ISSN 0097-8078, Water Resources, 2018, Vol. 45, No. 3, pp. 348–356. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © E.S. Grishantseva, L.P. Fedorova, 2018, published in Vodnye Resursy, 2018, Vol. 45, No. 3.

HYDROCHEMISTRY, HYDROBIOLOGY: ENVIRONMENTAL ASPECTS

Epiphyton Geochemistry in the Ivankovo Reservoir

E. S. Grishantseva[a], * and L. P. Fedorova[b]

[a] *Moscow State University, Moscow, 119991 Russia*

[b] *State Research Institute of Lacustrine and Riverine Fishery, Upper Volga Department, Konakovo, Tver oblast, 171253 Russia*

**e-mail: SHES99@mail.ru*

Received June 12, 2015; in final form, June 16, 2016

Abstract—Epiphyton chemistry was studied in the Ivankovo Reservoir; a large number of micro- and macroelements (Ag, Al, As, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, S, Sc, Sr, Ti, V, Y, Yb, Zn, W) were determined with the use of up-to-date analytical methods. Comparative characteristics of the geochemistry of macrophyte epiphyton of different ecological groups is given for the Ivankovo Reservoir. The potential of epiphyton as a biogeochemical indicator of anthropogenic impact on the water body is examined.

Keywords: microelements, macrophyte epiphyton, aquatic ecosystem, Ivankovo Reservoir

DOI: 10.1134/S0097807818030077

INTRODUCTION

Epiphyton is a community of microbiota (algoflora), which exists attached to macrophytes [8, 9]. Epiphyton, along with higher aquatic plants (HAP), plays an important role in production processes in water bodies and actively participates in the processes of migration and binding of metals and other pollutants entering the aquatic ecosystem. The bulk primary production of epiphyton in the biotopes of the littoral zone of reservoirs is higher, in terms of effective production, than the production of both plankton and microphytobenthos, ranking second after macrophyte production [6, 8, 9]. Epiphyton is most widespread in the littoral zone of water bodies, where it is often the only source of primary production. According to different data, epiphyton can provide from 10 to 70% of the total organic matter production in the water body [10, 16]. Epiphyte microflora commonly accounts for the maximal part of alga biomass in shallow water bodies and the littoral zone of large water bodies. In the Ivankovo Reservoir, shallow zone occupies a considerable portion (48%) of its area [7, 18]; this determines the high degree of water body overgrowth with HAP, on which epiphyton forms. The species composition and the structure of alga epiphyton have been studied well because these organisms can be used as water quality indicators in assessing changes in the hydrological–hydrochemical conditions in the water body [8, 9]. Macro- and microelements in epiphyton composition form an important component of matter fluxes into the food chains of organisms in aquatic ecosystems, they actively participate in biogeochemical processes [16]. However, studying epiphyton chemistry is not enough to understand its geochemical role in biogeochemical cycles of freshwater ecosystems.

Bioproducers (plankton, macrophytes, epiphyton, etc.) are a source of organic matter of sediments; in the course of their vital activity, they absorb and accumulate microelements. Elements–pollutants accumulate through sorption on the barrier of dead organic matter. The planktonogenic organic matter of lacustrine deposits is known to give start to the formation of fossil fuels and often shows oil-parent properties [11, 12]. Theoretical principles of studying the role of plankton in geochemical cycles of elements and sedimentation processes have been formulated in [2, 11, 12, 14]. Biogeochemical processes involving plankton in continental water bodies and sedimentation processes with its participation were studied in [12, 13]. However, the geochemical role of epiphyton in the formation of the microelement composition of bottom sediments in different aquatic ecosystems, including anthropogenic, such as reservoir, has not been determined.

This study is the continuation of many-year studies of the ecological–geochemical conditions of Ivankovo Reservoir ecosystem [4, 5, 17]. In addition to studying abiotic components (bottom sediments; soils on the drainage area; surface, bottom, and pore waters), studies should also embrace the biotic component of Ivankovo Reservoir ecosystem. The biogeochemical role of different types of higher aquatic plants of the Ivankovo Reservoir in microelement migration processes and the efficiency of their use in environmental monitoring is discussed in [5]. Considerable experience has been accumulated in the use of phytoplankton in biomonitoring aquatic ecosystem pollution by heavy metals. [16]. However, the difficult sampling of

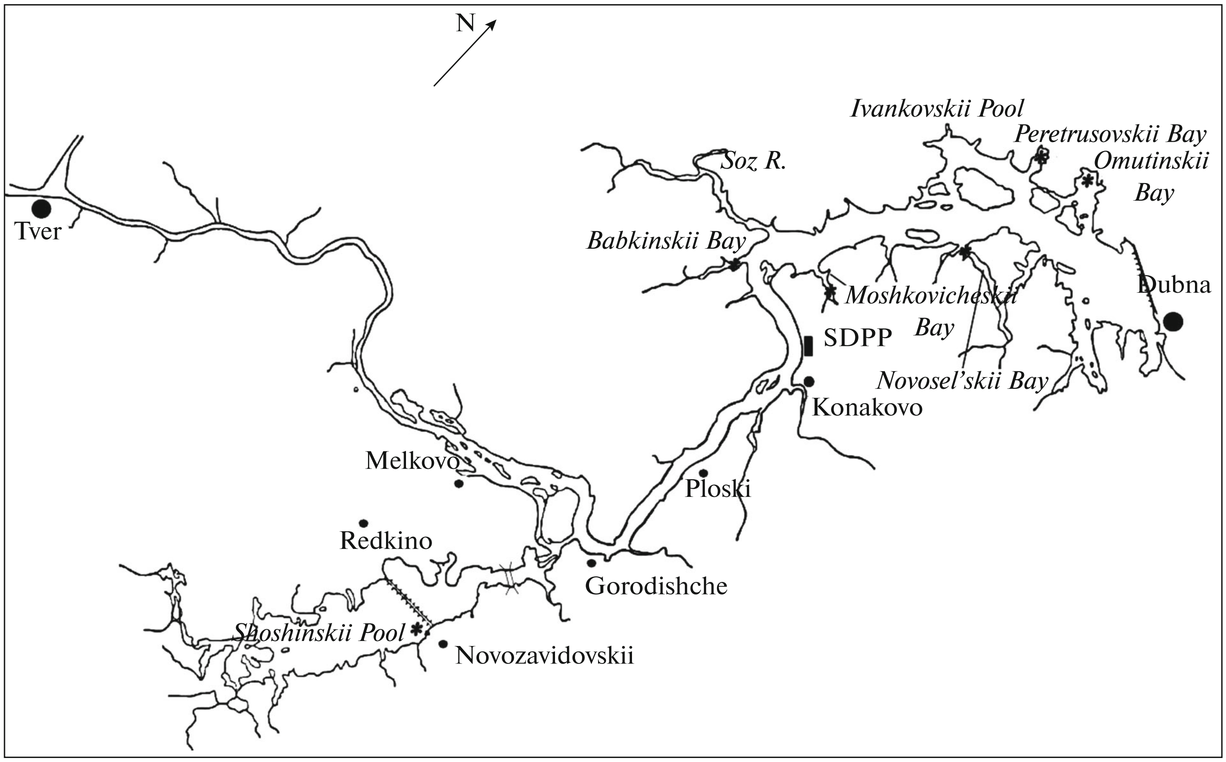

Fig. 1. Scheme of Ivankovo Reservoir sampling. Asterisks show stations of sampling epiphyton, macrophytes, and water.

plankton and the need to use special equipment hamper the use of plankton as an object of environmental monitoring and bioindication. Bioindication methods, based on the reactions of plankton communities, are applicable, primarily, to lakes and, with a great caution, to flow-through water bodies. In reservoir areas with riverine hydrodynamic regime, plankton has no time to form, so it consists mostly of species delivered from upstream reaches and, therefore, inherits the chemistry of the habitat [12]. It is very difficult to determine the habitat of individual plankton samples, because of its incessant motion with water masses. Epiphyton is functioning attached at the same place throughout its life cycle. In this case, the species composition of phytoplankton is known to be identical to that of epiphyton [9].

The objective of this study is to assess the biogeochemical role of epiphyton in the accumulation of microelements, and the perspectives of the use of epiphyton to assess the ecological-geochemical state of an aquatic ecosystem, based on the case study of the Ivankovo Reservoir.

This study is aimed at

determining the chemistry of epiphyton on macrophytes of different ecological groups, inhabiting the Ivankovo Reservoir, with the use of up-to-date analytical methods;

assessing the biogeochemical concentration function of epiphyton and the degree of accumulation of various chemical elements in epiphyton by biological absorption coefficients (BAC);

assessing the current ecological–geochemical conditions of different reservoir areas by microelement content of epiphyton;

assessing the potential of epiphyton in the biogeochemical indication of reservoir conditions.

MATERIALS AND METHODS

The Ivankovo Reservoir is located in Tver oblast between the cities of Tver and Dubna; the reservoir is used as a source of drinking water supply to Moscow. Field studies were carried out in the Ivankovo Reservoir in July 2005 and 2010. The object of studies was epiphyton—fouling algacenoses on macrophytes, growing in reservoir bays with different levels of anthropogenic impact: Babninskii, Peretrusovskii, Novosel'skii, Moshkovicheskii, and Omutninskii, as well as the Shoshinskii Pool (Fig. 1). The background objects were taken to be the bays of Babninskii, Peretrusovskii, and Novosel'skii, which are far from large pollution sources, suffer minor anthropogenic impact, and contain no controlled wastewater discharges. The station in the Shoshinskii Pool can be also referred to background area as it lies near Zavidovo National Park, upstream of potential pollution sources.

The species composition of Ivankovo Reservoir epiphyton have been well studied and found to be represented by the following algae, % of the total amount: diatoms (Bacillariophyta), 48; green algae (Chlorophyta), 28; blue-green algae (Cyanophyta), 12; and other species (pyrrophytic Pirrophyta, yellow-green Chrysophyta, green Chlorophyta, and euglena Euglenophyta), 12 [8]. As the hydrological–geochemical factors contribute much to the formation of epiphyton composition, the samples were divided into two groups by the growth conditions of host macrophytes: epiphyton from macrophytes from the group of aquatic–marsh plants and epiphyton from submerged macrophyte species. The examined macrophyte group contained the species of two ecoloigical groups: helophytes, i.e., aquatic–marsh plants (reed manna grass, club-rush, common reed grass, and narrow-leaved cattail) and hydrophytes, i.e., submerged plats (shining pondweed, clasping-leaved pondweed, dark green hornweed).

Some researchers believe macrophytes to be an inert surface for inhabiting by epiphyton, and epiphyton from different types of macrophytes to have the same species composition. It is supposed that, although the type of substrate and the species compositions of macrophytes have an appreciable effect on the algaflora that develops on them, but the hydrological–geochemical conditions of the habitat play a key role [1, 8, 9, 23]. Other researchers attribute the different composition of epiphyton algae on macrophytes of different types to the important role that the host macrophyte plays in epiphyton formation as a medium-forming factor [15, 21, 24]. Currently, there is no unified theory regarding the interrelation between macrophytes and epiphyton attached to it; therefore, the authors proceeded from the concept of neutral interactions, relying on the study [8], where it is noted that no confinement of epiphyton algae to certain macrophyte species was revealed in the Ivankovo Reservoir, i.e., epiphyton samples can be taken from any macrophyte species and no single species is to be chosen.

The above-root part of the plant was accurately cut under water, and next a hard brush and a plastic scraper were used to remove epiphyton samples into Petri dishes, and forceps were used to remove zoobenthos. The obtained epiphyton samples were dried in a dessicator (at $t = 105°C$), pulverized in an agate mortar, and stored in vellum packets. Next, the samples were decomposed in a microwave system Discover: a 250-mg weighted sample was poured by 5 mL of concentrated nitric acid, warmed to 200°C, incubated for 5 min, and cooled. The white flocks of silicic acid were filtered out through a paper filter and diluted to 25 mL. The concentrations of Ag, Al, Ba, Ca, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, S, Sc, Sr, Ti, V, Y, Yb, and Zn were determined by atomic-emission spectrometry with inductively coupled plasma (AES-ICP) on instrument IRIS Intrepid II XDL Duo (Thermo Electron Corporation, USA) in the Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences. The concentrations of As, Pb, and Cd were determined by atomic-absorption spectrometry with electrothermal atomization (ETAAS) on instrument Solar MQZ (Thermo Electron Corporation, США). High-purity standards (parts A and B) were used for measurements, sulfur was measured with the use of a standard made of sulfuric acid fixanal. Standard solutions for AES-ICP in the determination of main macro- and microcomponents were a 23-element standard solution 11355 ICP Multi Element Standard IV (Merck) (with concentration of elements 1000 ± 10 mL/L) and multi-element standard solutions ICP-MS 68 (parts A and B) (High-Purity Standards) (with concentrations of elements of 100 and 10 mg/L, respectively). The relative standard deviation varies from 0.1 to 10%, depending on the measured concentration: from 5 to 50 ng/mL, the error is 5–10%, and from 50 ng/mL to 20 μg/L, it is 0.1–3%.

In all bays, in addition to epiphyton samples, surface water samples were taken in 2010, which immediately after sampling were filtered through Vladipor membrane filter with a pore size of 0.45 μm and acidified by 0.1 mL of concentrated nitric acid per each 10 mL of sample to study by AES-ICP method. Elements As, Cd, and Pb were determined by ETAAS method. The concentrations of Cd, Ce, Co, Cr, La, Mo, Nd, Ni, Pb, Sc, V, Y, and Yb in natural water was determined by mass-spectrometry with inductively coupled plasma (ICP-MS), because the concentrations of these elements in water samples were below the detection limit of AES-ICP method. The analyses were made on ELEMENT-2 mass-spectrometer (Thermo Scientific) at the Chair of Geochemistry, Faculty of Geology, Moscow State University. In 2005, a limited number of elements, mostly, heavy metals (Cd, Co, Cr, Cu, Ni, Zn), were determined in surface-water samples.

Samples of higher aquatic plants (HAP) were taken in overgrowing bays. The above-root part of the plant was cut off, washed in flowing water, dried at room temperature, pulverized in a mill, and incinerated at $t = 450°C$. Ash samples were decomposed in a mixture of acids ($HF + HNO_3 + HCl$). The element composition was determined by mass-spectrometry with inductively coupled plasma on ELEMENT-2 instrument (Thermo Scientific) at the Chair of Geochemistry, Faculty of Geology, Moscow State University. The overall chemical composition of plant ash was determined by X-ray-fluorescent method on an AXIOS Advanced spectrometer [4].

RESULTS AND DISCUSSION

As is known, bioindication can be implemented both by the response of an organism and the accumulation of hazardous substances in the organism. In this case, the degree of environmental pollution is assessed by the level of pollutant accumulation in the organism [16].

The concentrations of microelements determined in the epiphyton of the Ivankovo Reservoir are given in Table 1. The series of macroelement concentrations in the epiphyton of aquatic–marsh waters in 2010 is as follows: Ca > K > P> Mg > Na > S, and that for microelements is Fe > Al > Mn > Ba > Ti > Sr > Zn > V > Li > Ce > Cr ≥ Cu > Ni > W > Pb > La > As > Nd > Y > Co > Sc > Yb > Cd > Mo > Ag. For the epiphyton of submerged plants, the series of macroelement concentrations in 2010 is as follows: Ca > Mg > K > Na > P > S; and that of microelements is Fe > Al > Mn > Sr > Ba > Ti > Zn > W > Li > Ce > Cu > As > V > La > Pb > Ni > Y > Cr > Nd > Co > Sc > Ag > Cd > Yb > Mo.

Compared with the epiphyton of submerged plants, most elements (especially, lithophilous and rare earth elements) show high concentrations in epiphyton of aquatic–marsh macrophyte species. This is due to the large portion of terrigenous suspension in the geochemical composition of epiphyton samples of aquatic–marsh plant species. The belt of aquatic–marsh plants lies immediately at the shore in the surf zone, in the site of intense shore transformation, which shows higher water turbidity. Macrophyte beds actively capture surface runoff and the suspension it carries and absorb organic and inorganic compounds. In the coastal zone, lithodynamic abiotic factors, such as precipitation of terrigenous suspension, have a considerable effect on the geochemical composition of epiphyte suspension. The sampling method used in this study does not allow one to prevent the incorporation of particles of terrigenous suspension into epiphyton samples; therefore, the contribution of the terrigenous component to the sample was assessed by the concentration of lithophilic, main petrogenic, and rare earth elements (Al, Fe, Na, K, Ti, Li, and Sc). Epiphyton samples taken from aquatic–marsh macrophyte species, are, geochemically, samples of epiphyte suspension, i.e., a mixture of solid particles of river suspension with algaflora organisms attached. E.P. Yanin [20] was the first to propose the use of epiphyte suspension to indicate technogenic pollution of rivers under the conditions of considerable anthropogenic impact. The comparison of the obtained data on heavy metal concentrations in epiphyton samples taken from aquatic–marsh macrophyte species and data in [20], obtained for rivers subject to technogenic impact of a large industrial center, showed that the epiphyton of the Ivankovo Reservoir contains lower concentrations of Cd (on the average, by a factor of 20), Cu (by a factor of 15), and Co (by a factor of 5), and the concentration of lithophilic elements lower than those in epiphyte suspension.

Epiphyton samples taken from submerged macrophytes from different bays, remote from the sources of anthropogenic impact (background areas) showed similar macro- and microelement composition and a low terrigenous component. The composition of epiphyton from submerged plants is close to the average composition of freshwater plankton, according to [9], thus confirming both the species and geochemical identity of epiphyton and plankton.

Studying the spatial distribution of microelements in the epiphyton of the Ivankovo Reservoir revealed the following regularities. The concentrations of microelements in the epiphyton sampled in Babninskii, Peretrusovskii, Novosel'skii, and Omutninskii bays, as well as in the Shoshinskii pool are very close to one another and to the average values. Maximal concentrations of microelements in epiphyton were obtained for Moshkovicheskii bay, receiving wastewater from the Konakovskaya State District Power Plant (SDPP) and municipal sewage from Konakovo C. Here, epiphyton shows high concentrations of Ba, Cd, Cu, Mg, Mn, Ni, Pb, S, Sr, and Zn, exceeding their background values by factors of 3–8.

The comparison of data of 2005 and 2010 showed that in 2005, epiphyton accumulated heavy metals (Cd, Cu, Ni, Pb, and Zn) in concentrations 3–160 times those in 2010. The concentrations of biogenic elements (P and S) were also higher in 2005. Similar concentrations were obtained for Al, As, Ce, K, La, Li, Mg, Na, Ti, and V. The concentrations of Ca and Sr in 2010 were higher than those in 2005 by factors of 14 and 2, respectively; this may be due to the space and time variations of hydrochemical characteristics and changes in the species composition of algaflora. The decrease in heavy metal concentrations in epiphyton in the study period is, most likely, a result of a decrease in the discharge volumes of pollutants into the Ivankovo Reservoir. According to data in [3], the volumes of wastewater discharges were 101.9 in 2007, 98.85 in 2008, 92.31 in 2009, and 92.3 million m^3 in 2010. As shown in [19], heavy metal pollution tends to decrease in all groups of aqual complexes in the Upper Volga reservoirs over the recent 10 years (up to 2011), a fact which is in a good correlation with a decrease in the anthropogenic press of wastewater on water bodies. In 2005, according to the author's data, the concentrations of heavy metals in water in the examined bays were far in excess of the concentrations obtained in 2010 for the same bays (Table 1) and amounted to 0.3 for Cd, 1 for Co, 55 for Cr, 14 for Cu, 7 for Ni, and 108 μg/L for Zn. Interestingly, the average concentrations of microelements in HAP in 2005 and 2010 were the same. This is due to the fact that higher aquatic plants are biological species more tolerant to pollution and to the specific features of their nutrition. Macrophytes absorb microelements from both water and polluted bottom sediments, while epiphyton accumulates elements only from water.

The comparison of the obtained microelement concentrations in macrophytes and epiphyton of submerged plants showed that most elements accumulate in epiphyton in amounts larger than in macrophytes (Ag, Ca, Ba, Cd, Co, Ce, Cu, Fe, Mn, Pb, La, Li, Sr, V, Zn, Y, and Yb). Equal concentrations were

Table 1. Geochemical composition of epiphyton in the Ivankovo Reservoir (n—...; aq-bog is for aquatic-bog macrophyte species, subm is for submerged macrophyte species, nd is for concentration was not determined)

Element	Ecological group of macrophytes	Average concentration in epiphyte suspension per dry mass		EF 2010	Average composition of freshwater plankton by [9], mg/kg, %	Clarke of clay shale [16]	Average concentration in macrophytes in 2010, mg/kg dry mass	Average concentration in water in 2010, μg/L	BAC for epiphyton	BAC for macrophytes
		2005 (n = 10)	2010 (n = 10)							
Ag, mg/kg	aq-bog	nd	<0.1	6	0.024	0.07	0.02	5	2×10^1	4
	subm	nd	0.145	72			0.06		3×10^1	1
Al, %	aq-bog	0.21	1.3	0.68	0.17	8	147	50	3×10^5	3×10^3
	subm	0.13	0.16	0.65			4250		3×10^4	8×10^4
As, mg/kg	aq-bog	3.5	11.2	3.5	1.3	13	2.13	<0.5	2×10^4	4×10^3
	subm	2.2	3.53	9			3.41		7×10^3	7×10^3
Ba, mg/kg	aq-bog	310	312	2.5	37	580	7.41	105	3×10^3	7×10^1
	subm	1196	332	18			24		3×10^3	2×10^2
Ca, %	aq-bog	1.3	2.21	5.8	1.43	1.6	4898	61000	3×10^2	8×10^1
	subm	1.64	22.9	465			49226		4×10^3	8×10^2
Cd, mg/kg	aq-bog	1	0.45	7	0.79	0.3	0.004	0.08	5×10^3	5×10^1
	subm	2.74	0.125	16			0.01		2×10^3	1.3×10^2
Ce, mg/kg	aq-bog	15	21.6	1.2	1.83	70	0.09	0.14	2×10^5	6×10^2
	subm	4	6.5	3			1.94		5×10^4	1.4×10^4
Co, mg/kg	aq-bog	5	6.2	1.3	0.89	19	0.03	0.17	4×10^4	1.8×10^2
	subm	6	0.5	0.9			0.63		3×10^3	4×10^3
Cr, mg/kg	aq-bog	16	19.5	0.9	12.6	90	5.45	0.42	5×10^4	1.3×10^4
	subm	10	1.3	0.5			3.4		3×10^3	8×10^3
Cu, mg/kg	aq-bog	80	19.5	1.8	18.3	45	0.64	6	3×10^3	1×10^2
	subm	137	3.7	3			5.7		6×10^2	9.5×10^2
Fe, %	aq-bog	0.77	1.33	1.18	0.13	4.72	209	320	4×10^4	6.5×10^2
	subm	0.8	0.17	1.17			1861		5×10^3	6×10^3
K, %	aq-bog	0.16	1.6	2.5	0.59	2.66	24053	4040	4×10^3	6×10^3
	subm	0.24	0.33	4			29528		8×10^2	7×10^3
La, mg/kg	aq-bog	6.75	12.2	1.6	1.08	32	0.04	0.06	2×10^5	6×10^2
	subm	4	2.9	3			0.86		5×10^4	1.4×10^4
Li, mg/kg	aq-bog	8	26.2	1.6	1.8	66	0.34	4	6×10^3	8×10^1
	subm	5.2	8.7	4.3			0.96		2×10^3	2.4×10^2
Mg, %	aq-bog	0.24	0.36	1	0.15	1.5	1523	15320	2×10^2	1×10^2
	subm	0.46	0.6	13			9767		4×10^2	6×10^2

Table 1. (Contd.)

Element	Ecological group of macrophytes	Average concentration in epiphyte suspension per dry mass		EF 2010	Average composition of freshwater plankton by [9], mg/kg, %	Clarke of clay shale [16]	Average concentration in macrophytes in 2010, mg/kg dry mass	Average concentration in water in 2010, μg/L	BAC for epiphyton	BAC for macrophytes
		2005 (n = 10)	2010 (n = 10)							
Mn, %	aq-bog	0.3	0.76	38	0.02	0.085	96	220	3×10^4	4×10^2
	subm	1.47	0.08	30			759		4×10^3	3×10^3
Mo, mg/kg	aq-bog	nd	0.2	0.3	0.71	2.6	0.01	0.25	8×10^2	3×10^1
	subm	nd	0.1	1.25			0.07		4×10^2	2×10^2
Na, %	aq-bog	0.1	0.23	1	0.54	0.96	694	5460	4×10^2	1.3×10^2
	subm	0.05	0.06	2			7031		1×10^2	1.2×10^3
Nd, mg/kg	aq-bog	nd	10.2	1.4	0.78	31	0.04	0.07	1×10^5	6×10^2
	subm	nd	0.64	0.7			0.82		9×10^3	1.2×10^5
Ni, mg/kg	aq-bog	35	16.7	1	3.7	68	2.42	0.84	2×10^4	3×10^3
	subm	52	1.94	1			1.63		2×10^3	2×10^3
P, %	aq-bog	0.17	0.39	23	1.27	0.07	2058	260	1.5×10^4	8×10^3
	subm	0.17	0.05	23			4849		2×10^3	2×10^4
Pb, mg/kg	aq-bog	140	12.6	2.6	28	20	0.23	0.35	4×10^4	6×10^2
	subm	350	2.07	3			0.92		6×10^3	2.6×10^3
S, mg/kg	aq-bog	0.5	0.34	0.0006	nd	2400	1850	2360	0.14	8×10^2
	subm	0.98	0.09	0.001			2808		0.04	1.2×10^3
Sc, mg/kg	aq-bog	1.7	3.12	1	0.33	13	0.008	0.01	3×10^5	8×10^2
	subm	4	0.37	1			0.24		4×10^4	2.4×10^4
Sr, mg/kg	aq-bog	86	202	2.8	85	300	2.4	350	6×10^2	7.5×10^0
	subm	297	607	66			122		2×10^3	3.5×10^2
Ti, mg/kg	aq-bog	58	245	0.2	127	4600	1.67	1	2.5×10^5	1.7×10^3
	subm	56	44.4	0.3			450		4×10^4	4.5×10^5
V, mg/kg	aq-bog	15.5	26.7	0.9	6.3	130	0.25	0.55	5×10^4	4.5×10^2
	subm	4	3.15	0.7			0.44		6×10^3	8×10^2
Y, mg/kg	aq-bog	10	9	1.5	0.65	26	0.03	0.04	2×10^5	7.5×10^2
	subm	4	1.4	2			0.72		3.5×10^4	1.8×10^4
Yb, mg/kg	aq-bog	nd	0.79	1	0.074	3.1	0.002	<0.01	8×10^4	2×10^2
	subm	nd	0.11	1			0.055		1×10^4	5.5×10^3
Zn, mg/kg	aq-bog	374	110	4.9	107	95	8.0	9	1×10^3	8×10^2
	subm	733	15.1	5			10		1×10^3	1×10^3
W, mg/kg	aq-bog	14	nd	nd	nd	1.8	nd	<10	–	–
	subm	<10	nd	nd			nd		–	–

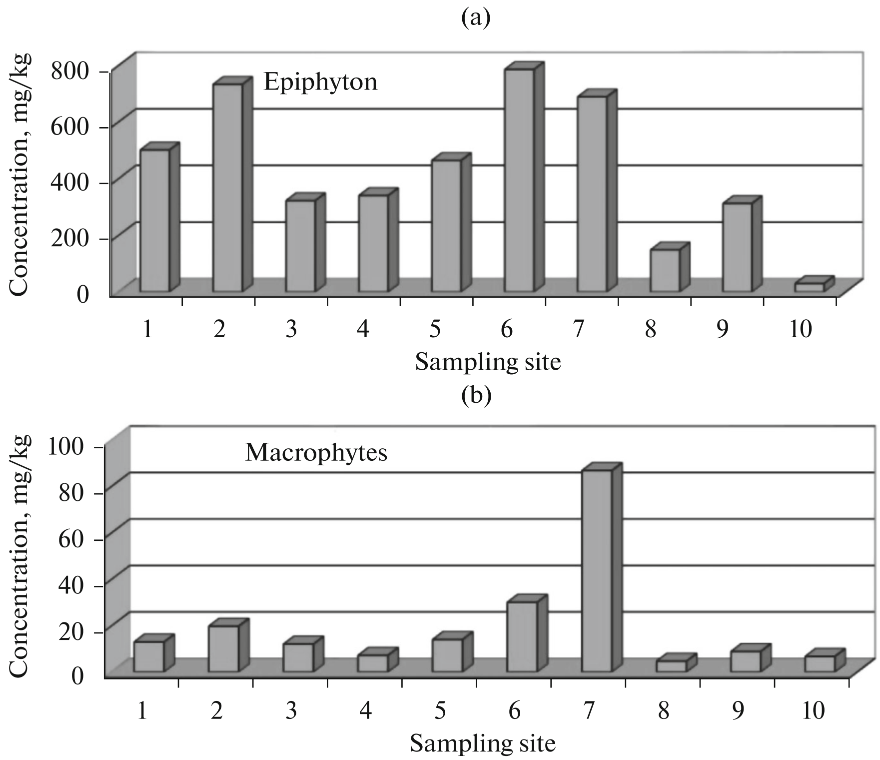

Fig. 2. Zinc distribution in epiphyton and macrophyte samples (for samples of 2005). Sampling sites: (1) Moshkovicheskii (reed manna grass), (2) Moshkovicheskii (water chestnut), (3) Babninskii (common floating pondweed), (4) Babninskii (water-bean), (5) Babninskii (bulrush), (6) Babninskii (common reed grass), (7) Omutninskii (dark green hornweed), (8) Omutninskii (narrow-leaved cattail), (9) Peretrusovskii (reed manna grass) bays, (10) Shoshinskii pool (reed manna grass).

recorded for Al, As, Co, Mg, Mo, Nd, Ni, and Sc. Macrophytes contain the amounts of K, Na, P, S, and Ti larger than those contained in epiphyton. The calculated coefficients of biological absorption for macrophytes confirm this regularity and show that, for most elements, epiphyton is better group concentrator than macrophytes. The spatial distribution of microelements in epiphyte suspension follows their distribution in macrophytes and has a similar character (Fig. 2). For example, both macrophytes and epiphyton show maximal concentrations of most microelements in Omutninskii Bay, where water and bottom sediments almost always contain high microelement concentrations. The Omutninskoe shallow area downstream of the island shows higher water turbidity and specific stagnant hydrodynamic conditions; the soil is represented by macrophyte silt, rich in organic matter. In other examined bays, where macrophytes contain microelements near their background concentrations, the concentrations of elements in epiphyton are also at a medium level. However, their spatial distributions show some differences. This is because macrophytes accumulate pollutants within a long vegetation period and receive them from both water and bottom sediments, while the microelement composition of epiphyton forms under the effect of surface water alone. Moreover, the biomass of epiphyte epibioses, unlike macrophyte, reproduces several times over vegetation period, i.e., it reflects habitat chemistry over the short period of its life cycle. For example, HAP in the zone near wastewater discharge from the Konakovskaya HDPP and Konakovo C. municipal facilities in Moshkovicheskii Bay contain medium concentrations of microelements Zn, Pb, Cu, Ni, while epiphyton samples show high concentrations of these elements, suggesting a volley type of water pollution in this site. Therefore, the geochemical composition of epiphyton is a good pollution indicator for water medium, where it lives for a short period, and it can be used to identify modern anthropogenic impact on an aquatic ecosystem.

The main bioindicator characteristics of aquatic ecosystem pollution in assessing environmental pollution by metals with the use of aquatic organisms are commonly taken to be the coefficients of biological absorption of metals in the organism, i.e., the ratio of their concentrations in the aquatic organism to its concentration in the medium, and the coefficients of metal concentrations in aquatic organisms in polluted areas relative to their concentrations in background areas [10, 16].

To assess the biogeochemical concentration function of epiphyton and the extent of accumulation of chemical elements in it, the biological absorption coefficients (BAC) were calculated as the ratio of element concentration in the dry mass of epiphyton to its concentration in water [2, 12, 16]: BAC = $C_{i\ \mathrm{ep}}/C_{i\ \mathrm{water}}$ ($C_{i\ \mathrm{ep}}$ is the concentration of the *i*th chemical element in epiphyton, mg/kg dry mass; $C_{i\ \mathrm{water}}$ is its concentration in water, mg/L). BAC is known to characterize the physiological demand of living organisms in chemical elements and the ability of living organisms to accumulate elements from the aquatic environment. The average values of the biological absorption coefficients obtained for the epiphyton of background bays of the Ivankovo Reservoir are given in Table 1. The biological absorption coefficients, calculated for epiphyton for most elements were far in excess of the respective values for macrophytes.

By the values of BAC in epiphyton, the elements are divided into two groups:

(1) BAC = $n \times 10^1$–10^2: Sr, Ca As S, Ag, K, Mg, Mo, Na, i.e., elements that weakly accumulate in epiphyton;

(2) BAC = $n \times 10^3$–10^5: Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Nd, Ni, P, Pb, V, Zn, W, Al, Ce, La, Sc, Ti, Y, Yb, i.e., elements that accumulate in epiphyton from natural water in considerable amounts.

At the sites of wastewater discharge in Moshkovicheskii Bay, the values of BAC were several times greater than the respective average values: by factors of 4 for Ba, 17 for Cd, 40 for Cu, 31 for Ni, 24–166 for Pb, and 81 for Zn. In the Omutninskii Bay, the biological absorption coefficients were also much higher than their average values: by factors of 4 for Ba, 29 for Co, 56 for Cr, and 65 for Cu. The variations of BAC values reflect the different degrees of anthropogenic load in different parts of the reservoir and the distinct ability of epiphyton to the bioaccumulation of large amounts of microelements and its bioindicator significance.

In the interpretation of analytical data to reveal the geochemical specifics of biological objects, the element composition of the object under consideration is often normalized by Sc as an element inert in hypergene processes [2, 12, 14]. The concentration effectiveness of chemical elements in a sample relative to the clarkes of clay shales is estimated with the use of enrichment factors (EF): EF = $(C_{Xi}/C_{X\mathrm{Sc}})_{\mathrm{sam}}/(C_{Xi}/C_{X\mathrm{Sc}})_{\mathrm{shale}}$ ($C_{Xi\ \mathrm{sam}}$ is the concentration of the chemical element in the study object, $C_{X\mathrm{Sc\ sam}}$ is the concentration of scandium in the study object, $C_{Xi\ \mathrm{shale}}$ is the concentration of chemical element in clay shale [22], $C_{X\mathrm{Sc\ shale}}$ is the concentration of scandium in shale.

By the values of EF, the elements are divided into groups:

EF ≤ 2: Al, Ce, Co, Cr, Fe, Mo, Nd, S, Sc, Ti, V, Yb, Ni, Y—weakly accumulate in epiphyton;

EF in the range 2–10: As, Cu, K, Pb, Zn Ce La Li Na—accumulate well in epiphyton compared with shales;

EF > 10: Ag, Ba, Ca, Cd, Mn, P Mg, Sr—accumulate in epiphyton in considerable amounts relative to the clarkes of clay shales. Therefore, the concentration function of epiphyton facilitates the enrichment of bottom sediments with biogenic macroelements, alkaline and alkaline earth elements, and other biogenic metals to a larger extent than the clarkes of clay shales do.

CONCLUSIONS

The geochemistry of epiphyton of macrophytes in the Ivankovo Reservoir was determined. The element composition of the epiphyton of submerged macrophytes is close to the average composition of freshwater plankton, and it corresponds to nonpolluted aquatic ecosystems. The majority of bays in the Ivankovo Reservoir show background concentrations of microelements in epiphyton. Exceptions are the bays of Moshkovicheskii, with suffers the effect of wastewaters, and Omutninskii, where higher microelement concentrations in epiphyton are governed by natural factors. Epiphyton samples are recommended to be taken from emophyte macrophytes, because the hydrodynamic conditions of the growth of macrophytes of this group prevent large amounts of terrigenous suspension from entering the sample. The macrophytes of wetland ecological group retain pollutants delivered by surface runoff and accumulate depositing suspension from roiled bottom sediments; therefore, the composition of epiphyte suspension from plants of this group characterizes the transport of microelements in the composition of solid river runoff.

Epiphyton meets all requirements to organisms used for bioindication and has some advantages over other organisms. Studying the microelement composition of epiphyton enables solving the problem of promptly assessing the present-day state of aquatic ecosystems, and characterizes the extent, composition, and the character of anthropogenic load onto aquatic ecosystem. The level of aquatic environment pollution can be assessed by the degree of pollutant accumulation in epiphyton, and the obtained data can be used for monitoring and retrospectively analyzing changes in the ecological state of the Ivankovo Reservoir. The ubiquitous occurrence of epiphyton, its fixation in a certain habitat, the relatively simple procedure of sample taking and preparation allow epiphyton to be recommended as an object of biomonitoring and bioindication of the anthropogenic effect on a water body. Epiphyton is a more informative study object for revealing volley pollution of aquatic environment than higher aquatic plant.

The values of BAC were used to identify chemical elements in the aquatic environment that accumulate in epiphyton in considerable amounts. The concentration function of epiphyton leads to the enrichment of bottom sediments with biogenic elements, in particular, alkaline and alkaline earth, as well as some microelements (Ag, Cd, Mn, Sr, As, Cu, Pb, Zn, Ce, and La).

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project no. 16-05-00542.

The authors are grateful to O.A. Tyutyunik (Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences) for her help in AES-ICP analysis.

REFERENCES

1. Belyaeva, P.G., Phytoperiphyton composition and structure in the Sylva R., Perm krai, *Bot. Zh.*, 2014, vol. 99, no. 8, pp. 903–916.
2. *Biogeokhimiya okeana* (Ocean Biogeochemistry), Monin, A.S., Lisitsyn, A.P., Eds., Moscow: Nauka, 1983.
3. *Gosudarstvennyi doklad Minprirody Rossii "O sostoyanii i ob okhrane okruzhayushchei sredy Rossiiskoi Federatsii v 2011 g."* (State Report of RF Ministry of Natural Resources "On the Environmental Conditions of the Russian Federation in 2011"). http://www.mnr.gov.ru/. Accessed February 2, 2016.
4. Grishantseva, E.S. and Safronova, N.S., Ecological–geochemical assessment of the state of the Volga Source of water supply to Moscow, *Water Resour.*, 2012, vol. 39, no. 3, pp. 305–321.
5. Grishantseva, E.S., Safronova, N.S., Kirpichnikova, N.V., and Fedorova, L.P., Regularities in the distribution of microelements in higher aquatic plants in the Ivankovo Reservoir, *Geoekol. Inzh. Geol. Gidrogeol. Geokriol.* 2010, no. 3, pp. 223–231.
6. Zhukova, A.A., Primary production of plankton, epiphyton, macrophytes, and microphytobenthos in littoral biotopes of Lake Naroch, *Vestn. BrGU*, 2005, no. 3, vol. 24, pp. 79–84.
7. Kazmiruk, V.D., Kazmiruk, T.N., and Brekhovskikh, V.F., *Zarastayushchie vodotoki i vodoemy: dinamicheskie protsessy formirovaniya donnykh otlozhenii* (Overgrowing Streams and Water Bodies: Dynamic Processes of Bottom Sediment Formation), Moscow: Nauka, 2004.
8. Kosyatova, V.A., Levshina, N.A., and Einor, L.O., Epiphyton of Macrophytes–Edificators of the Ivankovo Reservoir and its effect on quality formation of natural water, *Vodn. Resur.*, 1990, no. 3, pp. 81–88.
9. Kosyatova, V.A. and Einor, L.O., Epiphyton of freshwater bodies and its role in water quality formation, *Vodn. Resur.*, 1992, no. 5, pp. 110–120.
10. Kurilenko, V.V. and Osmolovskaya, N.G., Bioindication role of higher plants in the diagnostics of aquatic ecosystems: case study of small water bodies in St. Petersburg, *Water Resour.*, 2007, vol. 34, no. 6, pp. 718–724.
11. Leonova, G.A., Biogeochemical indicators of aquatic ecosystem pollution by heavy metals, *Water Resour.*, 2004, vol. 31, no. 2, pp. 195–202.
12. Leonova, G.A. and Bobrov, V.A., *Geokhimicheskaya rol' planktona kontinental'nykh vodoemov Sibiri v kontsentrirovanii i biosedimentatsii mikroelementov* (Geochemical Role of Plankton of Siberian Continental Water Bodies in the Concentration and Biosedimentation of Microelements), Novosibirsk: GEO, 2012.
13. Leonova, G.A., Bobrov, V.A., Lazareva, E.V., Bogush, A.A., and Krivonogov, S.K., Biogenic contribution of minor elements to organic matter of recent lacustrine sapropels (Lake Kirek as example), *Lithol. Miner. Resour.*, 2011, no. 2, pp. 99–114.
14. Lisitsyn, A.P., Fluxes of sedimentary matter, natural filters, and sedimentary systems of "live ocean," *Geol. Geofiz.*, 2004, vol. 45, no. 1, pp. 15–48.
15. Makarevich, T.A., Mikheeva, T.M., and Luk'yanova, E.V., Macrophytes as a substrate for periphyton, *Vestn. BGU*, 1986, Ser. 2, 1986, no. 3, pp. 30–33.
16. *Osnovy ekologii, bioindikatsii i biotestirovaniya vodnykh ekosistem* (Principles of Ecology, Bioindication, and Bioassaying of Aquatic Ecosystems) Kurilenko, V.V., Ed., St. Petersburg: Sankt-Peterb. Gos. Univ., 2004.
17. Safronova, N.S., Grishantseva, E.S., and Korobeinik, G.S., Hydrocarbon gases (C_1–C_5) and organic matter in bottom sediments of the Ivankovo Reservoir on the Volga River, *Water Resour.*, 2013, vol. 40, no. 3, pp. 285–296.
18. Tarasenko, L.V. and Lutsenko, M.A., Phytocenoses of Ivankovo Reservoir shallows, in *Biologicheskaya produktivnost' i kachestvo vody Volgi i ee vodokhranilishch* (Biological Production and Water Quality of the Volga and Its Reservoirs), Moscow: Nauka, 1984, pp. 161–162.
19. Tikhomirov, O.A., Formation, dynamics, and ecological state of aquatic complexes of lowland reservoirs, *Extended Abstract of Doctoral (Geogr.) Dissertation*, Moscow: Mosk. Gos. Ped. Univ., 2011.
20. Yanin, E.P., *Epifitovzves'—novyi indikator zagryazneniya rechnykh sistem tyazhelymi metallami* (Epiphyte Suspension as a New Indicator of Heavy Metal Pollution of River Systems), Moscow: IMGRE, 2002.
21. Cattaneo, A., Galanti, G., Gentinetta, S., and Romo, S., Epiphytic algae and macroinvertebrates on submerged and floating-leaved macrophytes in an Italian lake, *Freshwater Biol.*, 1998, vol. 39, no. 4, pp. 725–740.
22. Li Yuan-hui, Distribution patterns of the elements in the ocean: A synthesis, *Geochim. Cosmochim. Acta*, 1991, vol. 55, pp. 3223–3240.
23. Piirsoo, K., Vilbaste, S., Truu, J., et al., Origin of phytoplankton and the environmental factors governing the structure of microalgal communities in lowland streams, *Aquatic Ecol.*, 2007, vol. 41, no. 2, pp. 183–194.
24. Pip, E. and Robinson, G.G.C., A comparison of algal periphyton composition on eleven species of submerged macrophytes, *Hydrobiol. Bull.*, 1985, vol. 18, no. 2, pp. 109–118.

Translated by G. Krichevets