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Hydrogeochemistry and hydrobiology of technogenic reservoirs of mining territories of Eastern Transbaikalia

Vera Abramova[1*], *Ekaterina* Afonina[1], *Alexey* Kuklin[1], and *Svetlana* Borzenko[1]

[1]Institute of Natural Resources, Ecology and Cryology, Siberian Branch of the Russian Academy of Sciences, 16a, Nedorezova St., Chita, 672014, Russia

Abstract. The chemical composition of the waters of quarry lakes formed as a result of the development of the Zavitinskoye lithium-beryllium deposit located in Eastern Transbaikalia (Russia) has been studied. The studied waters of the ore pits are fresh with a neutral and slightly alkaline reaction, mainly of the magnesium-calcium sulfate type. It was found that the quarry waters contain high concentrations of lithium (Li) and strontium (Sr), in isolated cases of arsenic (As). Low concentrations of other metals in man-made waters are due to the neutralizing effect of carbonates of host rocks and ores, but this does not make them environmentally safe. The content of trace elements in the waters of quarries relative to the background contents, as well as the standards of maximum permissible concentrations (MPC) of chemicals for the waters of water bodies of fishery importance and sanitary and hygienic indicators were determined. A distinctive feature of the studied quarry lakes, as well as other man-made reservoirs, is the low species diversity of zooplankton and macrophytes, which is mainly due to the small catchment area, the steepness of the shores, the absence of shallow waters and other factors.

1 Introduction

The study of quarry lakes on mining territories is of great interest to researchers around the world. Such water bodies typically form as a result of mining of mineral deposits and mining activities. The quality of technogenic water bodies is characterized by a broad range of physicochemical conditions that differ from natural conditions, and can vary greatly depending on the geological, hydrogeological, and landscape-climatic features of mining territories, as well as the mineralogical-geochemical characteristics of the extracted raw materials. Many questions regarding the chemical composition, evolution, and functioning of these natural-technogenic systems continue to be highly relevant. The study of the hydrogeochemistry of technogenic water bodies is also important for addressing various environmental problems, including the improvement of water quality for multiple human uses, such as recreation, water supply, irrigation, cooling water reservoirs, and energy production. Of particular interest is the study of hydrobionts in technogenic water bodies,

* Corresponding author: vera_abramova79@mail.ru

which can serve as indicators of water quality and can sensitively respond to even short-term changes, including pollution. The Transbaikal region, as the oldest mining region in Russia with its wealth and diversity of mineral resources, offers ample opportunities for studying such objects. The hydrogeochemical characteristics of some of them have been discussed in previous works. However, the hydrobiological aspects of technogenic water bodies within the mining complexes of the Transbaikal region have not been studied extensively, and have only been presented by individual comprehensive studies. The goal of this work is to study the chemical composition of technogenic water bodies at the Zavitinskoye rare metal deposit, as well as the diversity of zooplankton communities that develop in complex eco-geochemical conditions of anthropogenic genesis.

2 Materials and methods

2.1 The characteristic of the study area

The Zavitinskoye lithium-beryllium deposit is one of the largest lithium reserves in Russia. The deposit is located in the Zavitaya River basin in the western part of the Borshchevokh Ridge, on the territory of the Shilkinsky district of the Transbaikal region. The climate of the area under investigation is markedly continental, with an average annual sum of atmospheric precipitation of about 350 mm and the spread of perennial permafrost of the island type.

The deposit is related to the Eastern Transbaikalian rare-metal pegmatite province. The pegmatite dikes of the deposit are localized in the sandstone-shale thickness of the Triassic and are associated with the Mesozoic Kukulbey granite complex. The main ore minerals of the Zavitinskoye deposit are spodumene ($LiAlSi_20_6$) and beryl ($Be_3Al_2Si_60_{18}$); accompanying minerals are petalite ($LiAlSi_4O_{10}$), columbite-tantalite ($FeTa_20_6$), and cassiterite (SnO_2). Ore mining at the deposit was carried out by the Transbaikal Mining and Processing Plant (ZabGOK) from 1937 to 1997 using an open-pit method. The beneficiation plant was located near the quarries, and the pulp was discharged into the tailings storage about 4 km east of the plant. From 1980 to 1989, the plant also processed imported ores from the Permakovskoye fluorspar-beryllium deposit (Republic of Buryatia) and fluorspar ores from Mongolian deposits. In 1997, due to the lack of demand for spodumene and beryllium concentrates, all work at the deposit was halted, and the plant was mothballed. The technogenic disturbed lands were not recultivated.

Currently, in the careers of the Zavitinskoye deposit at different elevations, two lakes have formed as a result of flooding, separated by a ridge of bedrock. The upper lake (hereafter K-1), with an area of 30.000 m^2, is located at an elevation of approximately 665 m. Its length and width are 552 m and 70 m, respectively, and its maximum depth is 11.3 m with a water transparency of 5.5 m. The lower lake (K-2) is larger in area (434 000 m^2) and is located at an elevation of 605 m with dimensions of 1230 m and 510 m in length and width, respectively. The maximum depth of the lower lake at the sampling point was 33 m with a water transparency of 7.0 m. The bottom of the quarry lakes is sandy with large rock fragments, and the shores are mainly steep. Various types of plants grow along the shores and slopes of the quarries. Currently, the quarry lakes are actively used by the local population of the nearby town of Pervomayskiy for recreation and fishing.

According to the data obtained during the operation of the Zavitinskoye mine, 11.815 million tonnes of tailings from beneficiation plants have accumulated. The average contents of traditional rare elements, such as beryllium, lithium, tantalum and niobium, located in tailings ponds, are 56. 652, 19 and 42 g / t, respectively. The wastes of the Zabaykalsky GOK are characterized by the largest reserves of lithium (7.703 tons) and tantalum (225 tons), as well as the second most significant reserves of beryllium (662 tons) and niobium (496 tons).

Currently, a project has been developed to use the already worked-out ore of the Zavitinskoye deposit and produce lithium concentrate at a new beneficiation plant. Later on, the obtained lithium will be used by the industry to create batteries.

2.2 Collection and processing of samples

The hydrochemical and hydrobiological testing objects were the waters of the two quarries and two tailings ponds left after the operation of the Zavitinskoye mine. Sampling was carried out in the coastal (depth up to 0.5 m) and central (deep water) zones of the technogenic reservoirs, except for the upper tailings pond where water samples were taken from the discharge well. The Ingoda river was chosen as the object of the regional hydrochemical background for this territory.

Water samples were collected in 1.5 L polyethylene bottles at sampling points where water temperature (T, °C), hydrogen ion concentration (pH) values, and redox potential (Eh) were measured. Water transparency was determined using a Secchi disk, and water depth was measured using an echosounder. For atomic absorption analysis, water samples were filtered through a 2-3 μm pore size paper filter and acidified to pH 2 with concentrated nitric acid (OSCH grade) before being transferred to 100 mL plastic cups. For mass spectrometric analysis using inductively coupled plasma mass spectrometry (ICP-MS), samples were filtered using a 0.45 μm pore size membrane filter under pressure with a syringe and transferred to 15 mL plastic tubes. Chemical-analytical studies of the water samples for macrocomponents and some trace elements were carried out using standard procedures at the certified laboratory of geoecology and hydrogeochemistry at the Institute of Natural Resources Ecology and Cryology, Siberian Branch of the Russian Academy of Sciences (Chita, Russia). The ICP-MS analysis was performed at the analytical center of the A.P. Vinogradov Institute of Geochemistry, Siberian Branch of the Russian Academy of Sciences (Irkutsk, Russia).

Zooplankton samples were collected and processed using standard methods. To assess the diversity and structure of zooplankton, they used species diversity indices such as Shannon (H'), dominance (Id), and Pielou's (e) indices. The structure of zooplankton communities was analyzed based on the composition and abundance of major taxonomic groups. Dominant species were defined as those accounting for at least 20 % of the total zooplankton abundance. Place the figure as close as possible after the point where it is first referenced in the text. If there is a large number of figures and tables, it might be necessary to place some before their text citation.

3 Results and Discussion

The obtained results on the chemical composition of the investigated waters and some of their physico-chemical parameters are presented in Table 1.

The analysis of the obtained data showed that water from the studied quarry ponds is characterized as fresh with an increased mineralization ranging from 1.23 to 1.84 g/L (Table 1). Based on the pH value, the water is classified as neutral (samples ZV-1, ZV-2, ZV-4) and weakly alkaline (sample ZV-3). As the overall mineralization of quarry water increases, caused by the accumulation of the SO_4^{2-} anion, as well as Ca^{2+} and Mg^{2+} cations, a decrease in the pH of water with increasing depth of the pond is observed. The values of the redox potential (Eh) also undergo changes with the depth of the pond, ranging from 231 to 168 mV in the upper quarry and from 121 to 130 mV in the lower quarry.

Based on the chemical composition, the quarry water belongs to the sulfate-magnesium-calcium type. The anion-cation composition of the upper and lower quarry water showed an excess of the maximum permissible concentration (MPC) for fishery water bodies based on the averaged values for the sulfate ion SO_4^{2-} (11.1 and 2.23 times), Ca^{2+} (1.8 and 1.5 times) and Mg^{2+} (2.23 and 1.7 times), respectively (Table 1). For Mg^{2+} cations, an excess of hygienic standards was also observed, with values 1.78 and 1.36 times higher than the norm, while for SO_4^{2-} ions, the excess was 2.22 and 1.63 times higher in the upper and lower quarries, respectively. When compared to background values, the excesses were 115 and 84 times for the sulfate ion, Ca^{2+} (22 and 18.5 times), and Mg^{2+} (54 and 1.68 times) in the upper and lower quarries, respectively (Table 1). Additionally, in the upper quarry pond, slight excesses of fluoride and ammonium ions were observed at a depth of 10.8 m. In the water of the lower quarry, a single case of slight excess of nitrites was recorded at a depth of 31 m, according to the MPC and background concentration (Table 1).

Table 1. Physico-chemical parameters of quarry lakes of the Zavitinskoye rare metal deposit and the background area (mg / L).

Parameters	**Quarry lakes**				**Back-ground**	**MPC */**, mg/dm^3**
	К-1		**К-2**			
	Sample number					
	ZV-1	**ZV-2**	**ZV-3**	**ZV-4**	**IN-1**	
Depth, m	0.5	10.8	0.5	31	0.5	n.n. / n.n.
pH	7.32	6.83	8.24	7.39	8.16	b.v. / from 6 to 9
T°C	18.2	–	21.0	–	15.4	n.n. / n.n.
Eh, мВ	231	168	121	130	210	n.n. / n.n.
CO_2, mg / L	6.39	13.1	3.87	15.9	5.42	n.n. / n.n.
HCO_3^-	28.3	39.8	114	136	62.5	n.n. / n.n.
SO_4^{2-}	952	1276	740	891	9.72	100 / 500
Cl^-	14.5	20.2	31.6	38.5	1.38	300 / 350
F^-	1.25	1.42	0.53	0.57	0.17	0.75 / 1.5
Ca^{2+}	293	360	245	299	14.7	180 / n.n.
Mg^{2+}	78.8	99.2	60.0	75.9	3.37	40 / 50
Na^+	22.9	29.9	32.3	41.7	5.58	120 / 200
K^+	13.0	15.7	11.3	14.4	1.0	50 / n.n.
NO_2^-	0.03	0.02	0.05	1.42	0.003	0.08 / 3
NO_3^-	0.43	0.37	2.51	2.98	0.51	40 /45
NH_4^+	0.17	0.89	<0.1	<0.1	<0.1	0.5 / 1.5
Σ ions	1404	1843	1238	1501	98.9	n.n. / 1500
Si	7.03	7.52	1.16	3.54	5.09	n.n. / 20-25
Li	2.97	3.73	2.16	2.41	0.009	0.08/ 0.03
Be	0.009	0.01	0.0004	$8 \cdot 10^{-6}$	$4 \cdot 10^{-7}$	0.0003/ 0.0002
Al	0.16	0.08	0.03	0.009	0.02	0.04/0.2
Mn	0.97	0.46	0.008	1.20	0.009	0.01/0.1
Ni	0.04	0.02	0.004	0.003	0.001	0.01/ 0.02
Cu	0.01	0.004	0.002	0.0004	0.002	0.001/ 1.0
Zn	0.45	0.37	0.03	0.03	0.44	0.01/5.0
As	0.005	0.001	0.008	2.39	0.001	0.05/ 0.01
Sr	2.08	2.76	2.97	3.63	0.12	0.4/7.0
Mo	0.0002	0.0002	0.002	0.0006	0.0006	0.001/ 0.07

Note. That a dash "-"- indicates no data, n.n. - means not regulated, b.v. - background value, MPC*- maximum permissible concentrations of substances for fishery water bodies [Federal norms "On Approval of Water Quality…", 2020], and MPC** - domestic drinking water use [Federal norms and sanitary rules 1.2.3685-21, 2021].

According to Table 1, the concentrations of microcomponents in quarry lakes range from a few micrograms to several milligrams per liter of water. The maximum concentrations of Li in the upper quarry waters were recorded at the surface and depth levels, at 2.97 and 3.73 mg / L, respectively. The Li concentrations in the lower quarry waters ranged from 2.16 to 2.41 mg / L. Additionally, the maximum concentrations of Sr in the quarry lakes were observed to be in the range of 2.08-2.76 mg / L for upper quarry water and 2.97-3.63 mg / L for lower quarry water. In all cases, the concentrations of lithium and strontium increased with the depth of the lakes. The water at the bottom of the lower quarry lake was found to contain a high concentration of As (2.39 mg / L). The concentrations of U in the quarry waters ranged from 0.04 to 0.10 mg / L. For a number of other metals, such as Be, Al, Mn, Ni, Cu, and Zn, a slight exceedance of the quality standards for water bodies with fish-farming importance and sanitary and hygienic norms was recorded (Table 1).

The background waters of the Ingoda River belong to fresh weakly alkaline water (pH 8.16) with mineralization of 98.9 mg / L. The chemical type of Ingoda River waters is magnesium-calcium carbonate. Unlike the explored technogenic reservoirs of the Zavitinskoye mine, most indicators of Ingoda River waters remain within normative values, except for slight MPC excesses for waters of fishery significance for Sr, Cu, Zn and Se (Table 1).

The study of zooplankton communities in the aforementioned technogenic reservoirs allowed for the examination of their species diversity and quantitative characteristics. Thus, the zooplankton of the upper quarry consisted of four species (rotifers-2, branched-1, copepods-1). The values of numerical density and biomass corresponded to 14.6-21.7 thousand individuals/m3 and 26.1-94.0 mg / m^3. *Keratella quadrata* Müller, 1786 (67-91 % of the total numerical density and 11-88 % of the total biomass) and *Cyclops vicinus* Uljanin, 1875 in naupliar and copepodite stages (6-33 % and 8-89 %) dominated. The diversity index values (H' = 0.77 bits/individual, Id = 0.70, e = 0.56) indicate signs of extreme ecological conditions with an intensification of the dominance of one species.

The fauna of the lower quarry's planktonic invertebrates included 16 species (*Rotifera* - 7, *Cladocera* - 7, *Copepoda* - 2). The quantitative indicators ranged from 17.5-22.1 thousand individuals/m^3 and 54.5-177 mg / m^3. In the pelagic zone, juveniles of *Cyclops vicinus* (63 % of the numerical abundance and 86 % of the biomass) and *Daphnia longispina s.str.* (O.F. Müller, 1785) (22 % and 12 %) were dominant, while in the littoral zone, *Keratella quadrata* (37 % and 12 %) and *Euchlanis dilatata Ehrenberg*, 1832 (26 % and 17 %) along with juvenile *Cyclopoida* (11 % and 11 %) were dominant. Based on the diversity indices (H'= 1.73 bit/ind., Id = 0.34, e = 0.80), the water body was classified as eutrophic with a balanced zooplankton community.

The research showed the correlation between the environment and the abundance of zooplankton species. Statistically significant Pearson coefficients were found for six taxa. *Rotifera Keratella quadrata* was positively related to metals (Cu, Mn, Zn) and negatively to Be and CO_2 contents, species *Hexarthra mira* and juvenile cyclopoids were positively associated with Al. The abundance of crustaceans *Daphnia longispina* and *Cyclops vicinus* were associated with depth, arsenic and nitrate content. Species number was correlated with pH, TDS, Si.

Among the higher aquatic vegetation in the upper quarry (K-1) to a depth of 3 m (at the exit of the technological road from the quarry), the growth of *Phragmites australis* (Cav.) Trin. ex Steud. was noted, in shallower areas – *Potamogeton perfoliatus* L. and *Myriophyllum spicatum* L.. Macroscopic algae are not marked. P. *perfoliatus* and P. *crispus* L. grow in the lower quarry lake (K-2) at depths up to 4-5 m, *Sparganium* sp. grows in shallower areas (from 2 m). *Lemna minor* L. grew in the near - lake zone. On aquatic vegetation, *Oedogonium* sp. was noted as an epiphyte. All aquatic plants in the quarry (K-2) were abundantly covered with mineral formations, presumably calcite.

4 Conclusion

Analysis of the conducted hydrogeochemical research of quarry lakes at the Zavitinskoye rare-metal deposit showed that their waters are fresh, neutral, and weakly alkaline. A significant increase in mineralization values and sulfate ion concentration was observed in the waters of the quarry lakes. The chemical type of water is sulfate magnesium-calcium. Alkaline pH values in the sulfate composition of quarry water indicate a high potential for neutralization of the surrounding rocks. Anomalously high concentrations of lithium, strontium, and arsenic were found among microelements, reaching 3.73, 2.97, and 2.39 mg / L, respectively. The mobility of beryllium in quarry waters is limited by high pH values; its maximum content was up to 0.01 mg / L.

Hydrobiological research has shown significant differences in zooplankton between shallow and smaller ponds in tailings and deep quarry lakes. In ponds, the species composition of plankton fauna (10-18 species) is formed by a littoral-phytophilic complex, while in quarries, it is a set of true planktonic forms (2-9 species). The quantitative indicators of hydrobionts in tailings (37.3-269 thousand individuals/m^3 and 256-515 mg / m^3) are higher than in quarry water bodies (14.6-22.1 thousand individuals/m^3 and 26.1-177 mg / m^3). The dominant complex of zooplankton, both in ponds and in quarries, consists of *Rotifera* and juvenile *Cyclopoida*.

Thus, it is necessary to further study the hydrogeochemical and hydrobiological parameters of the waters of the mining facilities of the Zavitinskoye deposit in order to obtain timely data on changes in their ecological and geochemical qualities

Hydrobiological studies have shown that the species composition of zooplankton in quarry lakes forms a set of truly planktonic forms (2-9 species). Quantitative indicators of hydrobionts in the upper and lower quarry reservoirs are 14.6–22.1 thousand copies/m3 and 26.1–177 mg / m^3, respectively. The dominant zooplankton complex is represented by *Rotifera* and juvenile *Cyclopoida.*

The reasons for such a small diversity of macrophytes in the studied quarry lakes may be the small catchment area, the restriction on the supply of biogenic elements (compounds N and P) and the almost absence of shallow areas available only on sections of technological roads.

Thus, it is necessary to further study the hydrochemical and hydrobiological parameters of the waters of the ore pits of the Zavitinskoye rare metal deposit in order to obtain timely data on changes in their ecological and geochemical qualities.

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