Features of the metal distribution in the technogenic and natural waters of the Novoshirokinsky deposit (Eastern Transbaikalia)

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Abstract. To identify the degree of impact of technogenic activity on the main water bodies located in the immediate vicinity of mining production, an analysis of the composition and pH of the water, the chemical components of which are normalized by the Order of the Ministry of Agriculture of the Russian Federation (dated 13.12.2016, No. 552 with amendments), was carried out starting on 10.03.2020.

1. Introduction

The impact of the mining industry during the extraction of minerals leads to a change in the chemical composition of underground and surface waters located in the zone influenced by this mining. The formation of the chemical composition of water within the developed ore deposits has its own characteristics, which are associated with the intensive decomposition of ore and rocks. Contrasting halos of scattering of many chemical elements are formed around ore zones in underground and surface waters. In halos and scattering streams, the dissolved substance changes the forms of its location, colloidal compounds are formed, solid phases are formed, and the chemical type of the water changes. In general, the decomposition of ore minerals leads to the scattering of many chemical elements, and water scattering halos with different lengths and contrasts are formed. The highest concentrations of metals are found in the interaction of groundwater with ore zones. In the underground waters located within the ore body, the concentration is maximum, and it decreases along the flow, depending on the distance from the ore body to the background concentration.

The purpose of the work is to study the composition of water in different water bodies for the ecological and geochemical assessment of the possible impact on the environment of anthropogenic activities. The main factors that determine the behavior of alkali metals are associated, firstly, with the proximity of the properties and sizes of Li ions with magnesium (Mg), a Rb, and Cs with potassium (K), which leads to their scattering in the minerals of the host elements (mainly silicates), and, secondly, with the formation of compounds with volatile components. This, in turn, contributes to their accumulation in residual melts and the formation of pegmatite deposits of rare alkaline elements [3].

Novoshirokinsky gold is a polymetallic deposit located in the Trans-Baikal Territory. The geological structure of the deposit involves intrusions of the Shakhtaminsky complex (J2-3), effusions of the Shadaron series (J2-3), and sedimentary deposits of the Akatuyev formation (J1-2
ak). The foundation of the Shirokin volcano-plutonic structure (UPC) is made up of Lower Cambrian deposits (limestones, dolomites, sandstones, quartzites). Their thickness exceeds 300 m [1–8].

Ore bodies have a length of up to 2000 m, with an average thickness of 0.5 to 5.5 m, and they spread to a depth of over 500 m. Intrusive and effusive rocks of the Novoshirokinsky volcano-plutonic complex are close to adakites in terms of their geochemical features. In the distribution of ore mineralization relative to the granitoid outputs of the Shakhtaminsky complex, the following lateral zonality is noted (as one moves away from the granitoid rods): quartz-pyrite-tourmaline association → quartz-pyrite with chalcopyrite, arsenopyrite → gold-polymetallic (productive). The host rocks are andesites and andesibasalts of the Shadoron series.

Testing at this facility was carried out in 2004, 2010, 2012, 2014, and 2017. The hydrochemical testing network covered all major water bodies falling within the zone of the alleged influence of mining production, including the water intakes of the settlements of Staraya and Novaya Shirokaya, mine water drainage and mine water, runoff from the off-balance sheet ore dump, and tailings water.

The hydro-grid of the described territory is represented by the Zhiltkovskaya and Shirokaya rivers and their tributaries. The catchment basins of the district's watercourses were significantly disrupted by gold mining carried out at the beginning of the last century on the Shirokaya River and the construction of the Novo-Shirokinsky (MPP) the end of the last century, which affects the water and hydrochemical regime of the watercourses.

The water supply of surface waters starting at the beginning of spring is provided by thawed snow waters and ice runoff. In the warm period of the year, the bulk of the supply comes from rainfall, and subordinate roles are played by the underground fractured waters of effusive formations and the fractured-vein waters of tectonic fault zones. In the summer and at the beginning of the winter period, groundwater is the only source of surface runoff, which mostly stops by December, and underground discharge mainly accumulates in ice [9].

2. Results and discussion

The concentrations of the main cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, and K$^+$) and anions (CO$_3^{2-}$, HCO$_3^-$, SO$_4^{2-}$, Cl$^-$, and F$^-$) in the water were determined by taking 1.5 L water samples in plastic bottles. To quantify the concentrations of the trace elements (Zn, Mn, Fe, Cu, Sr, Pb, Cd, Ag), 50 ml samples were also taken in plastic test tubes. For atmospheric precipitation sampling, a recess in the ground with a volume of about 2 L was prepared and covered with a clean plastic film; then, samples were taken in 1.5 L bottles and 50 ml plastic test tubes. The water was filtered through a filter with a pore diameter of 0.10 μm and the micro-component composition was acidified with high-purity HNO$_3$. The samples were hermetically sealed and sent to the laboratory, where they were analysed on the same day.

Laboratory analyses for cations and anions were performed by using potentiometric titration (CO$_3^{2-}$, HCO$_3^-$), atomic absorption (Ca$^{2+}$, Mg$^{2+}$), flame emission (Na$^+$, K$^+$), the potentiometric method (F$^-$), the titration method (SO$_4^{2-}$, Cl$^-$), and the photometric method (Si), while trace elements were determined by inductively coupled plasma mass spectrometry (ICP-MS). The total dissolved solids (TDS) were determined as the sum of the basic ions. Chemical analyses were performed at the accredited Geocology and Hydrogeochemistry Laboratory of the SB RAS Institute of Natural Resources, Ecology and Cryology (Chita, Russia).

Data on the metal content and chemical composition of the water, represented by the Kurlov formula [10], of the Novoshirokinsky deposit are presented in the table 1.

Table 1. The metal content in the waters of the Novoshirokinsky deposit (μg L$^{-1}$) and the chemical composition of the water according to the Kurlov formula.

| Samples          | Sr | Fe | Mn | Zn | Cu | Pb | Cd | Ag     | Chemical composition of water |
|------------------|----|----|----|----|----|----|----|--------|--------------------------------|
| Sub-basement waters and tailings dam waters |     |    |    |    |    |    |    |        | M0.11 HCO$_3$ 70.7SO$_4$ 20.4 Mg 48.1Ca 41.6  pH 7.2 |
| NSH-04-1         | 360| 910| 318| 162| 6.95| 16.3| 1.47| <0.02  |                                |

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| Sample  | Ca  | Mg  | Na  | pH  | SO  | HCO  | M |
|---------|-----|-----|-----|-----|-----|------|--|
| NSH-04-2 | 170 | 418 | 16.9 | 70.9 | 1.67 | <0.02 |
| NSH-10-1 | 57  | 5.8 | 0.71 | 13.5 | 1.41 | 9.02 | 0.26 |
| RM-12-09-02 | 380 | 94.2 | 13.7 | 16.1 | 9.87 | 4.38 | 0.45 | 0.10 |
| Surface waters | 242 | 186 | 11.8 | 23.2 | 3.15 | 0.10 |
| NSH-04-3 | 460 | 5 | 1.19 | 1.36 | 1.91 | <0.02 |
| NSH-04-4 | 70  | 697 | 7.96 | 18.3 | 0.82 | <0.02 |
| NSH-04-5 | 100 | 35 | 13.5 | 33  | 1.85 | <0.02 |
| NSH-04-6 | 370 | 42  | 12.9 | 23.9 | 0.3  | <0.02 |
| NSH-04-7 | 450 | 9  | 0.65 | 7.06 | 1.11 | <0.02 |
| NSH-04-8 | 190 | 73 | 4.32 | 14.3 | 0.92 | <0.02 |
| NSH-04-9 | 190 | 10 | 0.67 | 1.98 | 0.7  | <0.02 |
| NSH-04-10 | 150 | 6  | 4.23 | 4.84 | 0.15 | <0.02 |
| NSH-04-11 | 180 | 6 | 4.50 | 5.54 | 0.67 | 0.11 |
| Average | 240 | | 5.55 | 12.2 | 0.94 | 0.02 |

| Sample  | Ca  | Mg  | Na  | pH  | SO  | HCO  | M |
|---------|-----|-----|-----|-----|-----|------|--|
| Mine waters | 123 | 108 | 3.12 | 12.1 | 1.34 | <0.02 |
| NSH-04-12 | 120 | 4 | 5 | 5.88 | 7.46 | 2.31 | <0.02 |
| NSH-14-01 | 13700 | 84.0 | 1.68 | 0.31 | 0.1 | 1.06 |
| NSH-14-02 | 16000 | 123 | 8.30 | 1.03 | 0.23 | 32.0 |
| NSH-14-03 | 21900 | 28.0 | 2.27 | 0.39 | 0.09 | 31.0 |

Evolution of Biosphere and Technogenesis (2nd EBT 2021) IOP Conf. Series: Earth and Environmental Science 962 (2022) 012036 doi:10.1088/1755-1315/962/1/012036
Water samples taken from the tailings and sub-shaft runoff are mostly neutral; they are slightly mineralized. The samples taken from under the dumps are sulphate-bicarbonate, with predominant Ca and Mg cations. Samples from the tailings dump include sulphate, calcium-sodium-magnesium, and sodium-calcium. In all samples, there are increased amounts of iron, manganese, zinc, and lead. In some samples, MPC was exceeded for Fe (9–13 times), Mn (up to 4 times), Pb (up to 12 times), and Zn (2–42 times). The Sr content did not exceed the MPC in any sample. In a slightly alkaline sample from a tailings dump (2010), Cd exceeded the MPC (almost 2 times). Silver was also found in this sample and the lowest Sr content was noted. In all samples, there is an excess of Cu (7–17 times the MPC).

The natural waters of the territory are neutral and slightly alkaline; they are slightly mineralized. Almost all samples are bicarbonate, and several samples are sulphate-bicarbonate and bicarbonate-sulphate. Calcium and Mg predominate in all samples. For some samples, there is a slight excess in Sr (both samples were taken at water intakes). Almost all samples showed an excess of Fe (up to 30 times the MPC, except for the intake of the village of Staraya Shirokaya) and Mn (up to 12 times the MPC, except for samples from the intake). In the sample from the Zhitkovskaya River and the Coal Stream, the concentration of Cu exceeds the MPC by 8–14 times. For some samples, Zn exceeded the MPC by 3–60 times and Pb exceeded the MPC by 2–6 times. No excess Cd was detected.

The samples taken in the mine are also slightly mineralized; they include bicarbonate, sulphate-bicarbonate, magnesium, magnesium-calcium, calcium-magnesium, and sodium-magnesium. For mine waters, the greatest excess in Sr is observed in neutral waters (up to 42 times the MPC), although in slightly alkaline waters the MPC is also exceeded by up to 10 times. Cadmium concentrations do not exceed the MPC in all samples. In terms of samples, the MPC is exceeded for
Pb by 2–10 times and for Mn by 2–26 times; almost all samples have an excess of Zn (2–20 times the MPC). The concentration of Cu in all samples exceeds the MPC by 2–27 times.

According to Ag, which is not normalized according to the MPC, samples from the tailings dump were found to have concentrations of 0.10 (2009) and 0.26 μg L⁻¹ (2010). In surface waters, silver was found only in a sample from the Shirokaya River. In mine waters, the concentration of silver varies from 0.09 to 32 μg L⁻¹.

3. Conclusion
It is established that, depending on the values of the hydrogen index, the waters of the deposit in question are neutral and slightly alkaline. A comparative assessment of the MPC established for the reservoirs of fisheries showed that the contents of many metals in underground and surface waters located in the zone of influence of the developed deposit are higher than the normative value.

Possible sources of the contamination of surface and underground waters in the zone of influence of the deposit may be drainage waters coming from a tailings dump, a special dump of off-balance ores, and the drainage of mine waters. These elements have exceeded the MPC in the water because when mine waters interact with ore and host rocks, which are represented by hydroslude, galena, sphalerite, pyrite, siderite, and chalcopyrite, some of the chemicals pass into solution [9]. Abnormal concentrations of iron, manganese, zinc, lead, and copper have been found in the waters accumulating in the tailings dump and the special dump, which indicates the possibility of the contamination of the river network with these metals from surface or underground runoff from these structures. At the same time, strontium was found to exceed the MPC for both water intakes. Perhaps this is a consequence of reaching the zone of influence of polymetallic mineralization intakes.

Based on the data obtained, further monitoring of this deposit is necessary to assess the ecological and geochemical impact of the mining activity of the Novoshirokinsky mine.

Acknowledgments
The work was carried out in accordance with the State task for project of Basic research Programs of SB RAS, state registration number 121032200070-2.

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