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Geochemical Characteristics of the Modern State of Salt Lakes in Altai Krai

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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 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 WATEQ4F and Selektor-S 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).

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INTRODUCTION

Salt lakes in Altai krai have long been used as sources of nonore minerals (mirabilite, gypsum, soda, and halite). The complex research conducted there in the early 20th century has demonstrated that many of the lakes can be used as economic sources of these minerals. The early 1950s were marked by the beginning of works at soda and salt lakes in the Kulundinskaya steppe. For example, a sulfate plant operates at Lake Kuchukskoe and is Russia's largest producer of Na sulfate from natural mirabilite. The Burlinskii salt plant specializes in producing rock salt extracted from Lake Burlinskoe. The soda solutions of the Tanatarskie Lakes are utilized as a soda source by the Mikhailovskii soda plant [1, 2].

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, Kuchukskoe, and others. The alkaline and H_2S-bearing oozes of lakes Shchelochnoe and Baklan'e and the sapropel oozes of lakes Mel'nichnoe, Khor'kovskoe, and Malyi Utkul' are of balneological interest. The development of local and regional sanatorium and resort institutions in Altai krai resulted in the intense utilization and depletion of natural limnic materials: solid salt deposits, brines, mineralized oozes, and mud deposits [1, 3].

Starting in the 1980s, the salt lakes of the Kulundinskaya steppe serve as the source of biological materials of aquatic genesis, including invertebrate meal, as the most valuable brine shrimp crustacean *Artemia salina* L. [4].

The development of the mineral and biological resources of salt lakes in Altai krai induced the study of, first of all, the salt composition of the high-mineralization brines [5–8], the physicochemical characteristics of the medicinal mood [3], and the hydrobiological characteristics of the aquatic biota, such as its biomass, seasonal dynamics, etc. [9, 10]. In contrast to this, practically no biological research was conducted at the lakes, neither was determined the elemental composition of the interrelated components of the lacustrine ecosystems (for the brine, bottom deposits, and halophilic biological species). A.P. Vinogradov was the first to mention [11, p. 356] the halophilic brine shrimp *Artemia*: "…a very unusual species is the brine shrimp *Artemia salina*, whose masses inhabit many salt lakes, marine lagoons, and natural water bodies with high salt concentrations, particularly sulfates (saturated Na_2SO_4 solutions), for example, the Tambukanskie lakes, Karabugaz lagoon, lakes in the Kulundinskie steppes, etc. In lakes in the Barabinskaya steppe, *Artemia salina* forms sapropel deposits. The chemistry of the brine shrimp remains largely uncertain, which makes it particularly interesting to consider the likely only one available analysis of *Artemia salina* from a lake in Cordoba (Lake Mar Chiquita, Argentina), available from

Stuckert (1933). The eggs of the shrimps are rich in P, and the shells of the eggs contain much Ca. The ash was determined to contain 74.92% NaCl." In the publication quoted above, the researcher points out unusual chemical features of zooplankton and the zooplankton of salt lakes in particular: "…it is impossible to accurately enough separate this zooplankton from seawater, which is retained in and beneath its coverings, trunk segments, and valves, as well as in antennae. Because of this, a common disadvantage of all plankton analyses is that they involve some amounts of marine salts" [11, p. 352]. The authors of this paper also faced the problem of the impossibility of complete separating salts when the elemental composition of *Artemia salina*is determined, as was mentioned in our earlier paper [12].

The gap in the biogecohcemical study of the ecosystems of salt lakes in general and those in the Kulundinskaya steppe in particular led us to formulate the task of examining the elemental composition of interrelated components of the lacustrine ecosystems in both natural and anthropogenically disturbed environments. We also tried to assay the ecological state of the lakes using the method of biogeochemical indicating. This research was based on the results of the monitoring, conducted in 1998–2004, of the state of three salt lakes: Kulundinskoe, Maloe Yarovoe, and Bol'shoe Yarovoe [13–17].

The following tasks were formulated to be accomplished in order to solve the general problems:

—to elucidate the specifics in the enrichment of the living material of the lakes in trace elements relative to their concentrations in the habitat (brine and bottom deposits);

—to examine the distribution of the elements between the major chemical modes in the inorganic subsystem of the brine and to demonstrate their biological accessibility and potential ecological hazard for biological species;

—to assay the anthropogenic load onto the ecosystem of Lake Bol'shoe Yarovoe within the influence zone of the Altaikhimprom chemical plant with the application of conventionally accepted geochemical criteria.

MATERIALS AND METHODS

The salt lakes in question are situated in the northwest of Altai krai, in its steppe and most arid part: the Kulundinskii plain (Fig. 1, modified after [18]). The territory has the topography of a slightly depressed flatland that is weakly cut by watercourses and has the minimum elevations in the central portion of the depression. The surface topography of the plain was shaped under the effect of a large Quaternary water body, which systematically diminished. As the surface of the basin decreased, the exposed land surface was affected by water erosion, and outer terraces with insignificant altitudes were eroded more strongly and acquired a rolling topography. The depressed part of the flatland includes large salt lakes, such as Kulundinskoe, Kuchukskoe, Bol'shoe Yarovoe, and a number of smaller lakes, which are residual water bodies of the precursor large basin. The major rivers draining the area are the Kulunda, Kuchuk, Suetka, and their tributaries [2].

Lake Kulundinskoe is the largest salt lake in the Kulundinskaya steppe. It is a periodically flowing water reservoir, i.e., outlets its waters to Lake Kuchuk at high water. The lake is fed by the Kulunda and Suetka rivers and by snow melt waters (the lake does not freeze in wintertime). The bottom deposits of the lake contain mirabilite reserves [7].

Lake Bol'shoe Yarovoe fills a deep (~25 m) depression and has neither river feeding nor outlet. Its bottom deposits have a thickness of 0.6–1.5 m and consist of ooze. 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 [1].

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 [1].

The principal components of the ecosystems of the lakes were sampled in compliance with conventional techniques. Water samples were collected from the surface layer into polyethylene flasks, filtered through membrane filters with pores 0.45 μm in diameter on the Kuprin devise in order to separate particulate and solute metal species. The filtrates were conserved by means of adding concentrated reagent-grade HNO_3 (4 ml of acid per 1 l of the solution). The filters with particulate matter were packed into polyethylene pockets and stored in a fridge. The bottom deposits were sampled near the banks to depths of 30–50 cm, using cylindrical coring samplers with leaf shutters. The sediment cores were divided into 3-cm segments. Each sample was analyzed for natural moisture. Mesoplankton (*A. salina*) was sampled using a small plankton net. The net samples from the uppermost (0–5 m) brine level of Lake Bol'shoe Yarovoe were dominated by mature brine shrimps *A. salina* (up to 100% of the biomass). The ash contents of these samples was 28% on average. Samples of surface plankton from lakes Kulundinskoe and Maloe Yarovoe consisted of mature *A. salina*, diapausing cysts (eggs), and perhaps, also insignificant amounts of mineral particulate matter, which caused the remarkably higher ash contents of plankton samples from this lake (42 and 51%, respectively).

The major-component (cations and anions) composition of the brines was determined at the certified Laboratory for the Monitoring the Quality of Natural and Waste Waters at the VERKHNEOB'REGIONVODKHOZ federal institution.

The trace-element composition of the brine, bottom deposits, and biological material was analyzed at the

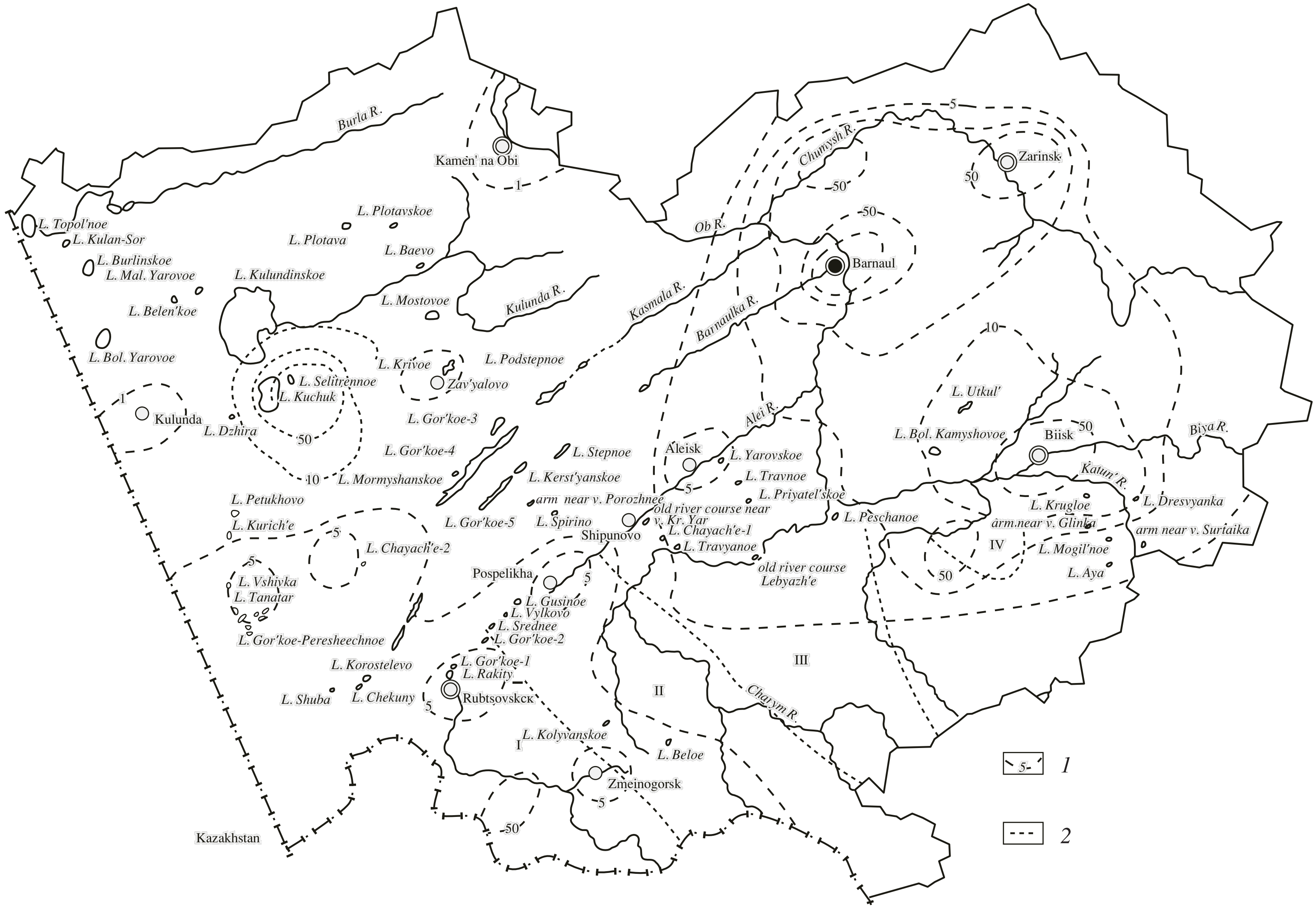

Fig. 1. Location map of salt lakes in northwest Altai krai (Modified after [18]). (*1*) Isopleths (t/km^2/year) for air contamination in Altai krai; (*2*) boundaries of zones (I) Rudnyi Altai base-metal, (II) Charysh–Korgon subzone, (III) Talitskaya rare-metal subzone, (IV) Belokurikha cluster of mineral deposits.

Analytical Center of the United Institute of Geology, Geophysics, and Mineralogy, Siberian Branch, Russian Academy of Sciences, with the use of a complex of precise analytical techniques, which were described in detail in [12, 19]. This allowed us to obtain data on the concentrations of approximately 40 elements (including several trace and major elements and REE) in the bottom sediments and mesoplankton of the salt lakes. Our analytical data are unique, because the mesoplankton samples were the first ever analyzed for a broad spectrum of elements, with all analyses conducted using the same samples and various analytical techniques, which enabled us to compare the results obtained by various methods.

In order to understand the specifics of the concentration of chemical elements in living matter in aquatic ecosystems with various salt compositions and geochemical environments, we calculated the chemical speciation of elements in the brines of the salt lakes using the WATEQ4F [20] and Selektor-S [21] computer programs. The application of two computer programs allowed us to bypass certain limitations commonly encountered when the speciation of chemical elements in solutions are calculated. For example, the WATEQ4F program is not suitable for calculating the speciation of elements in highly mineralized solutions and is not supplied with a thermodynamic database for the calculation of Hg speciation. Conversely, the Selektor-S program complex makes it possible to calculate equilibria in highly mineralized solutions, but its thermodynamic databases have some limitations in terms of the list of trace-element species. Because of this, the simultaneous utilization of the two computer program not only provides results in fairly good agreement with chemical analytical data but also allowed us to calculate the speciation of most major and trace elements in the brines of three salt lakes: Kulundinskoe, Maloe Yarovoe, and Bol'shoe Yarovoe.

Below we explain the notation usually applied in the calculation of the speciation of metals in aqueous solutions: Me^{2+}—hydrated ionic species, $MeCO_3^0$—neutral carbonate species, $MeHCO_3^+$—hydrocarbonate species, $Me(CO_3)_2^{2-}$—anionic carbonate species, $MeSO_4^0$—neutral sulfate species, $Me(SO_4)_2^{2-}$—anionic sulfate species, $MeOH^+$—cationic hydroxide species, $Me(OH)_2^0$—neutral hydroxide species, and $MeC1^+$—cationic chloride species.

In assaying the ecological state and conditions of the lakes, we used conventionally adopted geochemical criteria [22, 23], which enabled us to evaluate the anthropogenic pollution of the lacustrine ecosystems with heavy metals.

The concentration coefficient K_c 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:

$$Z_c = \sum K_c - (n - 1),$$

where K_c is the concentration coefficient (>1), and n is the number of elements with $K_c > 1$.

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. 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 [24]), in compliance with the approach [25–27], by the formula

$$EF = (x_i/x_{Sc})_{sample}/(x_i/x_{Sc})_{shale},$$

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.

It should be mentioned that a **principally new** approach employed in our research is the biochemical study of **a group of trace elements and REE**, which were inadequately poorly examined in aquatic living species but were fairly thoroughly examined in lacustrine–marine deposits. This allowed us to compare the concentrations of chemical elements in the mesoplancton and bottom sediments by normalizing to REE, including geochemically inert Sc, and to calculate the enrichment factors for the living matter.

SALT AND TRACE-ELEMENT COMPOSITION OF BRINES AND SPECIATION OF MAJOR AND TRACE ELEMENTS IN THEM

According to Alekin's classification [28], the waters of the lakes studied in the Kulundinskii steppe were ascribed to the chloride class, Na group, type III (Cl ≥ Na^+). The predominant major ions are Cl^- and Na^+. The overall salt concentrations in the brines (mineralization) increase in the following succession of lakes: Kulundinskoe, Bol'shoe Yarovoe, Maloe Yarovoe from 94 to 133 and 262 g/l, respectively (Table 1). The reason for the lower mineralization of the brine of Lake Kulundinskoe is the runoff of the Kulunda and Suetka rivers. The pH values range from near-neutral in lakes Maloe and Bol'shoe Yarovoe (7.10–7.28) to weakly alkaline (8.13) in Lake Kulundinskoe. Note that the high mineralization of the brine highly complicated its analysis for trace elements, including those of ecological importance (Cd, As, Pb, Ni, and Co).

The distributions of elemental species in the inorganic subsystem of brine of Lake Bol'shoe Yarovoe is characterized in Table 2. In our calculations, the source information was the major-salt (cations and anions) and trace-element composition of the brine, its oxygen concentration, and physicochemical parameters, such as Eh and pH, which were measured in field. Elemental species in the brine are dominated by hydrated ions and complexes with inorganic ligands.

Ca and Mg prevail in the brines of the lakes in the form of free ions (Ca^{2+} and Mg^{2+}) and are also contained (no more than 10%) as sulfate ($CaSO_4^0$ and $MgSO_4^0$) and hydrocarbonate ($CaHCO_3^+$ and $MgHCO_3^+$) complexes (less than 1%).

Na and K are contained in the brines mostly in the form of free ions (Na^+ and K^+) and as minor amounts of sulfate complexes ($NaSO_4^-$ and KSO_4^-; <1%).

Ba occurs predominantly in the form of sulfate complexes ($BaSO_4^0$) and ions (Ba^{2+}), and the concentrations of hydrocarbonate ($BaHCO_3^+$) and carbonate ($BaCO_3^0$) complexes are much lower.

Sr is contained in an ionic form (Sr^{+2}), which is the most readily accessible form for living organisms. However, when the pH changes from neutral to weakly alkaline in the succession of lakes Maloe Yarovoe—Bol'shoe Yarovoe—Kulundinskoe, the fraction of the Sr^{2+} species decreases from 92 to 65%. The sum of the sulfate ($SrSO_4^0$), carbonate ($SrCO_3^0$), and hydrocarbonate ($SrHCO_3^+$) complexes account for less than 5%.

Zn is contained in the solutions predominantly in the form of chloride complexes ($ZnCl_2^0$, $ZnCl_3^-$, and $ZnCl^+$) and as free ions (Zn^{2+}). The concentrations of

Table 1. Major ions and trace elements in the brines of salt lakes in Altai krai (as of July 2002)

Parameter	L. Kulundinskoe	L. Bol'shoe Yarovoe	L. Maloe Yarovoe
Mineralization, g/l	94	133	262
pH	8.13	7.28	7.10
Alkalinity, mg-equiv/l	22.5	–	7.5
Total hardness, mg-equiv/l	307	–	734
(HCO_3^-), mg/l	685	212	229
(SO_4^{2-}), mg/l	19880	4916	8450
(Cl^-), mg/l	34000	79000	160000
(PO_4^{-3}), mg/l	0.22	1.56	0.25
(NO_3^-), mg/l	4.6	0.2	7.0
(Ca^{2+}), mg/l	241	962	541
(Mg^{2+}), mg/l	3590	11700	8590
(Na^+), mg/l	25400	36000	91000
A1, mg/l	0.17	–	0.72
Ba, mg/l	0.05	0.31	0.11
Sr, mg/l	1.3	9.2	3.2
P, mg/l	0.35	0.53	0.54
Si, mg/l	6.6	4.7	2.7
Mn, mg/l	0.01	0.21	0.18
Cr, mg/l	0.011	–	0.016
Cu, mg/l	0.0079	–	0.0135
Fe, mg/l	0.25	0.89	0.41
Zn, mg/l	0.051	0.057	0.11
Hg, mg/l	0.00006	0.00008	0.00004

Note: Most analyses were done by titrometric and turbidimetric techniques at the laboratory for the Monitoring of the Quality of Natural and Sewage Waters of the VERKHNEOBREGIONVODKHOZ Federal State Enterprise (analysts T.M. Bulycheva, G.N. Krivolapova, and G.D. Veresova). Trace elements were analyzed by ICP-MS at the Laboratory of Analytical Chemistry, Analytical Center, United Institute of Geology, Geophysics, and Mineralogy, Siberian Branch, Russian Academy of Sciences (analyst L.B. Trofimov). Hg was determined by cold vapor atomic absorption (analyst Zh.O. Badmaeva). The Cd, As, Pb, Ni, and Co concentrations were below the detection limit of atomic absorption. Dashes mean the absence of data.

Table 2. Concentrations (%) of major elemental species in the brine of lake Bol'shoe Yarovoe

Species	Percentage, %	Species	Percentage, %
Ba		Sr	
Ba^{2+}	22.81	Sr^{2+}	91.97
$BaCO_3^0$	0.07	$SrCO_3^0$	2.63
$BaHCO_3^+$	2.17	$SrHCO_3^+$	1.47
$BaSO_4^0$	74.95	$SrSO_4^0$	3.93
Cu		Pb	
Cu^{2+}	1.0	Pb^{2+}	0.05
$CuCO_3^0$	36.83	$PbCO_3^0$	5.65
$Cu(CO_3)_2^{2-}$	0.02	$PbHCO_2$	0.44
$CuHCO_3^+$	5.84	$PbOH^+$	0.09
$CuOH^+$	0.97	$PbSO_4^0$	0.17
$Cu(OH)_2$	25.07	$PbCl^+$	14.65
$CuSO_4^0$	1.29	$PbCl_2^-$	28.4
$CuCl^+$	18.47	$PbCl_3^-$	45.15
$CuCl_2$	10.44	$PbCl_4^{2-}$	5.4
$CuCl_3^-$	0.07	Cd	
Zn		Cd^{2+}	0.01
Zn^{2+}	0.96	$CdSO_4^0$	0.02
$ZnCO_3^0$	1.31	$CdCl^+$	9.11
$Zn(CO_3)_2^{2-}$	0.01	$CdCl_2$	41.15
$ZnHCO_3^+$	1.41	$CdCl_3^-$	49.71
$ZnOH^+$	0.07	Fe	
$Zn(OH)_2$	0.01	$Fe(OH)_2^+$	43.65
$ZnSO_4^0$	1.42	$Fe(OH)_3^0$	55.41
$ZnCl^+$	18.18	$Fe(OH)_4^-$	0.94
$ZnCl_2$	24.19	Hg	
$ZnCl_3^-$	46.62	$HgCl_2$	0.5
$ZnCl_4^{2-}$	5.83	$HgCl_3^-$	2.7
		$HgCl_4^{2-}$	96.8

Note: The calculations were carried out by A.A. Bogusha and V.A. Bychinskii using the WATEQ4F and Selektor-S program complexes, respectively.

sulfate ($ZnSO_4^0$), hydrocarbonate ($ZnHCO_3^+$), and carbonate ($ZnCO_3^0$) species are lower. The weakly alkaline waters of Lake Kulundinskoe additionally contain hydroxide complexes [$ZnOH^+$ and $Zn(OH)_2$].

Cd is present in the brines mostly in the form of chloride complexes ($CdCl_2^0$, $CdCl_3^-$, and $CdCl^+$). The concentration of the (Cd^{2+}) ion and ($CdSO_4^0$) sulfate complexes are insignificant.

Cu is contained in the solutions mostly as carbonate ($CuCO_3^0$), hydroxide [$Cu(OH)_2^0$)], and chloride ($CuCl^+$ and $CuCl_2^0$) complexes. Hydrocarbonate ($CuHCO_3^+$), sulfate ($CuSO_4^0$), and free ionic (Cu^{2+}) species account for less than 5% of solute Cu species. A change in the physicochemical parameters of the solutions results in the regrouping of major Cu species. For example, if pH becomes more alkaline (lakes Maloe Yarovoe—Bol'shoe Yarovoe—Kulundinskoe), the fraction of carbonate ($CuCO_3^0$) and hydroxide [$Cu(OH)_2^0$)] species increases from 19 to 41% and from 7.2 to 51%, respectively, while the fraction of chloride complexes simultaneously diminishes.

Fe occurs in the solutions predominantly in the form of hydroxide complexes of Fe(III): $Fe(OH)_3^0$, $Fe(OH)_2^+$, and $Fe(OH)_4^-$. As pH varies from 7.1 to 7.28 and 8.13 (lakes Maloe Yarovoe—Bol'shoe Yarovoe—Kulundinskoe), the fraction of $Fe(OH)_2^+$ decreases from 50 to 8.5%, and those of $Fe(OH)_3^0$ and $Fe(OH)_4^-$ increase from 49 to 78 and from 0.5 to 13%, respectively.

Hg. It is expedient to consider the Hg speciation in more detail, because this element is the main potential ecotoxicant in Lake Bol'shoe Yarovoe. 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*.

The calculated speciation of metals in the inorganic subsystem of the brine of Lake Bol'shoe Yarovoe is dominated by free ions and chloride complexes, whereas the fractions of other species are much lower. The scheme presented for the ranking of metal species in surface waters depending on their toxicity for aquatic organisms (Fig. 2, after [29]) led us to conclude that the metals are contained in the brine of the lake in the most toxic and biologically easily accessible forms, which is

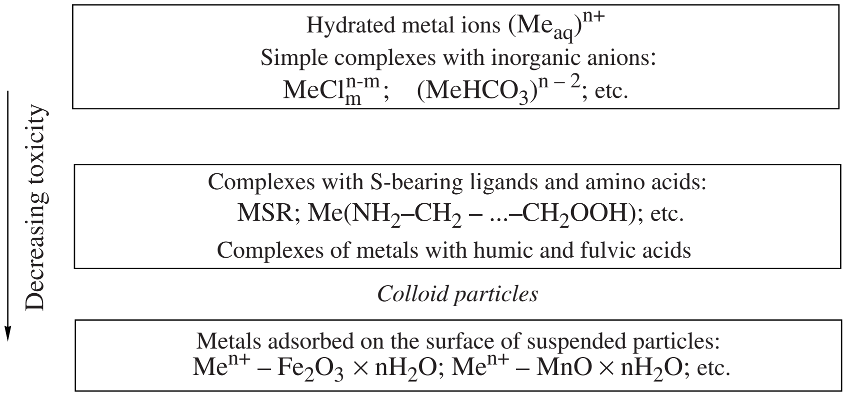

Fig. 2. Speciation of metals in surface waters (according to Budnikov [29]).

consistent with the conclusions drawn for fresh-water ecosystems [30–32].

DISTINCTIVE FEATURES OF THE ENRICHMENT OF CHEMICAL ELEMENTS IN THE MESOPLANKTON AND BOTTOM SEDIMENTS OF NATURALLY AND ANTHROPOGENICALLY DISTURBED ENVIRONMENTS

Lakes with natural (background) concentrations of chemical elements in components of their ecosystem. The problem of global environmental pollution (atmospheric transfer and precipitation of contaminants) becomes pressing for Altai krai in spite of the fact that this territory is characterized by one of the lowest levels of industrial airborne emissions in western Siberia [18]. Because of this, it is reasonable to distinguish there background areas affected only by transboundary atmospheric precipitates but not emissions from local industrial contamination sources. The geochemical parameters of this background state of lakes in Altai krai have not been examined thoroughly enough, which also pertains to salt lakes in the Kulundinskii steppe.

In determining the background parameters of the water bodies, we took into account, first of all, the distances from these bodies to local industrial contamination sources, and the ranges of elemental concentrations obtained for the aquatic biota were compared with the average values for aquatic organisms [11, 33] and with the average concentrations of these elements in biological species inhabiting uncontaminated waters [34, 35].

The background water bodies of the Kulundinskii steppe include lakes Kulundinskoe and Maloe Yarovoe, which were classed with this group on the basis of the results of long-term monitoring [13–17]. The concentrations of elements in the bottom deposits and mesoplankton of these lakes can be assumed as reference values, representing the geochemical background for this territory (Table 3).

The geochemical features of the examined materials (mesoplankton and bottom sediments) are revealed most clearly by the comparative analysis of the relative values, for example, the calculated enrichment factors *EF* (Table 4). The bottom sediments of lakes Kulundinskoe and Maloe Yarovoe are enriched in Na, whose *EF* is equal to ~6 and ~4, respectively. For all other alkaline and alkali-earth elements, the enrichment factors did not exceed 2 relative to the average concentrations of the elements in shale [24]. Low *EF*, no higher than 2 average concentrations in clay, occasionally 4–5, are typical of most trace elements in Lake Kulundinskoe. The sediments from lakes Maloe Yarovoe and Kulundinskoe generally have REE concentrations two times higher than the normalized REE concentrations in shale, a fact likely reflecting the geochemical specifics of terrigenous materials transferred by water and air masses.

Figures 3 and 4 present ranked *EF* values and display 3- to 8-fold enrichment of the mesoplankton in elements determining the salt composition of the brines: Br, Na, K, Ca, and Sr. In addition to salt forming, the mesoplankton is enriched in a group of so-called “volatile” elements [27], which are mostly chalcophile and are involved in atmospheric transfer (often for long distances), together with dust and emissions from industrial enterprises. These elements are Hg, Zn, Cu, Pb, Sb, and As. Upon precipitating onto water surface, these mobile elements are the most actively consumed by plankton, as follows from the relatively high *EF* values of these elements. However, the *EF* values for mesoplankton in lakes Kulundinskoe and Maloe Yarovoe are generally not high (not more than 8) and correspond to those typical of background water bodies [32].

Anthropogenically transformed Lake Bol’shoe Yarovoe. Biogeochemical studies in 1998–2003 indicate that the Altaikhimprom plant situated on the bank of this lake is responsible for ecologically unfavorable

Table 3. Elemental composition [mg/kg, %, anhydrous basis] of *Artemia salina* L. and bottom sediments from salt lakes Kulundinskoe and Maloe Yarovoe

Parameter	L. Kulundinskoe		L. Maloe Yarovoe		Average concentrations for shales [24]
Mineralization	94 g/l		262 g/l		
Material	*A. salina*	Precipitate	*A. salina*	Precipitate	
Ash content	42%		52%		
Na, %	2.1	2	10.5	1.7	0.96
K, %	1.68	1.3	1.05	2.3	2.66
Ca, %	1.14	1.1	0.92	0.6	1.6
Sc	1.55	4.4	1.68	6	13
Ti, %	0.092	0.2	0.152	0.28	0.46
V	23	55	30.5	50	130
Cr	12.6	52	10.5	50	90
Mn, %	0.0134	0.22	0.0152	0.023	0.085
Fe, %	0.44	1.1	0.58	1.75	4.72
Co	2.3	3.7	2.9	16	19
Ni	16.8	40	12.9	42	68
Cu	27.2	20	12.9	20	45
Zn	78	80	45	110	95
Ga	5.0	9	1.5	10	19
Ge	0.4	1	0.5	3	1
As	2.5	2	5.1	3.5	13
Br	75	25	164	30	20
Rb	31.5	80	11.2	100	140
Sr	196	300	79	102	300
Y	8.0	39	2.05	23	26
Zr	83	230	34.5	90	160
Nb	2.1	5	1.53	7	11
Mo	0.8	4	0.3	2	2.6
Cd	**0.54**	**0.08**	**0.13**	**0.07**	**0.3**
Sb	0.25	0.8	0.66	1.5	1.5
Cs	0.84	2	0.51	2.6	5
Ba	104	312	102	285	580
La	7.95	20	7.9	28	32
Ce	16.8	49	16.9	79	73
Nd	7.5	19.5	7.65	27	31
Sm	1.38	4.2	1.9	5	5.7
Eu	0.37	1	0.27	1.25	1.2
Tb	0.38	0.5	0.46	0.66	0.85
Yb	0.92	2.4	2.45	2.4	3.1
Lu	0.104	0.36	0.255	0.35	0.48
Hf	0.84	7	1.18	3.4	4.6
Ta	0.21	1.14	0.355	0.77	0.8
Th	1.7	5.7	4.3	5.7	12
Hg	**0.29**	**0.01**	**0.12**	**0.01**	**0.015**
Pb	**3.77**	**11**	**3.08**	**11**	**20**

Note: Zn, K, Ca, Ti, V, Ga, As, Y, Zr, Nb, and Mo were determined by XRF (analysts V.A. Bobrov, Yu.P. Kolmogorov, and M.A. Fedorin); Na, Fe, Sc, Cr, Co, Se, Br, Rb, Sr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, and Th were analyzed by INAA (analyst V.A. Bobrov); **Cd** and **Pb** were determined by atomic absorption AAS (analyst V.N. Il'ina); **Hg** was analyzed by cold vapor atomic absorption CVAAS (analyst Zh.O. Badmaeva); dashes mean the absence of data.

Table 4. Enrichment factors EF of various chemical elements

Element	L. Bol'shoe Yarovoe			L. Maloe Yarovoe		L. Kulundinskoe	
	A. salina		Precipitate, site 1	*A. salina*	Precipitate	*A. salina*	Precipitate
	site 3	site 1					
Br	68.9	41.5	2.8	68.94	3.25	38.65	3.69
Na	29.96	46.10	5.16	82.07	3.84	18.30	6.16
K	5.18	3.12	1.16	2.96	1.87	5.28	1.44
Ca	9.85	2.59	1.93	4.43	0.81	5.93	2.03
Hg	1208	203	3	112.93	2.17	234.23	2.95
Cd	27.6	12.0	0.8	5.91	0.55	5.62	0.79
Sb	23.6	11.1	5.2	3.4	12.17	1.41	1.58
Mn	26.9	6.2	1.3	1.39	0.59	1.32	7.65
Zn	6.63	4.54	2.18	3.94	2.51	8.14	2.49
Ni	3.48	2.03	1.14	1.45	1.34	2.07	1.74
Cu	3.50	2.77	1.51	2.19	0.96	2.34	1.31
As	3.94	2.55	1.43	3.03	0.58	1.62	0.45
Sr	5.25	1.52	2.06	2.04	0.74	5.15	2.95
Ti	0.86	0.84	1.48	2.57	1.32	1.68	1.28
V	0.61	0.68	0.60	1.82	0.83	1.49	1.25
Cr	1.40	0.92	1.79	0.88	1.20	1.76	1.71
Fe	1.00	0.81	0.77	0.95	0.80	0.78	0.69
Co	2.49	1.89	1.95	1.20	1.82	1.02	0.58
Sc	1	1	1	1	1	1	1
Ga	0.83	0.73	1.30	0.62	1.14	2.22	1.40
Rb	1.13	0.79	1.33	0.62	1.55	2.01	1.69
Y	0.91	0.85	1.55	0.61	1.92	2.57	4.43
Zr	1.48	1.11	3.10	1.67	1.22	4.30	4.25
Nb	1.07	1.01	1.13	1.07	1.38	1.60	1.34
Mo	1.06	1.06	2.38	1.52	1.67	2.70	4.55
Cs	1.34	1.66	4.02	0.79	1.13	1.41	1.18
Ba	1.22	0.86	1.55	1.36	1.06	1.51	1.59
La	0.98	0.86	1.26	1.91	1.90	2.09	1.85
Ce	0.92	0.83	1.36	1.78	2.34	2.17	1.98
Nd	0.95	1.16	1.20	1.91	1.89	2.04	1.86
Sm	1.04	0.97	1.30	2.56	1.90	2.03	2.18
Eu	1.25	0.99	1.93	1.81	2.26	2.58	2.46
Tb	1.67		1.09	4.17	1.68	3.72	1.74
Yb	1.27	0.89	1.57	6.10	1.68	2.49	2.29
Lu	1.23	0.69	1.68	4.10	1.58	1.83	2.25
Hf	1.71	0.90	2.69	1.97	1.60	1.53	4.50
Ta	1.48	1.38	2.32	3.45	2.09	2.20	4.21
Pb	0.98	0.62	1.70	2.95	1.19	2.28	1.63
Th	0.85	0.81	0.77	2.79	1.03	1.20	1.40

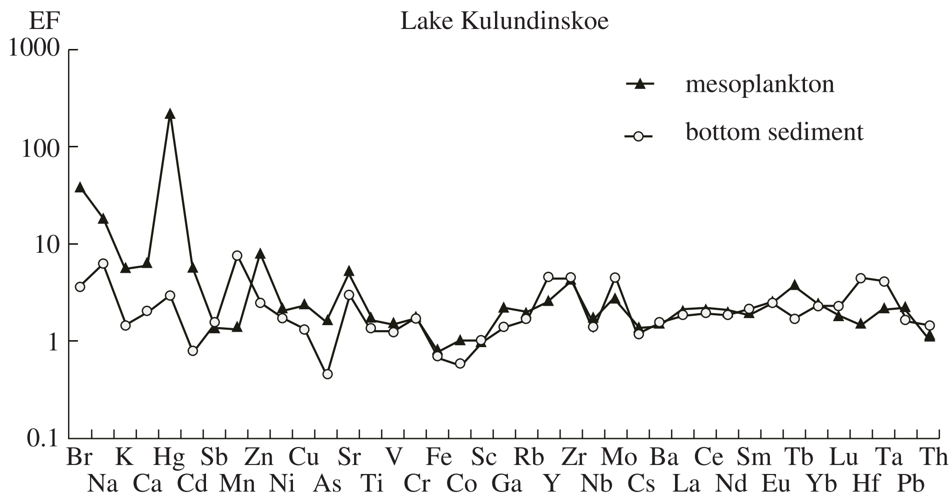

Fig. 3. Ranking of chemical elements according to their enrichment factors *EF* in mesoplankton and the upper layer of bottom sediments in Lake Kulundinskoe.

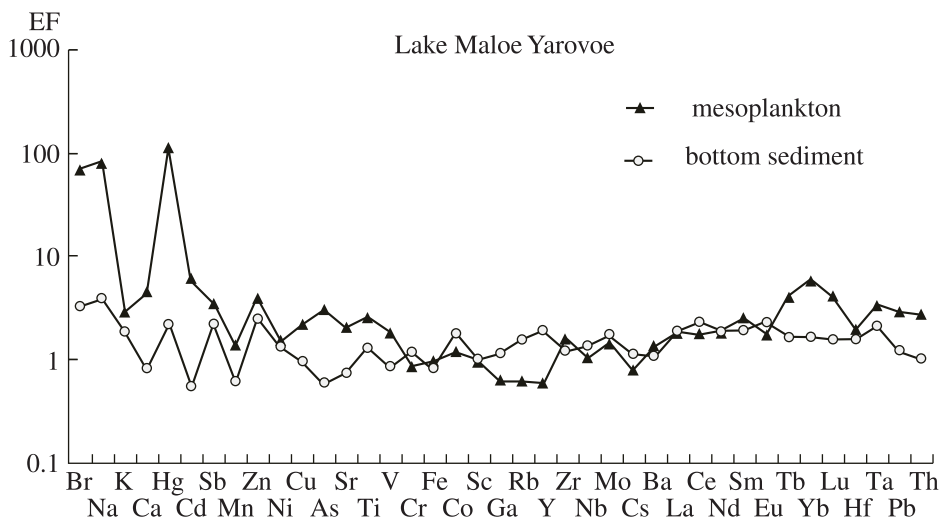

Fig. 4. Ranking of chemical elements according to their enrichment factors *EF* in mesoplankton and the upper layer of bottom sediments in Lake Maloe Yarovoe.

conditions within the influence zone of the plant in the lake [13–17]. This plant is one of the most active producers of chemicals (including Hg oxide) in Russia [36]. 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 *A. 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. 5). 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 potential point sources of Hg contamination in the lake.

Data on the elemental composition of the mesoplankton (*A. salina*) and bottom sediment of the background part of the lake (site 1) and in the immediate influence zone of disposals from the plant (site 3, bank dumps of solid disposals) are presented in Table 5.

The Hg concentrations of mesoplankton 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 and Kulundinskoe, which clearly highlights the anthropogenic sources of high Hg concentra-

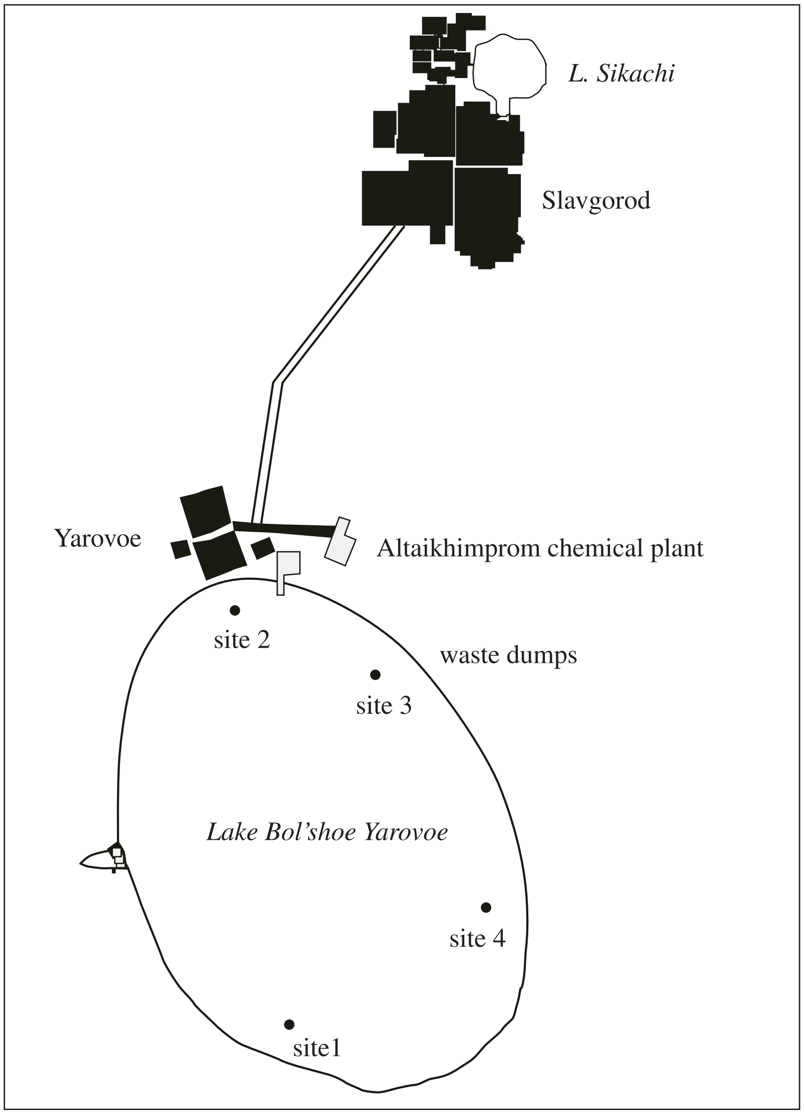

Fig. 5. Monitoring sites at Lake Bol'shoe Yarovoe.

tions in the mesoplankton of Lake Bol'shoe Yarovoe (Fig. 6).

The bottom sediments of Lake Bol'shoe Yarovoe are enriched in Na (*EF* = 5). The *EF* for all other alkaline and alkali-earth elements do not exceed 2 relative to the concentrations of the elements in the shale. Low enrichment factors (no higher than 2 clarkes for shale) are also typical of most trace elements.

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. 7). 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 [36].

Using the calculated concentration coefficients K_c, we developed formulas of geochemical associations for both the zooplankton 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 from 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

Table 5. Elemental composition [mg/kg, %, dry mass] of *Artemia salina* L. and bottom sediments from salt lake Bol'shoe Yarovoe

Parameter	L. Bo'shoe Yarovoe			Average concentrations for shales [24]
Mineralization	133 g/l			
Sampling site	Contamination zone (site 3)	"Background" zone site 1	"Background" zone site 1	
Material	*A. salina*	*A. salina*	precipitate	
Ash content	28%	28%		
Na, %	2.05	4.8	1.6	0.96
K, %	0.98	0.84	1	2.66
Ca, %	1.12	0.42	1	1.6
Sc	0.92	1.31	4.2	13
Ti, %	0.028	0.042	0.2	0.46
V	5.6	9	25	130
Cr	8.5	7.6	52	90
Mn, %	0.163	0.055	0.035	0.085
Fe, %	0.338	0.385	1.18	4.72
Co	3.4	3.65	12	19
Ni	16.8	14	25	68
Cu	11.2	12.5	22	45
Zn	43	44	67	95
Ga	1.1	1.4	8	19
Ge	0.6	0.55	3	1
As	3.6	3.5	6	13
Br	98	80	18	20
Rb	11	11.2	60	140
Sr	93	46	200	300
Y	1.7	2.3	13	26
Zr	18	17.7	160	160
Nb	0.85	1.12	4	11
Mo	0.2	0.28	2	2.6
Cd	**1.1**	**0.55**	**0.07**	**0.3**
Sb	2.1	1.68	2.5	1.5
Cs	0.5	0.83	6.5	5
Ba	50	50	290	580
La	2.2	2.8	13	32
Ce	4.8	6.18	32	73
Nd	2.1	3.65	12	31
Sm	0.42	0.56	2.4	5.7
Eu	0.106	0.12	0.75	1.2
Tb	0.10	0.76	0.3	0.85
Yb	0.28	0.28	1.57	3.1
Lu	0.04	0.034	0.26	0.48
Hf	0.56	0.42	4	4.6
Ta	0.08	0.112	0.6	0.8
Th	0.73	0.98	3	12
Hg	**2.3**	**0.46**	**0.01**	**0.015**
Pb	**1.6**	**1.9**	**11**	**20**

Note: Zn, K, Ca, Ti, V, Ga, As, Y, Zr, Nb, and Mo were determined by XRF (analysts V.A. Bobrov, Yu.P. Kolmogorov, and M.A. Fedorin); Na, Fe, Sc, Cr, Co, Se, Br, Rb, Sr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, and Th were analyzed by INAA (analyst V.A. Bobrov); **Cd** and **Pb** were determined by atomic absorption AAS (analyst V.N. Il'ina); **Hg** was analyzed by cold vapor atomic absorption CVAAS (analyst Zh.O. Badmaeva); dashes mean the absence of data.

Table 6. Integral contamination indicator Z_c for the bottom sediments of Lake Bol'shoe Yarovoe

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

Table 7. Qualitative scale for river contamination according to the intensity of the accumulation of chemical elements in bottom deposits (according to Yanin [37])

Contamination indicator	Anthropogenic contamination level	Toxicological hazardousness level
$Z_c < 10$	Weak	Permissible
$10 \le Z_c < 30$	Intermediate	Moderate
$30 \le Z_c < 100$	High	Hazardous
$100 \le Z_c < 300$	Very high	Very hazardous
$Z_c \ge 300$	Extremely high	Extremely hazardous

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 for 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 6) were ranked according to the classification proposed by Yanin [37] (Table 7). 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 ($10 \le Z_c < 30$) 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.

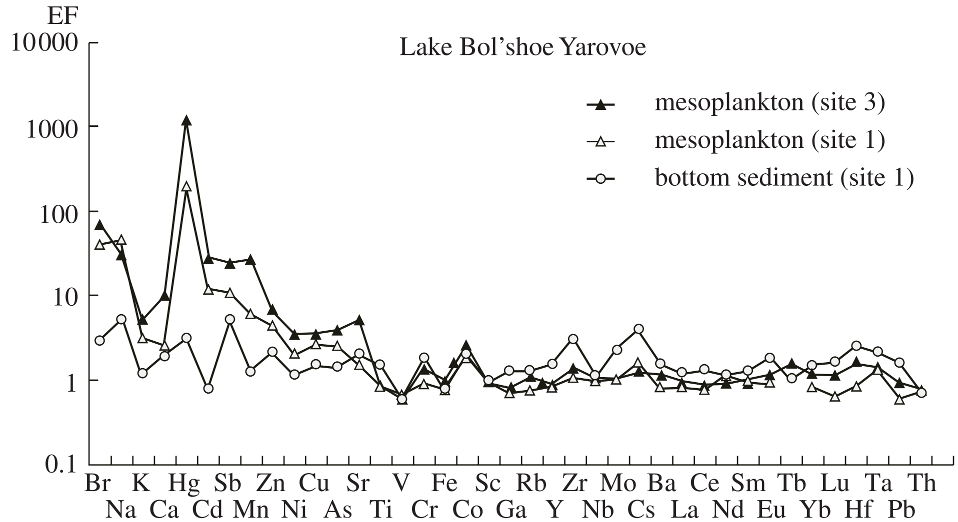

Fig. 6. Ranking of chemical elements according to their enrichment factors *EF* in mesoplankton and the upper layer of bottom sediments in Lake Bol'shoe Yarovoe.

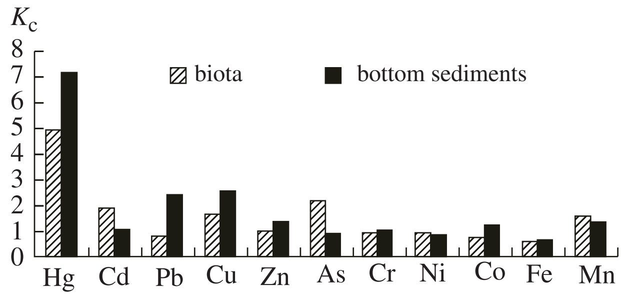

Fig. 7. Concentration coefficients K_c for mesoplankton and bottom sediments within the influence zone of the Altaikhimprom chemical plant in Lake Bol'shoe Yarovoe (site 3).

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 8).

Table 8. Hg contents in the zooplankton and bottom deposits of Lake Bol'shoe Yarovoe

Sampling site	1998	2004
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**

Notes: * Mesoplankton,
** bottom deposits.

CONCLUSIONS

(1) The mesoplankton of salt lakes actively concentrates brine-forming elements, such as Br, Na, K, and Ca. 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. At the same time, the bottom deposits are relatively poor in As, Hg, Cr, Fe, and Co.

(2) Ecologically significant elements (Hg, Cd, Pb, and Zn) are contained in the brines as solute (geochemically mobile) species, which are the most easily accessible for living organisms. The calculated *EF* values point to 100-fold enrichment of the mesoplankton of lakes Maloe Yarovoe and Kulundinskoe 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 sevenfold enrichment of the bottom sediments in Hg within the nearest influence zone of the chemical plant and the fivefold 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).

(4) The studying of the elemental composition of aquatic organisms, for example, plankton, is sometimes (for instance, in highly saline waters) advantageous over the immediate measuring the concentrations of trace elements in brine samples.

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