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Heavy Metals in Freshwater Ecosystem of the Kenon Lake (Transbaikal Territory, Russia).

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ABSTRACT

In the modern period the economic activity makes significant changes in the abiotic components of the lake ecosystem. It defines the conditions for hydrobionts life. Our research has important ecological significance in the operation of thermal power plant. Water environment, trophic level of aquatic organisms and its food objects are fundamental factors for heavy metals bioaccumulation. The heavy metal concentrations in water of the Kenon Lake are quite low. Hydrophytes maximally accumulate heavy metal (Hg, As, Pb, Zn, Cr, Cu, Cd, Mn). Most of heavy metals (Cr, Cu, Zn, As, Cd, Hg, Pb) are accumulated in the sediments. Pb is accumulated in plankton chain. Hg and Zn are moved from the lowest to the highest levels of the lake ecosystem.
Keywords: Water reservoir-cooler of combined heat and power plant (CHP); hydrochemistry; hydrobiology; heavy metals (HM); biological accumulation.

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INTRODUCTION

Heavy metals (HM) are released into environment from a wide range of natural and anthropogenic sources. Aquatic ecosystems are normally at the receiving end and in many cases, with lakes as intermediaries [1]. They have an adverse effect on water ecosystems: they change water quality [2, 3, 4], are accumulated in hydrobionts [5, 6, 7, 8] change biological diversity and population structure [9, 10]. The accumulation of toxic metals to hazardous levels from the simultaneous uptake and elimination of the in aquatic biota has become a problem of increasing pollutant [11].

Heavy metals flows of ponds inside of urban area are difficult for understanding owing to difficulties with identification of source of contamination. Urban and industrial areas are always accompanied by construction and power plants (for example, CHP) placing. Today we have no enough information about sources of contamination in Kenon Lake and heavy metals influence on water ecosystems, especially on fish, because fish is an important commodity and an important source of protein. TPP return water and their ash dumps are one of the heavy metals sources. Forthcoming Transbaikalia development, including power development, will inevitably have negative influence on water ecosystems. Understanding of the processes in water ecosystems including migration of heavy metals helps to decrease ecological risks on the stage of work planning. So, the main aim of this work is evaluation of heavy metals migration in Lake Kenon ecosystem, this lake has been used as CHP's cooler pond for 50 more years.

MATERIALS AND METHODS

Description of the study area

Kenon Lake is used as cooler pond for the CHP-1. Except thermal pollution, an additional pollutant is constructed - it is the CHP-1 ash-disposal area located 3 km to the north-west from CHP, it has no filtration screen [12]. Its filtration loss quantity is estimated to be 550m^3/hour [13]. Over 10 10^{-6} m^3 of ash wastes is been accumulated [14]. Infiltrated waters of ash-disposal area flow into the lake and may have technogenic influence on lake ecosystem.

The work describes morphologic, hydrochemical characteristics and species composition of hydrobionts communities in Kenon Lake [15]. To analyze heavy metals influence on lake ecosystem, from 2012 till 2015 the author has been taking water, bottom sediments and hydrobionts samplings in 5 points of the lake (Figure-1).

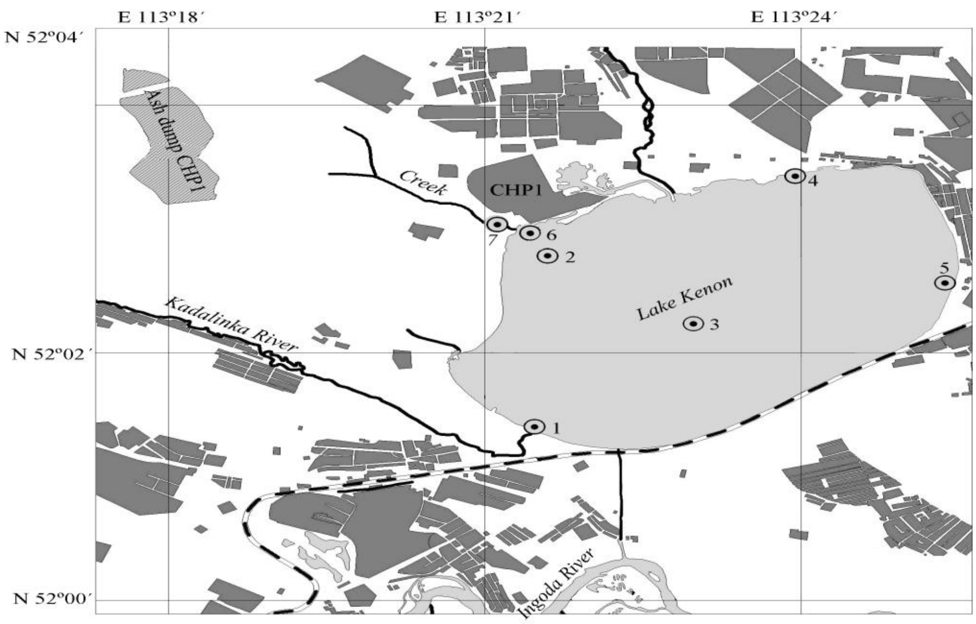

Figure-1-Schematic map of the location of sampling stations, 1 - Kadalinka river 2 - influence of CHP warm waters, 3 - the open part, 4 - Northern coastal, 5 - Eastern coastal, 6 - discharge of CHP heated water, 7 - drainage creek

Sampling methods

Water samplings were taken in lake different horizons with plastic Patalas water-sampler (V = 6 l). Water was filtrated through membrane filter to 15 ml plastic cryovials, acidified (Nitric acid 65% Suprapur, Merck), filtrated to pH less 2. Samplings of Hg (V = 15 ml) was preserved with a mix of nitric acid and 0.01% potassium dichromate.

Bottom sediments samplings were taken from bottom sediment surface level using Petersen dredge, gripping area is 0.025 m^2. Samplings were dried in drying chamber ES-4620 till having constant weight.

Phytoplankton was collected with net trawling, mesh opening 87 µm, net inside has bolting cloth cone, its mesh opening 106 µm. Green algae (*Tetraëdron minimum* (A. Br.) Hansgirg*, Tetrastrum komarekii* Hindak, *Scenedesmus quadricauda* (Turp. Brebisson)) and *Oocystis* genus species dominated in quantity (70-98%), dinoflagellates (*Ceratium hirundinella* (O.F.M.) Bergh) dominated in biomass (70-98%). Concentrated samplings with capron screen (mesh opening 87 µm) were weighted and dried in drying chamber ES-4620 till having constant weight.

Zooplankton was collected by the method of total catching in vertical direction using Juday net (entry-hole diameter 24 cm, screen filter cone with mesh of 60 µm). Zooplankton community included *Ceriodaphnia quadrangulata* (O.F. Müller) - 36-55%, *Neutrodiaptomus incongruens* (Poppe) - 13-30% and others. After separating large zooplankton fraction by a screen with mesh of 112 µm, small plankton consisted of algae, nauplii of Cyclops and diaptomus, detritus. Dried till having constant weight large and small plankton organisms were separately analyzed on heavy metal contain.

Zoobenthos main biomass was consisted by chironomids larvae (*Chironomus* spp.). Zoobenthos coastal communities is consisted by amphipoda (*Gmelinoides fasciatus* (Stebbing) and *Gammarus lacusrtis* Sars) and mollusks (*Lymnaea* spp.). Larvae were sampled with Petersen dredge in the lake deep zone, amphipoda and mollusks were gathered in the lake coasts. Cleaned of foreign particles organisms were dried till having constant air dried weight without dividing into organs and tissues.

Charophyceae occuped the biggest lake areas. They grew in the whole lake perimeter. *Potamogeton* sp. communities dominated in central and eastern zones. Plant samples were cleaned with filtered water to remove foreign particles, and then they were dried by air till having dry condition.

Catching fish was made a standard set of nets. Dominate fish (*Carassius auratus gibelio* (Bloch), *Leuciscus waleckii* (Dybowski) и *Perca fluviatilis* Linnaeus) with differences in composition in the food bolus were researched (Table 1).

Table 1. The main food components of dominant species (% by weight of the bolus)

Fish species	The main food components
Perca fluviatilis (n = 25)	Amphipods, larvae and pupae of chironomids (15-20%), fish (80%)
Carassius auratus gibelio (n = 25)	Charophyceae, filamentous (50%), ostracods, small chironomids (10%), cyclops (5%), detritus (35%)
Leuciscus waleckii (n = 20)	Pondweed (80%), detritus (20%)

Collected fish muscles samplings were dried in drying chamber till having constant weight, chamber temperature was 65 °C.

Dried organisms samplings were placed into sterile tubes without any preservatives, the tubes are sent to Analytical Certification Test Center of the Technology and Microelectronic Problem and High-pure Materials Institute of the Russian Academy of Sciences. Water samplings, bottom sediments and hydrobionts samplings elemental compositions were determined using atomic emission iCAP-6500 Thermo Scientific (USA) and mass-spectrum X-7, Thermo Elemental (USA) analysis methods. They used the Certified Reference Material “Trace Metals in Drinking Water” (High-Puriy Standards, USA); SRM, EK-1 (registration number

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COOMET 0065-2008-RU); Oriental Basma Tobacco Leaves (INCT-OBTL-5) and Oriental Polish Virginia Tobacco Leaves (INCT-PVTL-6); SRM, Baikal perch tissue, BOk-2 (registration number COOMET CRM 0068-2009-Ru) for quality control. We studied content of medium- and high-toxic elements, such as Hg, As, Pb, Zn, Cr, Cu, Cd, Mn.

Data process

We calculated biophility coefficient (BC) and trophic amplification coefficient (TMF) for heavy metals. BC is a relation of heavy metal content in organism to its content in environment (in water and bottom sediments), formula: BC = HM (organism) / HM (environment), HM (organisms) - is element content in a researched organism or organ, HM (environment) is element content in environment (in water and bottom sediments). Trophic amplification coefficient (TMF) is a relation of element content in a predator to element content in a prey. Formula: TMF = HM (predator) / HM (prey), HM (predator) is element content in predator's organism or organ, HM (prey) is element content in prey organism.

Data static handling was held using STATISTICA 10 computer program for Windows (Copyright © StatSoft, Inc) and Excel, significance level $p < 0.05$.

RESULTS

Mercury (Hg) content

Mercury (Hg) was not accumulated in bottom sediments, its maximum concentration was in plankton and besides concentration of mercury (Hg) was high in small (feed) plankton fraction than in large-sized zooplankton (Table 2).

Table 2 Mean concentrations of the chemical elements in components of the Kenon Lake ecosystem

Components	Unit	Cr	Mn	Cu	Zn	As	Cd	Hg	Pb
Bottom sediments, damp 70%, n = 5	µg/kg	13874	33	24535	43243	8979	75	25	12072
	S.D.	2114	10	3351	3694	2474	9	20	2375
Water, n = 10	µg/l	1.00	4.00	0.86	2.70	8.60	0.03	0.18	0.16
	S.D.	0.00	1.78	0.11	1.04	0.77	0.00	0.08	0.07
Phytoplankton n = 5	µg/kg	1213	3930	13700	7612	73	2852	11	1849
	S.D.	143	2653	7248	392	20	152	13	195
Chara sp., n = 10	µg/kg	200	170563	1066	3488	2388	5	5	320
	S.D.	94	12327	255	1144	663	1.4	2.8	381
Potamogeton sp., n = 10	µg/kg	65	24528	422	1306	171	4	4	66
	S.D.	43.0	15330	95.6	202.0	77.7	1.2	0.6	39
Zooplankton, (<112 µ), n = 5	µg/kg	803	19879	4070	7624	164	1767	1989	46787
	S.D.	1044	25028	1154	3894	107	981	2070	28124
Zooplankton, (>112 µ), n = 5	µg/kg	543	9044	3865	9229	145	1843	1503	73781
	S.D.	317	6901	1710	3114	47	1555	1307	75303
Amphipods, n = 7	µg/kg	86	4920	9970	10400	554	5	16	70
	S.D.	15	3030	1170	1130	227	2	8	36
Chironomus spp., n = 7	µg/kg	500	23500	3570	14900	875	18	7	464
	S.D.	300	18100	1600	5200	500	19	1	200
P. fluviatilis, n = 6	µg/kg	41	433	338	11583	<DL	<DL	78	6
	S.D.	12	512	32	1090	ND	ND	30	3
C. auratus gibelio, n = 6	µg/kg	43	192	228	15532	16	<DL	51	92
	S.D.	9	39	57	9190	1.4	ND	17	17

L. waleckii, n = 8	µg/kg	120	240	600	8950	<DL	<DL	71	19
DL, bottom sediments	µg/kg	600	0.1	800	500	80	40	5	80
DL, water	µg/l	4	1	4	9	1	0.09	0.2	0.4
DL, biota	µg/kg	20	50	40	70	10	4	4	10
MAC, Russia	µg/l	20	10	1	10	50	5	0.01	6
US EPA CCC	µg/l	11-74	ND	9	120	150	0.25	0.77	2.5

Note: DL - the detection limit of the method, ND - not determined, MAC - the maximum permissible concentration in fishery waters [16], US EPA CCC - maximum concentration of the element in water for permanent aquatic communities to occur without harmful impact [17].

High mercury (Hg) content was in *P. fluviatilis* and *L. waleckii*, these fish-predators have pelagic way of life and inhabit in pondgrass. Food relations of C*. auratus gibelio* is connected with bottom organisms that inhabit in charophyceae (Figure-2).

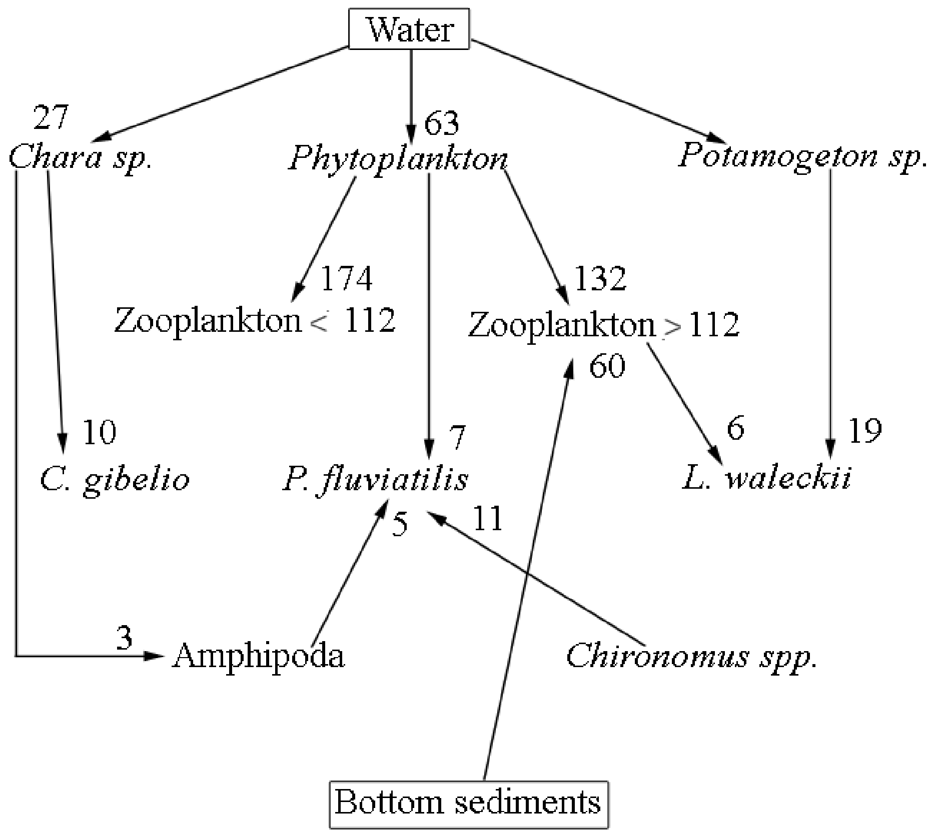

Figure-2-Mercury (Hg) concentration in the ecosystem

Zinc (Zn) content

Zinc (Zn) was accumulated in plankton and bottom sediments. Charophyceae had stronger accumulation ability than *Potamogeton* sp. The maximum concentration of zinc (Zn) was in *C. auranus gibelio* and *P. fluviatilis* muscles (Table 2). Zinc (ZN) was accumulated in fish through bottom sediments, then through hydrophytes, detritus and benthos organisms (Figure-3).

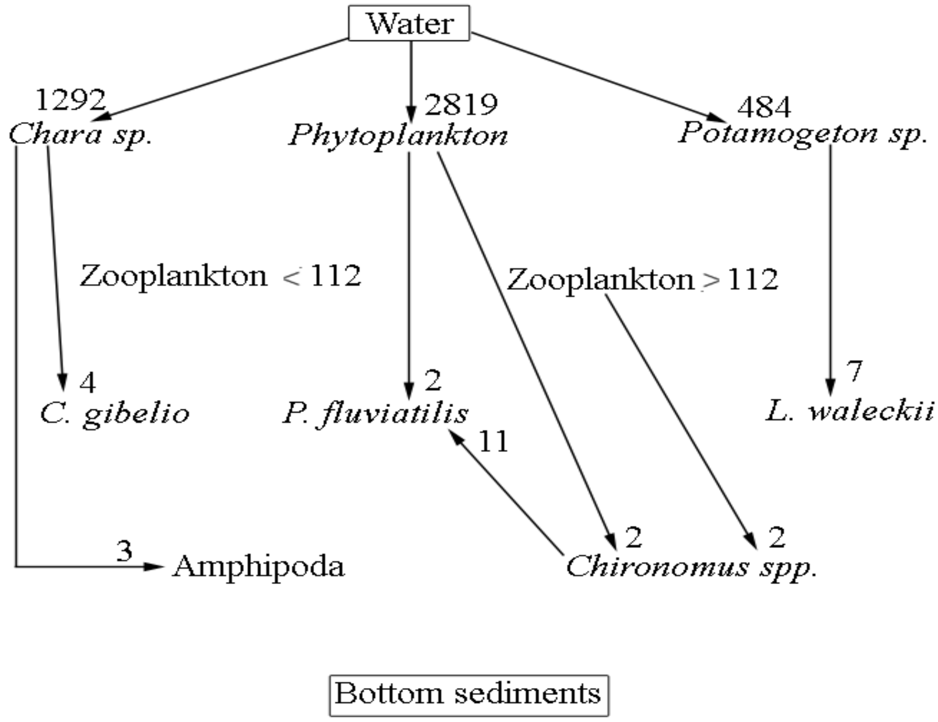

Figure-3-Zinc (Zn) concentration in the ecosystem

Lead (Pb) content

Lead (Pb) was deposited in bottom sediments and accumulated in plankton community and charophyceae (Table 2, Figure-4). The concentration of lead (Pb) was high in large-size zooplankton than in small feed plankton and was high in chironomids than in amphipods. Lead (Pb) was mainly accumulated in fish muscles.

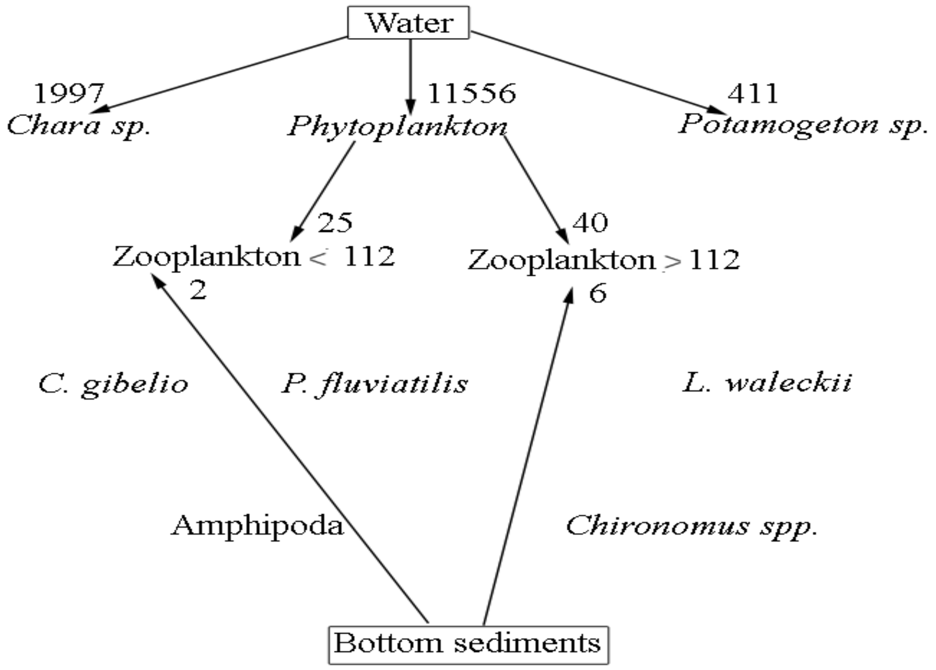

Figure-4-Lead (Pb) concentration in the ecosystem

Chromium (Cr), Manganese (Mn), Copper (Cu), Arsenic (As), Cadmium (Cd) contents

There were a following content of HM in water: Cu > As > Cr > Mn > Cd, in bottom sediments: Cu > Cr > As > Cd > Mn, in plankton: Mn > Cu > As > Cr > Cd, in *Chara* sp.: Mn > As > Cu > Cr > Cd, in Chironomus larvae: Mn > Cu > As > Cr > Cd, in amphipods: Cu > Mn > As > Cr > Cd, in mollusks: Mn > Cu > Cr > As > Cd. Metals was mostly accumulated in phytoplankton and charophyceae (Figure-5). Arsenic (As) and Cadmium (Cd) was not accumulated in perch and ide muscles. There were a following content of HM in fish muscles: *P. fluviatilis* – Mn > Cu > Cr; *C. auratus gibelio* – Cu > Mn > Cr > As; *L. waleckii* – Cu > Mn > Cr (Table 2).

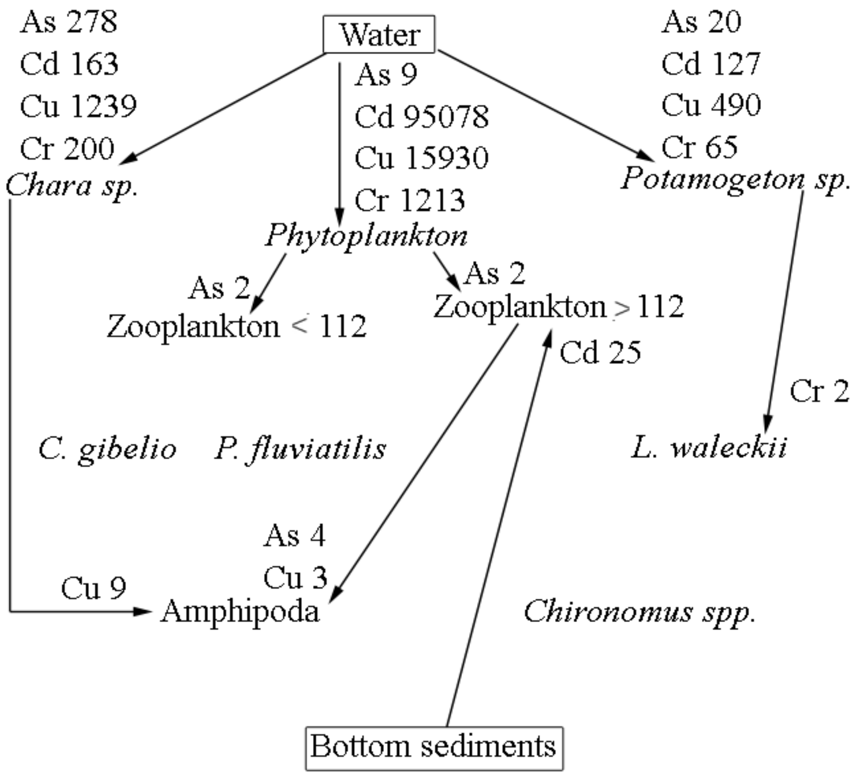

Figure-5-Chromium (Cr), Copper (Cu), Arsenic (As), Cadmium (Cd) concentrations in the ecosystem

DISCUSSION

Biobarrier is one of the classes of geochemical migration of elements. Geochemical barrier is determined as a space territory that has a rapid decrease of chemical elements migration intensity and has their concentration [18]. Living organisms of water ecosystems are participants of geochemical elements migration. Chemical elements that flow into water ecosystems through a system of trophic relations selectively accumulate in organisms.

Mercury (Hg)

Dissolved mercury (Hg) flows into the lake (0.38 µg/l) with the CHP-1 ash dump filtered water [12]. According to MAC [16] mercury (Hg) concentration in water is 18 times exceeded, but it less than USA standards. Mercury (Hg) content in European part of Russia, the Caucasus and the Tien Shan freshwater ecosystem water, that our work [2] describe as background, does not exceed 0.05 m. Mercury (Hg) concentration in water of the Kenon Lake are 3.6 times higher (Table 2). Mercury (Hg) persists in water ecosystem for a long time [19]. Mercury (Mg) deposits may create a long-time risk for water ecosystems and environment [20]. For example, as a result of mercury (Hg) burst release into the Nura River, Central Kazakhstan, in the latter part of twentieth century, water pollution is still determined within the limits of 0.2 до 0.5 µg/l [21]. Bioaccumulation of mercury (Hg) from water by hydrobionts has the following direction: phytoplankton – zooplankton – perch (Fig. 2). Mercury (Hg), which through passive adsorption [22] enters in phytoplankton, accumulated in zooplankton. Plankton rapidly responds even on short-time water environment pollution [10]. Mercury (Hg) contenting in plankton (Table 2) is within the limits for American lakes [23] small plankton, exceeds Siberian ponds indexes [10] and is lower than zooplankton pollution index for lake Big Yarovoye, that is influenced by chemical plant wastes [24]. Mercury (Hg) contenting in perch (Table 2), is higher than in lake Chany and the Baikal lake, Chyvyrkuyskiy gulf [25], but is lower than in Bratskiy water storage (that subject to mercury pollution) perch [8].

Mercury (Hg) in bottom sediment enters into hydrobionts through macrophytes and benthos organisms (Fig. 1). This way of mercury (Hg) accumulation is confirmed by several authors [22, 26]. Different types of macrophytes (*Potamogeton* sp. and *Chara* sp.) differently accumulate mercury (Hg), this fact corresponds with other research [27]. Mercury (Hg) content in charophyceae from Kenon Lake is higher than macrophytes from Altai lakes [24]. Compared with other ponds data [28, 29], average mercury (Hg) content in *Lymnaea* spp. is at the same level with lightly polluted ponds. Crucian muscle mercury (Hg) accumulation 40 times exceeds this index for Chany Lake [25], it may be compared with the indexes of having industrial pollution ponds [8].

Zinc (Zn)

Bioaccumulation has the following direction: bottom sediments – hydrophites – crucian and ide (Table 1). In relation to another ponds [30, 31] average contented of zinc (Zn) in *Chironomus* spp. Chironomids are comparable with lightly-polluted ponds. Vegetation as a combination of autotrophic organisms and mineral nutrition includes available forms of HM into biochemical processes [32]. Fish gets and accumulates zinc (Zn) through macrophytes in the Kenon Lake (Fig. 2). In crucian food bolus we found charophyceae remains, in ide – pondweed. In mentioned above fish species muscles zinc (Zn^0 content is 2-5 times higher than those in some reservoirs [25, 31, 33, 34]. But risk assessment based on national and international permissible limits and provisional tolerances for weekly intake of Zn revealed that the concentrations of this metal in muscle were relatively low and would not pose hazards to human health.

Lead (Pb)

Inorganic lead (Pb) is one of the most common environmental pollutants. Lead (Pb) flows into the lake with the CHP-1 emissions. The CHP-1 annual average fuel rate is 3.6 10^{-6} tons of brown coal. During burning 1000 tons of coal 5 tons of lead emits into atmosphere [35]. Incoming lead (Pb) is accumulated in bottom sediment and is partly held by charophyceae. Lead (Pb) levels in the examined fish muscles are more than in fish from drainage canals [31] and Manila Bay [36] (Table 2). Its following accumulation occurs in plankton community (Fig. 2).

Chromium (Cr), Manganese (Mn), Copper (Cu), Arsenic (As), Cadmium (Cd)

The concentration of chromium (Cr) in Lake Kenon is 2-3 times is higher than in northern Finnish lakes with domination of summer rotator complex, but lower than in lakes with domination of cladocerans [37]. Copper (Cu) is a very important microelement for phytoplankton community. It is involved in photosynthesis and takes part in cells growths [38], these all cause copper (Cu) concentration in phytoplankton. However, with the increased use of copper (Cu)-based antifouling (AF) paints, copper has become a potential threat to freshwater organisms. Blue-green algae are very sensitive to copper (Cu) content [39, 40]. Maximum accumulation of arsenic (As) is registered in bottom sediments. Bioconcentration of arsenic (As) is marked in plankton food chain (Table 2, Fig. 2.). Manganese (Mn) involving into biochemical cycle of water ecosystems, in case of high concentration toxically influence on organisms [2]. As a result of techno genesis, manganese (Mn) enters into environment and at the end accumulates in natural water [41, 42]. Manganese (Mn) migrates in acid medium and actively precipitates on formed oxygen barrier by water vegetation and during breathing cycle of *Chironomus* spp. larvae. Cadmium (Cd) in phytoplankton shows maximum growth of concentration related to water; it increases its concentration 95000 more times.

Hydrobionts as a geochemical barrier

The most important barrier on the way of bottom sediment elements to water is water vegetation [41]. This is connected with macrophyte ability to accumulate HM both from water and bottom sediments [5, 43-45]. Accumulate of heavy metals in sediments and in some water plants indicates that plant organs are good bioindicators of metal pollution in sediments of Kenon lake. Elements actively accumulate in plankton trophic chain in water. They enter into zooplankton filtration organism through phytoplankton. Fish, as food resource, actively consummated by human, are able to accumulate toxic elements (e.g. mercury (Hg)). Searching for food fish destroy vegetation bottom cover, this may lead to secondary pollution of ecosystem by HM.

CONCLUSION

The heavy metal contamination of water ecosystems is a potential threat to the living systems. The study of natural water bodies under the CHP anthropogenic influence promotes to the knowledge accumulation about the possibilities of its sustainable development. The results of this study is needed to develop methods of protecting the food chain from the toxic substances penetration in dangerous concentrations, to determine the possibility of the use of aquatic organisms as HM bioindicator and the responses of organisms to pollution.

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