The Features of Heavy Metal Accumulation in Water, Bottom Sediments and Biota of the Cherkalov Sor Bay at Lake Baikal

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Abstract

The seasonal dynamics of heavy metals (Fe, Mn, Zn, Cu, Cr, Ni, Co, Cd, Pb) in water, bottom sediments is shown; their concentrations in the higher aquatic plants (*Elodea canadensis*) and in zoobenthos (*mollusca bivalvia*) from the Cherkalov Sor bay of Lake Baikal are analyzed. It was established that the maximum permissible concentrations for fishery water bodies are exceeded for Fe, Mn, Zn, Cu in water all year long, for Pb during spring tide. The concentrations of all these metals in bottom sediments in fractions <60 mm exceeds the background values by 20–50 %, accumulation of Cd is almost 3 times higher. It is shown that redistribution of Mn, Zn, Cu, Cd is substantially affected by aquatic plants and mollusca.

INTRODUCTION

A substantial role of shallow bays in the formation of the quality of water entering a lake and in the ecological status of water body causes the necessity to investigate the pollution of bays. One of the most impartial and reliable parameters of pollution of a water body and the index of general anthropogenic load on it is the content of heavy metals (HM) in water, bottom sediments (BS) and in biota. Unlike organic substances, HM are not prone to degradation and can only migrate and accumulate in the components of a natural ecosystem. Accumulation of HM in BS at a level above the maximum permissible concentrations and the background brings danger for water quality due to the possibility of secondary pollution, that is, ejection of microelements from BS in water [1–3]. High HM concentrations in BS have unfavourable effect on the biological components [4–6]. Since hydrobionts actively accumulate chemical compounds, including HM, from water, the information about the concentrations of HM in natural water is important for better understanding of the effect of metal-containing compounds on water organisms. A true picture of water quality and ecological status of a natural water body and a stream should include a complex evaluation of the concentrations of various chemical compounds in the components of the water ecosystem.

The goal of the present work is to determine the concentrations of heavy metals in the ecosystem of the Cherkalov sor bay (Istomin sor) and to reveal the character of their accumulation in the chain: water – plants – zoobenthos – BS.

OBJECTS AND METHODS OF INVESTIGATION

The Cherkalov Sor bay is a water body of the lakeside region which is separated from Lake Baikal by a narrow sand spit partitioned

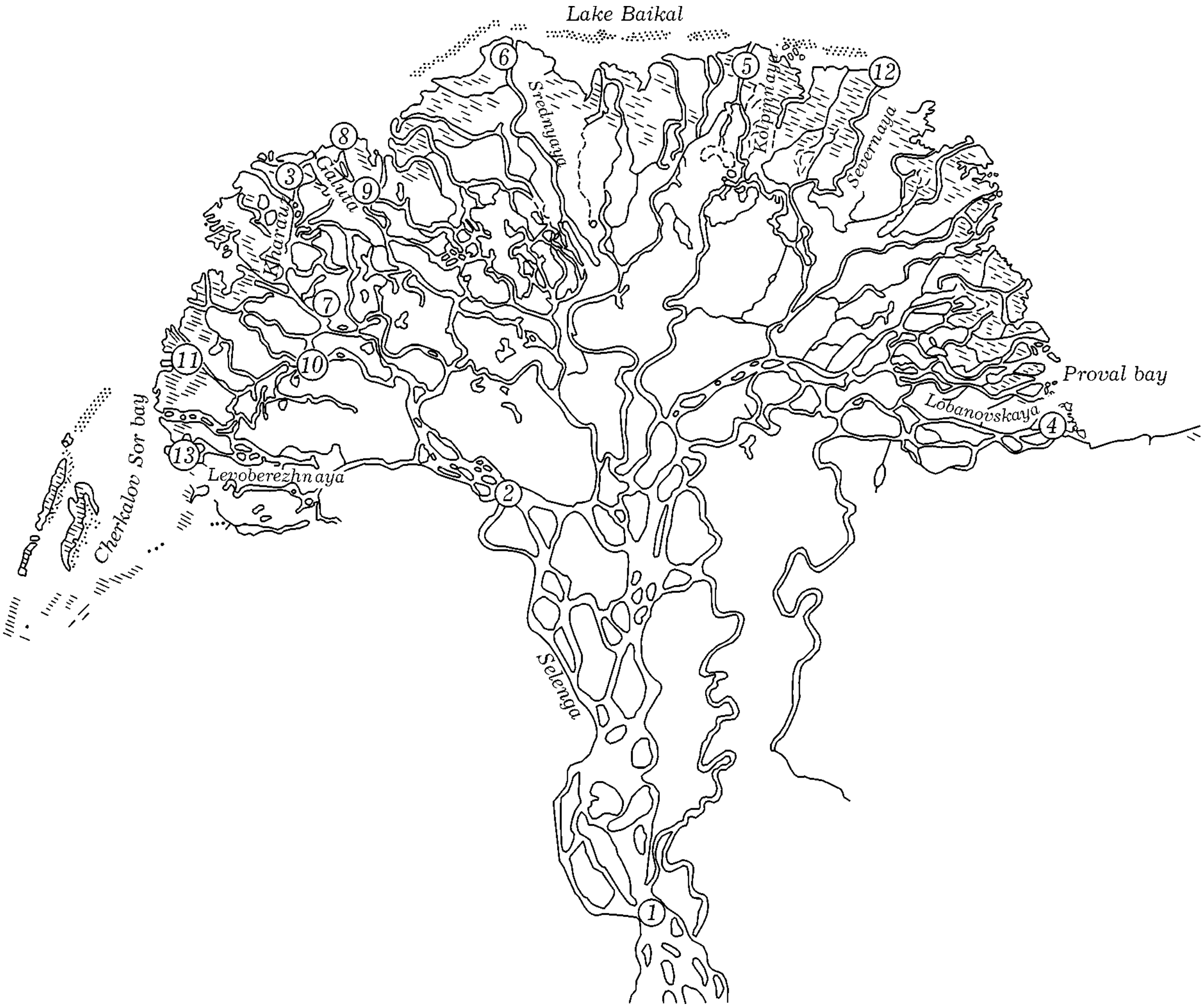

Fig. 1. Schematic map of the Cherkalov Sor bay of Lake Baikal: *1* – the Selenga River, Kabansk settlement, *2* – the Selenga River, Murzino settlement, *3* – the channel of the Kharauz River, mouth, *4* – the Lobanovskaya channel, mouth, *5* – the Kolpinnaya channel, mouth, *6* – the Srendyaya channel, mouth, *7* – Lake Zavernyaikha, *8* – the Galuta channel, mouth, *10* – the Selenga River, Semenovskiy island, *11* – the Shamanka channel, mouth, *12* – the Severnaya channel, mouth, *13* – the Levoberezhnaya channel, mouth.

by several breaks (Fig. 1). The maximal depth of the water body is at 2.5 m, prevailing depth is 2.0 m, surface area is 14 km^2. Lifting of the level of Lake Baikal due to the construction of the Irkutsk hydroelectric power plant caused substantial reformation of sand islands and spits which formerly were separating the bay from the lake. As a result, the hydrodynamic regime and the conditions of alluvium deposition changed; the soil and plant ecosystems were excluded from the natural development. Flood of low rushy islands in the lakeside region caused putrefaction of aquatic vegetation, flood of dumps resulted in extraction of HM and other components from flooded soil into water. At the same time, the Cherkalov sor bay is intensively used for fishing and for fishery activities.

Water was sampled with the help of bathometer, conserved by adding concentrated nitric acid of the "os. ch." reagent grade (specially pure) in the amount of 4 ml of the acid per 1 l of solution, and filtered through the blue ribbon paper filter. The samples of bottom sediments were collected with the help of Peterson dredger and placed in double polyethylene bags in order to exclude the loss of volatile elements and superfine fractions. The samples of higher aquatic plants (*Elodea canadensis*) and mollusca (*mollusca bivalvia*) were collected for analysis in July. After sampling, the mollusca were frozen and delivered to the laboratory where they were prepared with the instruments made of organic glass. Aggregated samples of the muscle tissue

TABLE 1

Some average chemical parameters ($M \pm d$) of surface water and bottom sediments of the Cherkalov Sor bay

Macroelements		Biogenic elements		Microelements		
Parameter	Content, mg/l	Parameter	Content, mg/l	Element	Water, mg/l	Bottom sediments, mg/kg
Na	5.9 ± 0.3	NO_3^-	0.07	Cu	15.2	16.9
K	1.3 ± 0.2	NH_4^+	0.02	Zn	35.3	55.6
Ca	20.6 ± 0.6	NO_2^-	0.002	Mn	40.1	902.0
Mg	5.3 ± 0.2	PO_4^{3-}	0.02	Cd	0.3	0.8
HCO_3^-	99.8 ± 1.5	BO	18	Co	0.5	14.2
SO_4^{2-}	8.6 ± 1.1	PO	4.8	Ni	9.0	35.1
Cl^-	1.5 ± 0.5			Cr	2.0	134.7
pH	7.7 ± 0.4			Pb	8.1	16.0

and the samples of internals (liver, intestines, spleen, kidneys) were collected from several individuals (25 to 40 specimens). Periphytons of clam shells were preliminarily cleared away for analysis. After that, the samples were washed, placed into boiling distilled water for 1 min; then the shells were separated from the bodies of the mollusca. Raw samples of the bodies were weighed, fixed with ethanol, evaporated after 6–12 h and dried at T = 105 °C till the dry state; then the samples were burnt by wet combustion according to Kjeldal' procedure in nitric acid ("os. ch." reagent grade) for 12–18 h, in some cases for 24 h (till complete decomposition of the sample mass).

Overall content of heavy metals (Fe, Mn, Zn, Cu, Cr, Ni, Co, Cd, Pb) was determined by means of atomic abdsorption photometry with flame atomization using the spectrophotometers of SOLAAR company. A mixture of acetylene with air was used for flame atomization. The analyses were performed three times. The State standards for emission analyses of microelements in biological objects SVMT-02 No. 3170–85 were used as reference samples. The coefficients of HM accumulation with respect to BS were calculated using equation $K = C_x / C_0$, where C_x and C_0 are concentrations of an element in the ash of a sample under investigation and in BS, respectively, mg/kg. To calculate the HM accumulation coefficient with respect to water, we used the ratio of metal concentration in the body of a hydrobiont (mg/kg of the raw mass) to that in water (mg/l).

RESULTS AND DISCUSSION

The Cherkalov Sor bay is a site where the fore-delta of the Selenga gets conjugated with the lakeside streams from southern Baikal. Investigation showed that in summer the warmer water entering Lake Baikal from the Selenga River is distributed over the lake surface mixing gradually with the water of Lake Baikal. The thickness of the layer of mixed water at a distance of 3–7 km from the Selenga streams does not exceed 10–15 m. In some cases, under the action of wind, admixture of the river water is detected at a depth up to 50 m [7]. However, during the spring thermobaric situations, the formed density fluxes deliver warm water with higher salt content form the Selenga to deeper sites down to 1000–1200 m. In summer, intensive growth of cyanobacteria is observed in water; water is characterized by high pH values (7.7 ± 0.4) (Table 1).

Investigation of the chemical composition of water from the Selenga showed that the concentration of sulphates in water is 8.4 mg/l as a mean, while in the 1950s it was 6.5 mg/l and in 1970s 12.4 mg/l [8]. The fraction of sulphates and monovalent cations in the Selenga water has increased while the fraction of hydrocarbonates and calcium has decreased. The flux of sulphates with the river water into Baikal increased by about 25 % in comparison with the 1950s [9]. A comparison of the data shown in Table 1 with the data reported in [8] shows that the surface water of the Cherkalov

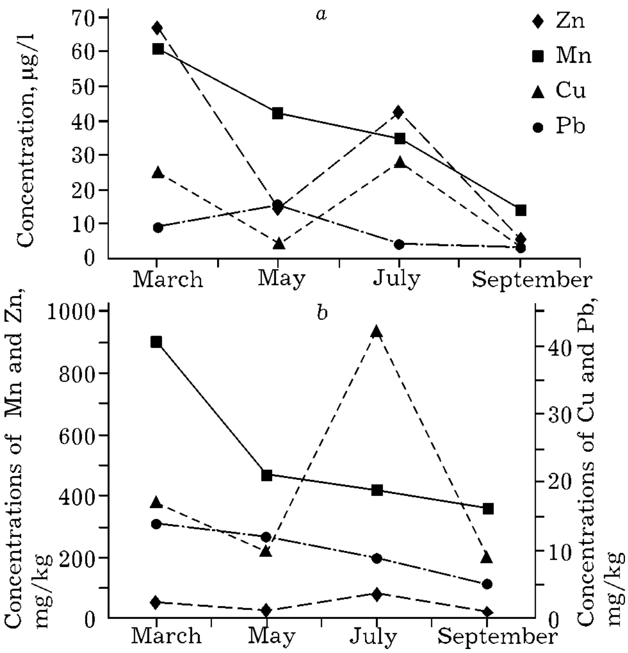

Fig. 2. Seasonal dynamics of Zn, Mn, Cu, Pb in the Cherkalov Sor bay of Lake Baikal: *a* – in water, *b* – in bottom sediments.

Sor bay is close in composition to the Selenga water. In it evident that under the action of anthropogenic factors the natural chemical composition of the Selenga water and the ratio of macrocomponents underwent noticeable changes.

The results of investigation of the seasonal dynamics of chemical elements in the water of the Cherkalov Sor bay (for the data of 2002 as an example) are shown in Figs. 2, 3. The obtained data were compared with the MPC for fishery water bodies [10], mg/l: Fe 50, Mn 10, Zn 10, Cu 1, Pb 6. The highest concentrations of Mn, Zn, Cu in the bay water is observed in winter: 61, 67, 21 mg/l, respectively, which exceeds the MPC by a factor of 6.2, 6.3 and 21, respectively. During the open water period, the concentrations of these elements in water decrease. For instance, in autumn the concentration of Mn in water decreases smoothly to 1.5 MPC (see Fig. 2, *a*). During the spring high water, the concentrations of Zn and Cu decrease by a factor of 4–8, but in summer they increase again: up to the winter value for Cu and by 60 % for Zn. In autumn the concentrations of these metals in water decrease to the MPC level for Zn and to 3 MPC for Cu. The maximal concentrations of Pb (see Fig. 2, *a*) and Fe (see Fig. 3) in water are observed during the spring flood; they are equal to 16 and 525 mg/l, respectively, which exceeds the MPC for fishery water bodies by a factor of 2.5 for Pb and 10.3 for Fe. In autumn, the concentration of Fe in water decreases to 2 MPC (see Fig. 3). The concentration of Pb in the water of the Cherkalov Sor bay decreases to MPC in summer and in autumn. The seasonal dynamics of Co is similar to those of Zn, Cu, Mn, and does not exceed the MPC. As far as Cd is concerned, its concentration in water does not exceed 0.5 mg/l; in autumn it decreases to 0.003 mg/l.

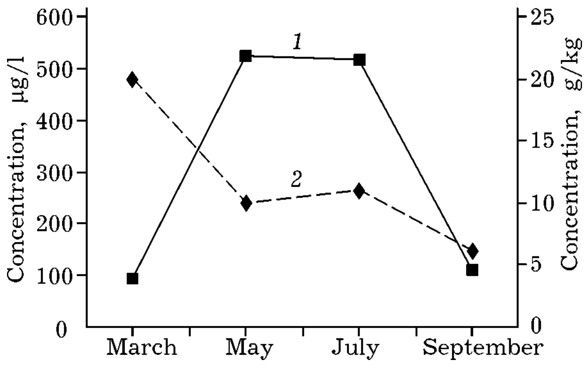

Fig. 3. Seasonal dynamics of Fe concentrations in the Cherkalov sor bay of Lake Baikal in water (*1*) and in bottom sediments (*2*).

The data obtained provide evidence that the seasonal dynamics of the variations of Zn and Cu concentrations in water is characterized by a decrease accompanying an increase in water flow during the spring flood, while the concentrations of Fe and Pb increase substantially during this period. The minimal concentrations of all the elements in water is observed during the autumn low-water season.

We consider total concentrations of HM though only their ion forms possess the toxic effect. All the HM under investigation are characterized by the ability to form complexes (<50 %). In addition, physicochemical conditions can vary during the seasonal dynamics of the ecosystem and in long-term trends; heavy metals can pass into solution [11]. In spite of the discovered potentially dangerous concentrations of the above-mentioned elements in water, the data obtained allow us to assume that they generally depict only the short-term pollution of natural water and cannot be considered as indicators of the presence of HM in macrophytes, animals with a long life cycle.

TABLE 2

Concentrations of heavy metals in different granulometric fractions of bottom sediments in the Cherkalov Sor bay, mg/kg

The size of fraction, mm	Fe	Mn	Zn	Cu	Pb	Ni	Co	Cr	Cd
$2R = 0.05$ (silt)	31 000	1010	102	44.7	19.4	41.4	25.6	180	0.87
$0.05 < 2R = 0.1$	18 000	900	55.5	16.9	16.8	35.5	18.9	135	0.56
$2R > 0.1$	7360	470	41.5	13.5	12.3	21.4	16.7	87.8	0.29
Background concentration [12] (silt)	27 000	900	340	30.0	21.0	50.1	20.0	90.2	0.27

Granulometric analysis of the BS of the Cherkalov Sor bay showed that the relative content of fractions with particle size 0.05 mm and less is 68 %. The fraction of aleurite fraction with particle size 0.01–0.1 mm is 25–30 %, the fraction of larger particles (>0.1 mm) of psammitic fraction does not exceed 12 %. The seasonal dependence of the dynamics of HM accumulation in the fractions with particle size £0.1 mm is shown in Fig. 2, *b* and 3. Maximal accumulation of the elements under consideration (except Zn and Cu) in BS was observed in winter; the open water period is characterized by a decrease in the accumulation of these elements (by 50–60 % of the values observed in winter). The maximal accumulation of HM in winter is: Fe – 17.9 g/kg, Pb – 16.8 mg/kg, Mn – 902.4 mg/kg. Unlike these elements, maximal accumulation of Zn and Cu is observed in summer; the values are 55.5 and 16.8 mg/kg, respectively. In autumn, accumulation of these elements in BS decreases by a factor of 4 as a mean. During the ice period the accumulation of Zn and Cu does not exceed 50 and 40 %, respectively, of the values characteristic of the summer period.

The income of microelements from water into BS is to a high extent determined by the presence of the fraction with particle size <0.05 mm. The data on pollution of BS provide evidence that the concentrations of almost all the metals increase with a decrease in particle size (Table 2). Comparison of the observed values with the background level [11] of this fraction shows that the concentrations of Fe, Mn, Co increased by a factor of 1.1–1.3, Cu 1.5, Cr 1.9, Cd 3.2. The particles of small-sized fractions (<0.05 mm) readily adsorb Fe, Mn, Cr, Ni, Pb, Cu, Cd, therefore, the particles of pelitic fraction are the main adsorbing material for HM. So, we observe a general trend of an increase in the number of metals the concentrations of which exceed the background levels of the given geochemical province. The fractions with particle size ³0.1 mm are represented by the sand material, are characterized by the minimal concentrations of the metals under investigation and take almost no part in self-purification of water environment. For Cu and Cd, the probability of secondary income from BS is high, which is caused by changes in physicochemical and hydrodynamic conditions of water environment and limited to the zones of active silt accumulation.

Almost all the groups of organisms inhabiting water bodies can be used for hydrobiological analysis of water quality. Higher aquatic plants are also able to absorb and accumulate the substances of different chemical nature and therefore to serve as the objects of investigation of pollution with HM.

The data on the concentrations of heavy metals in the ash of the examined hydrobionts are listed in Table 3. The concentrations of HM are characterized by positive correlation with each other (0.44–0.95, $P < 0.05$), which is an indirect evidence of the common (industry-related) source of the major part of HM in the environment. It is known that the main part of plant ash is composed of the elements which form large amounts of easily mobile compounds under the given natural conditions and provide vital functions of the given hydrobionts.

Concentrations of heavy metals in *Elodea canadensis* of the current year changes in the following sequence: Mn>Zn>Cr>Cu>Pb >Ni>Co>Cd. In the ash of the plants of the previous year, the sequence is different: Mn>Cr>Zn>Cu>Pb>Ni>Co>Cd. One can see

TABLE 3

Concentrations of heavy metals in the ash of Elodea canadensis and bivalve mollusca, mg/kg

Component	Cu	Zn	Mn	Cd	Co	Ni	Cr	Pb
Elodea, 2002	159	464	34 700	0.7	15.2	26.8	204	51.2
The same, 2001	63.2	84.1	88 500	1.6	7.8	9.5	139	25.1
Muscles of mollusca	220	1900	7500	21.1	16.1	25.2	45.2	35.1
Internals of mollusca	100	920	13 200	6.2	5.3	8.3	26.1	15.7
Periphytons of mollusca	38.0	88.9	1160	0.9	17.5	28.1	105	172

that the highest concentrations in higher aquatic plants are those of Mn, Zn, Cr, while the minimal values are characteristic of Co, Cd.

One can see in the data listed in Table 3 that the concentration of Mn in the ash of the last year's plants is 2–2.2 times higher than that in freshly connected plants. A similar picture is observed with the distribution of Cd. An attempt to explain an increase in the metal content of the last year's plants by a decrease in ash content (due to washing the mobile chemical elements K, Na, Ca, P out) failed because the ash content of fresh and hibernated plants is approximately the same.

The distribution of metals over the tissues of mollusca varies, too: the highest concentration of the major part of metals is observed in muscles (see Table 3). Mean concentrations of all the elements in the muscles is nearly 2–2.5 times higher than that in internals. Unlike other elements, the concentration of Mn in internals is 1.8 times higher than that in muscles. In general, the concentrations of HM in muscles and internals changes in the following sequence: Mn>Zn>Cu>Cr>Pb>Ni>Cd>Co. For periphytons, the sequence is somewhat different: Mn>Cr>Zn>Cu>Ni>Co>Pb>Cd. One can see that the highest concentration in the internals of mollusca is characteristic of Mn and Zn, in periphytons, of Mn and Cr.

TABLE 4

Accumulation coefficients for heavy metals in *Elodea canadensis* and mollusca of the Cherkalov Sor bay with respect to the concentrations of heavy metals in water

Element	Elodea		Mollusca	
	2002	2001	Muscles	Internals
Cu	1300	520	630	290
Zn	1600	300	2300	1100
Mn	108 000	277 000	8100	14 400
Cd	300	670	3100	900
Co	3800	1800	1400	460
Ni	400	130	120	40
Cr	12 700	8700	980	570
Pb	800	390	190	85

Accumulation coefficients *K* are usually larger in water bodies with relatively low concentrations of HM in environment [12]. Among the investigated HM, maximally high accumulation coefficient *K* in *Elodea canadensis* with respect to water is observed for Mn, Cr. Co, and the minimal one for Cd, Ni (Table 4). The accumulation coefficients *K* for the metals under investigation obtained with respect to the concentrations of HM in water are ranged in the following order: Mn>Cr>Co>Zn>Cu>Pb >Ni>Cd. With respect to the concentration of HM in BS, the order is different: Mn>Cu>Zn>Pb>Cr>Cd = Co>Ni (Table 5). In general, the concentrations of HM in *Elodea canadensis* are characterized by the positive correlation with the concentrations of HM in water and in bottom sediments.

On the contrary, the accumulation coefficient *K* exhibits not so unambiguous dependence on the concentration of the corresponding HM in water. A more close connection is observed between the accumulation coefficients with respect to the concentrations in BS on the concentrations of HM in bottom sediments.

So, the coefficients of accumulation in *Elodea canadensis* calculated with respect to the content of metal compounds in BS are more representative than the accumulation coefficients obtained by comparing with the concentrations of HM in water.

In the case of mollusca, on the basis of the accumulation coefficient *K* calculated with re-

TABLE 5

Accumulation coefficients for heavy metals in *Elodea canadensis* and mollusca of the Cherkalov Sor bay with respect to metal concentrations in bottom sediments

Element	Elodea		Mollusca		
	2002	2001	Muscles	Internals	Periphytons
Cu	9.4	3.7	13	5.9	2.2
Zn	8.3	1.5	34	16	1.6
Mn	38	98	8.3	14	1.3
Cd	0.8	2.0	26	7.7	1.1
Co	0.8	0.4	0.8	0.3	0.9
Ni	0.7	0.2	0.7	0.2	0.8
Cr	1.5	1.0	0.3	0.2	0.8
Pb	3.2	1.5	0.2	0.9	1.1

spect to the concentrations of HM in water (see Table 4), the investigated HM are ranges in the following order: Mn>Cd>Zn>Co>Cr>Cu>Pb>Ni – muscles, Mn>Zn>Cd>Cr>Co>Cu>Pb>Ni – internals. A similar order obtained with respect to the concentration of HM in bottom sediments (see Table 5) is as follows: Zn>Cd>Cu>Mn>Co>Ni>Cr>Pb – muscles, Zn>Mn>Cd>Cu>Pb>Co>Ni>Cr – internals, Cu>Zn>Mn>Cd = Pb>Co>Ni = Cr – periphytons.

It follows from these data that the dependence of the coefficient of HM accumulation in mollusca on the concentrations of the corresponding HM in water and in BS is ambiguous. The difference in the orders of HM accumulation is likely to be explained by the existence of the species-specificity of concentrating and by the features of the mollusca as filterers and inhabitants of silt. (High accumulation coefficients of a series of metals – Mn, Zn, Cu – by mollusca should be noted.)

It is known that water organisms can be separated into three groups on the basis of the coefficients of biological accumulation K calculated with respect to the concentrations of HM in bottom sediments: macroconcentrators ($K > 2$), microconcentrators ($1 < K < 2$), and deconcentrators ($K < 1$) [12]. On the basis of the data obtained by us, we may assume that the higher aquatic plant Elodea canadensis is a macroconcentrator with respect to Mn, Zn, Cu, Pb, and microconcentrator for Cr. The mollusca belong to macroconcentrators of Mn, Zn, Cu, Cd and deconcentrators for Co, Ni, Cr, Pb.

It is known that Mn is represented in the silt solutions mainly (75–95 %) by ions not bound in complexes, which increases the rate of its molecular diffusion [13] and assimilability substantially. For Zn, a high degree of binding in complexes with organic substances is characteristic, which allows us to refer this metal to the group of less mobile elements. The concentrations of this metal in silt solutions is 10–40 times higher than in the water volume.

CONCLUSIONS

The MPC for fishery water bodies are exceeded in the surface water of the Cherkalov Sor bay for Fe and Pb by a factor of 10.1 and 2.5, respectively, during the spring flood, for Mn and Zn 6.2–6.7 during the winter low water period, for Cu all year round. Investigation of the concentrations of HM in various granulometric fractions of BS showed that the concentrations of almost all the metals increase with a decrease in particle size. A comparison of the available data for 2002 and 1983 on the concentrations of HM in BS shows that the pollution of the water body has increased. The concentrations of all the metals in the BS fraction £60 mm exceed the background level by 20–50 % while accumulation of Cd has increased by a factor of 3 [11]. The higher aquatic plant *Elodea canadensis* has a substantial effect on redistribution of Mn and to a less extent of Zn and Cu. An increase in the accumulation of Mn and Cd is observed in the plants of the previous year. The majority of the metals under investigation are accumulated in the soft tissues of mollusca; however, Mn, Zn, Cu, Cd have rather high accumulation coefficients ($K > 2$).

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