BIOFACIES ROLE OF PLANKTON AS NATURAL REMEDIATION MECHANISM OF HIGH-MINERALIZATION WATER CONTAMINATED WITH MERCURY (by the example of the Bolshoe Yarovoe lake, Altay Territory, Russia)

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Abstract – A complex of analytical methods (atomic absorption spectroscopy AAS, synchrotron radiation X-ray fluorescence SR-XRF, and instrumental neutron activation analysis INAA) were used to conduct for analyses of 40 trace elements. In compliance with the conventional biogeochemical methods, enrichment factors EF were calculated for plankton relative to the average concentrations of elements in continental clay (shale) preliminarily normalized to Sc. In order to understand the concentration specifics of trace elements in living organisms inhabiting aquatic ecosystems of variable salt composition and geochemical characteristics, chemical speciation of elements was calculated for the brines of salt lakes by the WATERQ4F (3) and Selektor-S (4) computer programs. The enrichment of plankton in Hg in Lake Bol'shoe Yarovoe is caused not only by the chemistry of the mineralized brine (bittern), as follows from the Hg speciation in it, but also by anthropogenic contamination (Hg-bearing wastes from the Altaikhimprom chemical plants in the town of Yarovoe).

INTRODUCTION. Biogeochemical studies in 1998-2003 indicate that the Altaikhimprom plant situated on the bank of this lake is responsible for ecologically unfavorable conditions within the influence zone of the plant in the lake (5–7, 9). This plant is one of the most active producer of chemicals (including Hg oxide) in Russia (11). Near the plant, the township of Yarovoe houses one of Russia's unique physiotherapeutic mud baths, which was established with the use of the mud produced in the lake with the participation of the dying brine shrimp Artemia salina. In this context, it is particularly important to evaluate the impact of wastes from the chemical plant on the ecosystem of the lake. Its biogeochemical sampling was carried out at five sites, some of which were situated within the near influence zone of the plant (sites 2 and 3) and others located at various distances from the contamination source (Fig. 1). We also sampled the solid wastes accumulators and the holding ponds for sewage in the sanitary protection zone of the plant considering them as the as the potential point sources of Hg contamination in the lake.

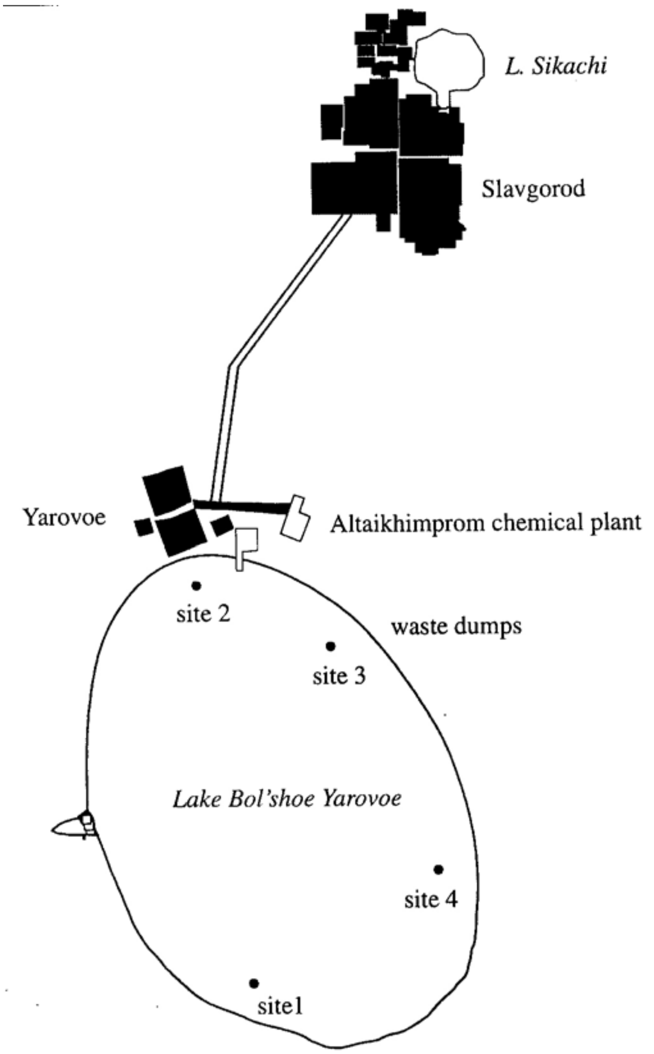

Fig. 1. Monitoring sites at Lake Bol'shoe Yarovoe.

MATERIALS AND METHODS. Salt lakes in Altai krai have long been used as sources of nonore minerals (mirabilite, gypsum, soda and halite). Sanatoria and spa resorts were constructed at the salt lakes of the Kulundinskaya steppe, which contain specific bottom deposits: medicinal ooze or mud, whose resources and reserves in the area are quite significant. The valuable medicinal materials can be produced on lakes Bol'shoe and Maloe Yarovoe, and others.

Lake Bol'shoe Yarovoe fills a deep (~25 m) depression and has neither river feeding nor outlet. The major component of the natural water budget of the lake is the spring runoff from the catchment area, outlets of groundwaters, and summer and winter atmospheric precipitates; the only water outlet if its evaporation. Its bottom deposits have a thickness of 0.6-1.5 m and consist of ooze.

Lake Maloe Yarovoe fills a deep geometrically shaped rounded depression and has no outlet. The floor of the lake is sandy, with the thickness of the ooze deposits reaching 0.1-0.2 m.

According to Alekin's classification (1), the waters of the lakes studied in the Kulundinskii steppe were ascribed to the chloride class, Na group, type III ($Cl^{-} \geq Na^{+}$). The predominant major ions are Cl^{-} and Na^{+}. The overall salt concentrations in the brines (mineralization) increase in the following succession of lakes: Bol'shoe Yarovoe and Maloe Yarovoe from to 133 and 262 g/l.

In assaying the ecological state and conditions of the lakes, we used conventionally adopted geochemical criteria (12, 14), which enabled us to evaluate the anthropogenic pollution of the lacustrine ecosystems with heavy metals.

The *concentration coefficient Kc* was applied as a measure of the level of anomalous concentrations of certain elements in the bottom sediments and biological matter. The

concentration coefficient was calculated as the ratio of the concentration of element *i* in the material C_i to the average background concentration of this element C_b:
$K_c = (C_i)/(C_b)$,

where C_i is the concentration of chemical element *i* in the contaminated zone, and C_b is the background concentration of this element.

The *integral contamination indicator* Z_c characterizes the effect of a group of elements and can be used when a polyelemental anthropogenic or natural anomaly is examined
$Z_c = \Sigma K_c - (n - 1)$,
where K_c is the concentration coefficient (>1), and n is the number of elements with $Kc > 1$.

The *geochemical association formula GAF* was employed to characterize the qualitative (elemental) composition of a geochemical anomaly within the influence zone of an individual source of anthropogenic contamination. GAF is a set of chemical elements ranked according to their K_c values, with these values K_c of no less than 1.5, i.e., elements with concentrations higher than 1.5 background values. The elements of a geochemical association are grouped according to the K_c values, with the boundaries of the ranges roughly corresponding to logarithmic scale with a step of 0.5 units, i.e., 0.5, 1.5–3, 3–10, 10–30, 30–100 etc., as can be seen when various objects are compared.

The *enrichment factors EF* of mesoplankton and bottom deposits from the lakes were calculated with the preliminary normalizing of the concentrations of all elements to the average concentration of Sc, a geochemically inert rare-earth element, and to the analogous average ratio in shales (according to (10), in compliance with the approach (2, 8), by the formula (13):
$EF = (x_i/x_{Sc})_{sample}/(x_i/x_{Sc})_{shale}$,
where $(x_i)_{sample}$ is the concentration of element *i* in the sample, x_{Sc} is the Sc concentration in the sample, $x_{i\ shale}$ is the concentration of element *i* in the shale, and $x_{Sc\ shale}$ is the Sc concentration in shale.

REZULTS AND DISCUSSION. The Hg concentrations of mesoplankton from lake Bol'shoe Yarovoe within the influence zone of the plant (site 3) are 5 to 10 times higher than those in mesoplankton from the "background" part of the lake (site 1) and in that from lakes Maloe Yarovoe (Fig. 2), which clearly highlights the anthropogenic sources of high Hg concentrations in the mesoplankton of Lake Bol'shoe Yarovoe (Fig. 3).

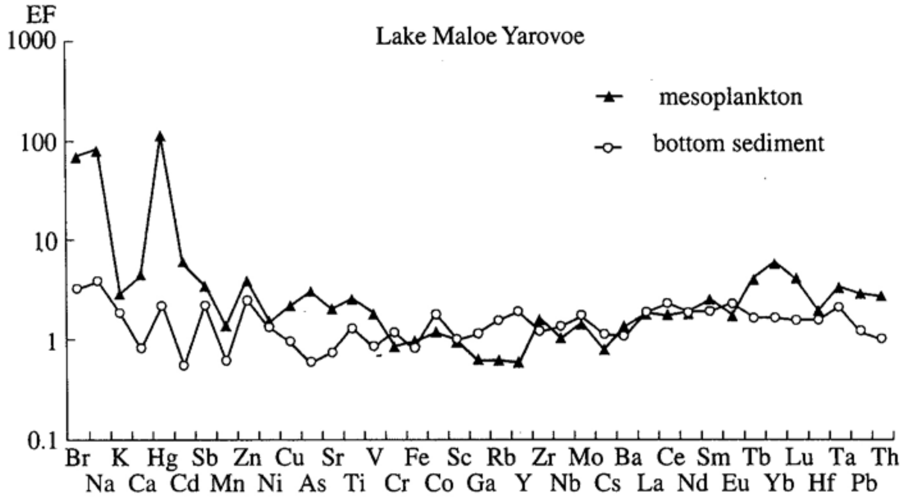

Fig. 2. Ranking of chemical elements according to their enrichment factors EF in mesoplankton (*A. salina*) and the upper layer of bottom sediments in Lake Maloe Yarovoe.

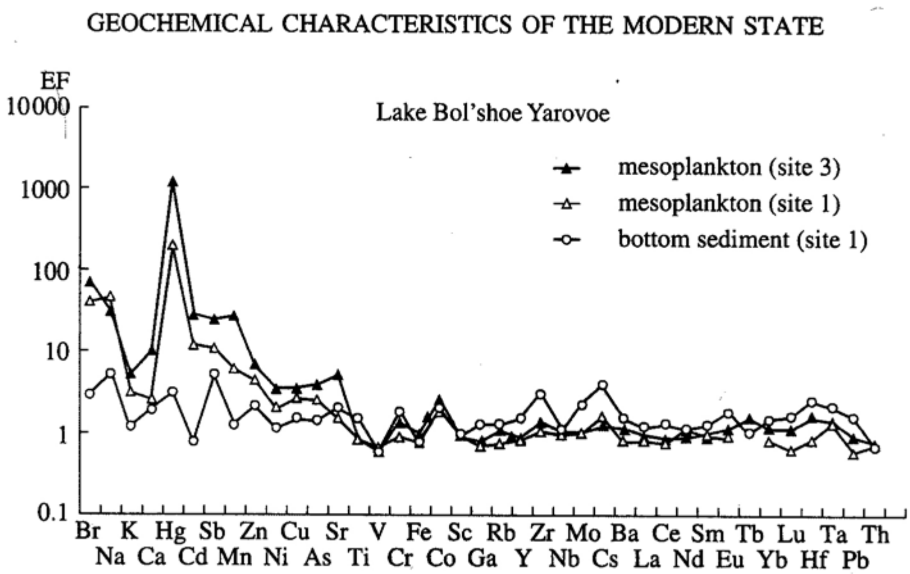

Fig. 3. Ranking of chemical elements according to their enrichment factors EF in mesoplankton (*A. salina*) and the upper layer of bottom sediments in Lake Bol'shoe Yarovoe.

The calculated concentration coefficients K_c reveal seven-fold Hg enrichment in the bottom sediments of Lake Bol'shoe Yarovoe in the nearest influence zone of the plant and five-fold enrichment in the mesoplankton relative to the background part (Fig. 4). The major diffuse sources of "anthropogenic" Hg in the lake seem to be solid-waste dumps on the lake banks, particularly during the snow-melting period, which is also consistent with the results of other researchers (11).

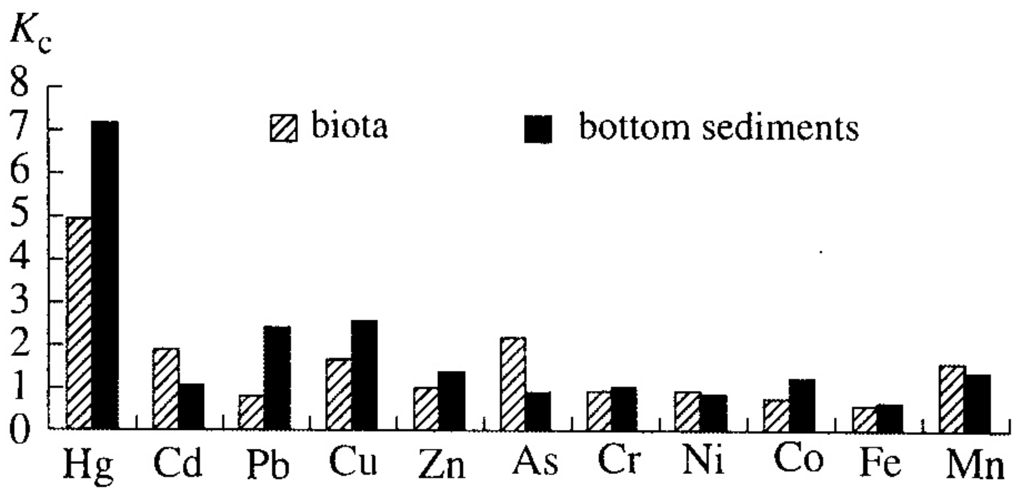

Fig. 4. Concentration coefficients Kc for mesoplankton (*A. salina*) and the upper layer of bottom sediments within the influence zone of the Ataihimprom chemical plant in Lake Bol'shoe Yarovoe (site 3).

Using the calculated concentration coefficients K_c, we developed formulas of geochemical associations for both the mesaplankton and the bottom sediments. In these coefficients, numerals near element symbols denote the values of the concentration coefficients $K_c > 1.5$.

Geochemical Association for the Mesoplankton of Lake Bol'shoe Yarovoe

Site 2: $\mathbf{Hg_{2.43}}$
Site 3: $\mathbf{Hg_{4.98}} > As_{2.24} > Cd_{1.93} > Cu_{1.69} > Mn_{1.65}$
Site 4: $\mathbf{Hg_{1.83}} > As_{1.65} > Cd_{1.56}$

As can be seen form this formula, the major contaminant of mesaplankton in the lake is Hg at all of the sites. The broadest spectrum of contaminating elements (Hg, As, Cd, Cu, and Mn) with $K_c > 1.5$ was detected in mesoplankton from site 3 near the lakefront dumps of the Altaikhimprom chemical plant.

Geochemical Association of Bottom Deposits in Lake Bol'shoe Yarovoe:

Site 2: $\mathbf{Hg_{5.5}}$
Site 3: $\mathbf{Hg_{7.17}} > Cu_{2.58} > Pb_{2.43}$
Site 4: $\mathbf{Hg_{2.5}} > Pb_{1.57}$

It should be emphasized that the K_c of elements in the association in both the living matter and the bottom sediments are generally relatively low, but nevertheless, they indirectly testify that the elements, particularly Hg, are potentially hazardous for the ecosystem of the lake.

The calculated integral contamination indicators Z_c (Table 1) were ranked according to the classification proposed by Yanin (14) (Table 2). This allowed us to class the bottom sediments of Lake Bol'shoe Yarovoe within the influence zone of the chemical plant (site 3) with medium contaminated ($10 \leq Z_c < 30$) and weakly contaminated (sites 2 and 4; $Z_c < 10$). These integral contamination indicators Z_c are characterized as moderate and permissible in terms of toxicological hazardousness.

Table 1

Integral contamination indicator Z_c for the bottom sediments of Lake Bol'shoe Yarovoe

Site	Integral contamination indicator for the bottom sediments **(Z_c)** of Lake Bol'shoe Yarovoe
2	6.60
3 (contamination zone)	**11.54**
4	4.01

Table 2

Qualitive scale for river contamination according to the intensity of the accumulation of chemical elements in bottom deposits (according to Yanin (14)

Contamination indicator	Anthropogenic contamination level	Toxicological hazardousness level
Zc <10	Weak	Permissidle
10 ≤ Zc < 30	Intermediate	Moderate
30 ≤ Zc < 100	High	Hazardous
100 ≤ Zc < 300	Very high	Very hazardous
Zc ≥300	Extremely high	Extremely hazardous

It should also be stressed that the situation with contamination of mesoplankton and bottom deposits in the lake did not change with time during our biogeochemical monitoring (in 1998–2004) (Table 3).

Table 3

Hg contents in the mesoplankton (*Artemia salina*)* and bottom sediments** from salt Lake Bol'shoe Yarovoe

Sampling site	**1998 year**	**2004 year**
site 1 (background)	0.64* 0.054**	0.46 – 0.84* 0.006 – 0.017**
site 3 (influence zone of the chemical plant)	1.5* 0.77**	1.1 – 2.3* 0.019 – 0.12**

It is also important to mention that Hg is contained in the brine of Lake Bol'shoe Yarovoe predominantly in solute form, and only its minor amounts are contained in the particulate matter. Inorganic Hg species in this system are chloride complexes: ~92–96% $HgCl_4^{2-}$, ~2.7–5.9% $HgCl_3^{-}$, and ~0.25–2.5% $HgCl_2^{0}$. These species predetermine the elevated biological accessibility of Hg, which makes this element toxic for living organisms, including the halophilic brine shrimp *Artemia salina*.

To determine mercury speciation in salt waters sediments and zooplankton of the Lake Bolshoe Yarovoe the method of thermal analysis with atomic absorption spectrometry detection was applied (Table 4). A Lumex RA-915+ mercury analyzer equipped with pyrolytic attachment RP-91C was used.

Table 4

Methylmercury and total mercury ($\mu g g^{-1}$) in the mesoplankton (*Artemia salina*) and bottom sediments from salt Lake Bol'shoe Yarovoe

Sample	Methylmercury	Total mercury
Mesoplankton (site1)	1.50 ± 0.30	1.60 ± 0.20
Mesoplankton (site 2)	1.60 ± 0.30	1.30 ± 0.20
Mesoplankton (site 3)	2.50 ± 0.50	2.30 ± 0.30
Lake sediment (site1)	0.53 ± 0.10	0.53 ± 0.07
Lake sediment (site 2)	0.30 ± 0.05	0.32 ± 0.04
Lake sediment (site 3)	0.27 ± 0.05	0.22 ± 0.03
Lake sediment (site 4)	0.19 ± 0.05	0.22 ± 0.03

CONCLUSIONS. (1) The accumulation of potential ecological toxicants (Hg, Cd, Zn, and Cu) is related to the fact that their predominant species in the brines of salt lakes are mobile chloride complexes and free ions, which can be readily consumed by plankton.

(2). The calculated EF values point to 100-fold enrichment of the mesoplankton of lakes Maloe Yarovoe in Hg and 1000-fold enrichment of the mesoplankton of Lake Bol'shoe Yarovoe in this element. This obviously demonstrates an anthropogenic source of Hg in the ecosystem of Lake Bol'shoe Yarovoe.

(3). The concentration coefficients @K@c calculated for components of the ecosystem of Lake Bol'shoe Yarovoe demonstrate the seven-fold enrichment of the bottom sediments in Hg within the nearest influence zone of the chemical plant and the five-fold enrichment of this element in the mesoplankton relative to the values for the "background" area. According to the anthropogenic contamination level of bottom deposits in the influence zone of the Altaikhimprom chemical plant in Lake Bol'shoe Yarovoe, these deposits were provisionally classified as moderately contaminated. The deposits at the "background" area were classified as weakly contaminated. In terms of toxicological hazardousness, these sediments are ascribed to moderately and permissibly hazardous, respectively. The major diffuse anthropogenic sources of Hg are lakeside dumps of solid wastes (which become particularly hazardous during snow melting).

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