northwestern coast of the Sea of Japan in July 1997. Samples were taken simultaneously from the same depth at several stations located in the middle horizon of the littoral zone and differing in the intensity of technogenic impact (Fig. 1). These stations formed a line extending from the north to the south through the Lidovka and Rudnaya bays and the coastal area located 8 km to south of the latter. In general, algae were collected at the same sites as in previous years. Station 1 was on the southern bench of Lidovka Bay. The Lidovka River flowing to this bay is much less affected by technogenic factors than the Rudnaya River. Stations 2 and 3 were located in Rudnaya Bay at different distances from the estuary of the river that brings dissolved and suspended pollutants. Station 4 was on the southern end of Cape Briner at the entrance of the bay, approximately 4 km away from the river estuary. Stations 5 and 6 (kekurs named Two Brothers and the Monastyr' rock) were located 1 and 8 km away from Cape Briner, respectively. The first and the last stations served as control ones.

The weather in the period before taking samples of algae remained stable. Of the mass species of brown algae typical for northern Primorye, *Fucus evanescens* and *Scytosiphon lomentaria* growing at all the stations were chosen. The algae were collected and prepared for analysis according to the standard procedure (Khristoforova, 1989). The contents of Fe, Zn, Pb, and Cu were determined by atomic absorption spectrophotometry (Hitachi 180–70; error of method 7–10%). The results are the averages of three replications. Concentrations of the metals are expressed as μg/g dry weight.

Heavy metal pollution of the marine environment in the study region is accounted for by atmospheric fallout and river discharge. The principal sources of air and surface water pollution in the village of Rudnaya Pristan' are gases and dust emitted from the lead and cadmium smeltery built in the 1930s, at which obsolete technologies of lead smelting and purification of lead-containing waste gases are still employed. On average, 40 metric tons of lead are released into the atmosphere each year (*Doklad* ..., 1996), and its content in the air within the area exceeds the maximum admissible concentration (MAC) by a factor of 10–12. The effect of gas and dust emissions is observed in the area of up to 100 km^2, and a zone with strongly disturbed ecosystems (approximately 5–8 km^2 in area) was formed within a radius of 2 km along the direction of prevailing winds (Elpat'evskii *et al.*, 1976).

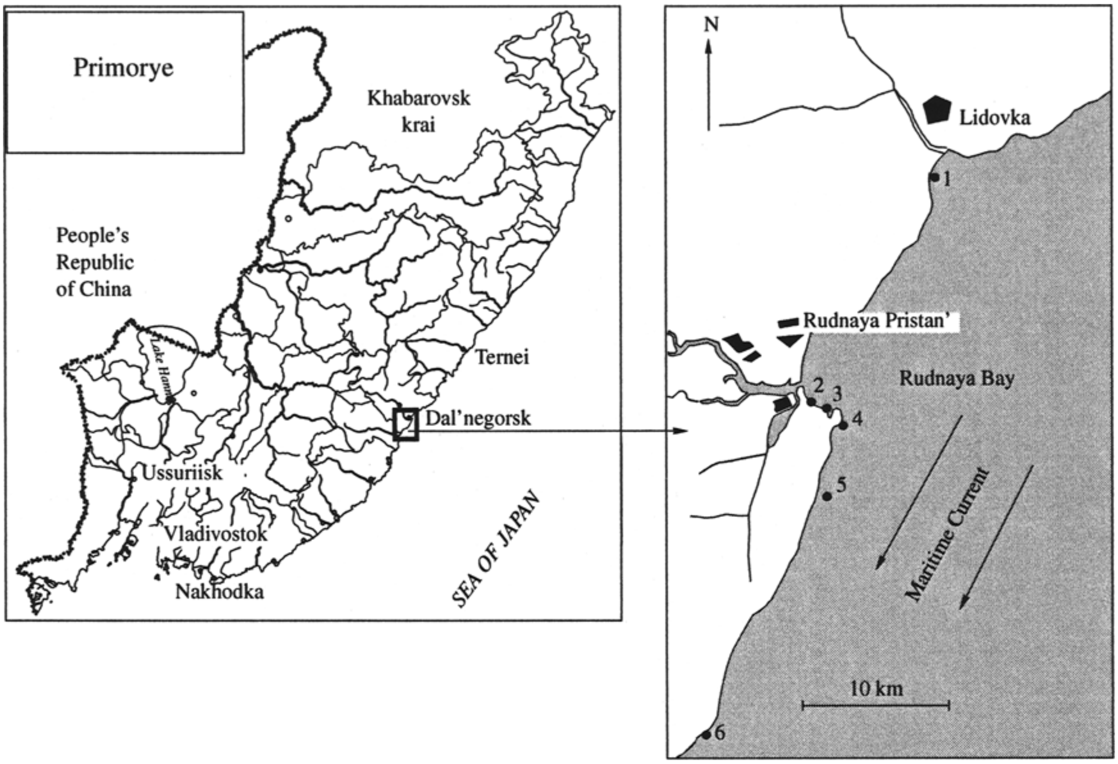

Fig. 1. Region of studies.

Waters of the Rudnaya River are polluted with ions of metals and their compounds. Zinc content exceeds MAC by a factor of 13–50; in 1995, this excess was even 100-fold. Such an extremely high level of pollution with zinc was explained by its washing out of the dumps of the Primorskii mine, which was put out of operation without proper conservation. In general, technogenic macroelements in the Rudnaya River estuary account for 40–50% of their total content in water; in cases of Zn, Pb, and Cu (microelements), the corresponding proportions are 90, 80, and 75%, respectively (*Dolgovremennaya programma* ..., 1993).

The river brings up to 20000 t of various technogenic elements to Rudnaya Bay, thus polluting both sea water and bottom sediments. Mn, Zn, Pb, and Cd concentrations in bottom sediments of the bay exceed the background values by a factor of more than 10. According to recent data, heavy metals accumulated in the sediments can serve as a source of secondary environmental pollution for at least 50–100 years after the cessation of technogenic impact.

Brown algae adequately reflect spatial changes of metal contents in the water. Table 1 indicates that pollutant concentrations in *Scytosiphon* collected in 1997 were maximal at the second station (*Fucus* disappeared from this station because its ecotope was destroyed during the construction of a gravel road, which changed the morphology of the coastal bench). At greater distances from the source of pollution, the content of metals in the algae decreased. For example, Cu and Zn concentration in *Scytosiphon* collected at the mouth of Rudnaya Bay (station 4) were more than twice as low as at station 2. The minimal contents of metals, as expected, were detected in the algae collected at the northernmost station, in Lidovka Bay.

The ability of macrophytic algae to accumulate metals depends both on the form in which the metal is found in the environment and on specific morphological and biochemical features of the macrophyte. The comparison of microelement compositions of two algal species indicated that *Scytosiphon* concentrates more Fe and Pb, whereas *Fucus* concentrates more Zn and Cu. In coastal waters, Fe and Pb are mainly found in suspended particles and, hence, are easily adsorbed on *Scytosiphon* plants, which have a large specific surface area (Khristophorova, 1985). Hence, iron and lead contents in *Scytosiphon* are two to five times higher than in *Fucus*. This difference in heavy metal concentration is especially obvious at stations 1, 2, and 6, which are strongly affected by the terrigenous flow. Insoluble metal hydroxides settled on the thalli are transformed into ionic forms due to the acidification of a thin surface layer by CO_2 during respiration, and these ionic forms are fixed in plant cells (Patin, 1977; Khristoforova *et al.*, 1981). Zn and Cu in the sea are mainly in the dissolved state, and fleshy *Fucus* thalli accumulate them more intensely than *Scytosiphon*, as the binding of these metals by brown algae depends directly on the

Table 1. Changes of metal contents in brown algae from Rudnaya Bay and adjacent water areas, µg/g dry weight

Station number	Species of algae	Year	Fe	Cu	Zn	Pb
1	*F. evanescens*	1978**			55	7.0
		1980**			83	12.0
		1989	88 ± 15	2.5 ± 0.5	93 ± 10	9.7 ± 1.4
		1997	50 ± 3	1.8 ± 0.0	61 ± 1	5.8 ± 0.6
	S. lomentaria	1979*	500	4.4		26.0
		1989	525 ± 59	3.3 ± 0.1	42 ± 1	10.6 ± 0.0
		1997	82 ± 4	1.8 ± 0.1	9 ± 0	7.3 ± 0.2
2	*F. evanescens*	1976**			790	37.2
		1978**			1100	40.7
		1979***	50	8.9	915	21.2
	S. lomentaria	1997	387 ± 43	7.4 ± 1.0	207 ± 10	26.4 ± 2.0
3	*F. evanescens*	1997	79 ± 6	8.4 ± 0.1	834 ± 4	14.3 ± 1.9
	S. lomentaria	1997	150 ± 6	3.5 ± 0.2	67 ± 15	14.1 ± 0.2
4	*F. evanescens*	1976**			169	13.1
		1978**			245	13.8
		1979***	65	5.2	230	12.8
		1987	69 ± 6	2.1 ± 0.2	215 ± 17	12.8 ± 1.3
		1989	49 ± 45	4.7 ± 1.2	235 ± 38	10.2 ± 2.0
		1997	59 ± 5	2.7 ± 0.2	171 ± 14	8.2 ± 0.8
	S. lomentaria	1987	185 ± 111	2.1 ± 0.2	56 ± 4	14.0 ± 0.1
		1989	517 ± 96	7.3 ± 1.4	121 ± 7	30.0 ± 2.0
		1997	295 ± 29	2.9 ± 0.4	94 ± 7	21.8 ± 1.2
5	*F. evanescens*	1997	102 ± 10	4.1 ± 0.2	190 ± 4	11.7 ± 0.9
	S. lomentaria	1987****	265 ± 11	2.7 ± 0.3	77 ± 7	25.3 ± 7.5
		1989	264 ± 15	5.2 ± 0.6	95 ± 1	28.2 ± 13.1
		1997	130 ± 9	3.0 ± 0.9	52 ± 0	12.3 ± 0.8
6	*F. evanescens*	1979*	95	3.6	130	9.3
		1997	40 ± 2	2.6 ± 0.2	119 ± 6	6.8 ± 0.3
	S. lomentaria	1979*	185	2.0	62	20.0
		1997	175 ± 3	2.9 ± 0.3	45 ± 1	11.8 ± 0.4

* Khristophorova, 1985.
** Khristoforova, 1987.
*** Khristoforova, 1989.
**** Khristoforova *et al.*, 1990.

content of alginates in the thalli (Khristoforova *et al.*, 1990).

In the 1990s, the total amount of pollutants dumped into the Rudnaya River basin decreased due to recession. However, the input of heavy metals to the river did not change significantly: their amount either remained the same or decreased slightly (Table 2). At the same time, the volume of atmospheric emissions decreased essentially: in Dal'negorsk, for example, this volume in 1995 was 66% lower than in 1990 (*Doklad* ..., 1996).

As the main mass of pollutants enters the marine environment with airborne particles settling from the atmosphere (lead is a good example), the decrease of heavy metal emissions in the lower air layers was immediately reflected in the chemical composition of the brown algae. Comparing the amounts of metals in algae with those detected in previous years, we revealed a decrease in the concentrations of Zn, Pb, and Cu (Table 1, Fig. 2). In *Fucus* thalli from Cape Briner, for example, these concentrations in 1997 proved to be 1.5–2 times as low

Table 2. Parameters of discharge into the Rudnaya River basin (*Doklad* ..., 1995, 1996)

Ingredients	1992	1993	1994	1995
Total, million m^3/year	20.78	19.967	18.038	16.889
Polluted discharge, t	20.57	19.91	17.97	16.825
Fe	3.396	15.61	7.033	6.93
Cu	0.053	0.054	0.062	0.06
Zn	2.241	1.781	2.498	2.299
Pb	0.2898	0.304	0.295	0.2273

as in 1979. In *Scytosiphon*, the contents of these metals also decreased.

Differences in metal concentrations between algae collected in 1989 and 1997 were especially pronounced (in 1989, technogenic pressure reached its peak). This can be illustrated using an example of *Scytosiphon* from station 4: Zn, Pb, and Cu concentrations in its thalli decreased by factors of 1.3, 1.4, and 2.5, respectively. In general, the mining industry steadily developed in the region until 1989, and this period was characterized by a significant technogenic impact on the environment, as reflected in high concentrations of zinc in algae and their slight annual variation (except for 1976, in which zinc content in macrophytes was lower). The data on lead are somewhat contradictory. In some cases, its content in algae increased with a decrease in zinc concentration, and vice versa. It should be noted, however, that the bulk of Pb comes to the sea from the atmosphere, and the efficiency of its retention by industrial filters has been increasing from year to year owing to the improvement of dust traps. This process, stimulated by severe penalties for air pollution, became especially noticeable after environmental agencies operating at different levels were organized in 1988. Taking these facts into account, it can be concluded that the amount of lead in the environment is not directly associated with the intensity of the production process. Moreover, it is known that even putting the enterprise out of operation does not prevent the release of lead into the atmosphere, as its compounds are present in automobile exhausts and in dust, which is the secondary source of air pollution.

It is apparent that a decrease in the level of water pollution with airborne heavy metals in Rudnaya Bay resulted in the improvement of local chemical and ecological conditions. Concentrations of Zn and Pb in algae decreased especially strongly at station 1 (the control station was not affected by water flowing from the Rudnaya River). Changes observed at the other stations are less pronounced, which is probably explained by secondary water pollution with metals accumulated in bottom sediments.

Thus, our investigations in 1997 confirmed the previous data on the pattern of sea water pollution with heavy metals in Rudnaya Bay and adjacent coastal areas. The minimal concentrations of metals were found in macrophytes from Lidovka Bay, and the highest concentrations were found in algae growing near the Rudnaya River estuary and the lead and zinc smeltery. Long-term observations on the content of heavy metals in macrophytes growing in this area of northern Primorye indicated the improvement of local environmental conditions with respect to Zn, Pb, and Cu concentrations, which is explained by reduced industrial activity in the region, the use of more efficient dust traps and filters in recent years, and, hence, the decreased discharge of these metals into the sea.

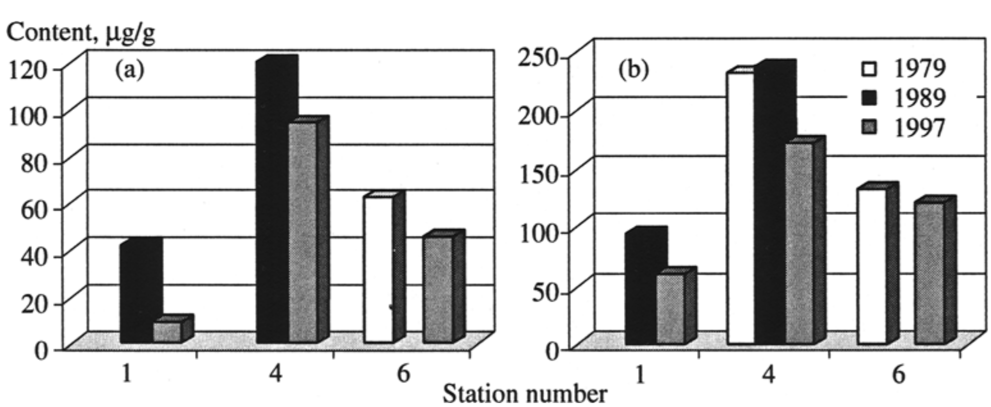

Fig. 2. Zinc contents in thalli of (a) *Scytosiphon* and (b) *Fucus*.

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