The dynamics of the chemical composition of surface water in the zone of influence of North-West Phosphorous Company JSC

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Abstract. Long-term monitoring studies of the chemical composition of water of Lake Komarinoe (Murmansk Region, North-West Russia) have been carried out in order to assess the quality of surface water in the territory of the development of the apatite-nepheline deposit Oleniy Ruchey. A clear reliable tendency has been revealed to increase the pH water value, mineralization, the content of basic ions, nitrate ion NO₃⁻ in recent years, as well as a number of trace elements (Sr, Cu, Mo, F), several times higher than the maximum permissible concentrations of harmful substances for water of fishery ponds. According to the content of nutrients, the lake is characterized at the present time as eutrophic. The sharp increase in the content of compounds of the biogenic element (nitrogen) can lead to the bloom development of potentially toxic algae and cyanobacteria. Lake Umbozero, which receives water from Lake Komarinoe, is also at risk of developing water bloom processes and pollution.

1. Introduction

The mining industry is one of the most powerful factors in the anthropogenic transformation of the environment, including natural waters. The quality of natural waters in adjacent areas is deteriorating as a result of the development of mineral deposits. The consequences of the impact of the technogenic influence of mining enterprises on natural waters are summarized in reviews [1], [2], [3], [4]. Changes in the chemical composition of surface waters are caused by both the influx of pollutants from surface technogenic reservoirs (settling ponds, massifs of dump rocks, etc.) and the violation of the natural hydrodynamic and hydrochemical regime of surface and ground waters [5], [6], [7]. In the spent mountainous areas, processes take place that increase mineralization and alter the chemical composition of mine waters. Mine waters carry compounds to the Earth surface that are sources of natural water pollution.

The North-West Phosphor Joint-Stock Company (SZFK JSC) was established by PJSC Acron in 2005 to implement a project creating a new phosphorus raw material base in the Murmansk Region. In November 2006, SZFK JSC has obtained a license to use the mineral resources of the deposits of apatite-nepheline ores Oleniy Ruchey and Partomchorr. In 2012, the construction of the first stage of the mining was completed, commissioning was carried out in the buildings of the processing plant, and the first tons of apatite concentrate were obtained. Since June 2013, SZFK JSC has fully satisfied the needs of Russian chemical enterprises of the Acron Group in phosphate raw materials (https://www.szfk.ru/).
The aim of this work is to assess the quality of surface water in the territory of the development of the apatite-nepheline deposit Oleniy Ruchey on the example of Lake Komarinoe.

2. Materials and methods
The chemical composition of water of Lake Komarinoe was studied in the period 2011–2019. Samples of lake waters were taken by employees of SZFK JSC on average 4 times a year. Analysis of water samples was carried out in the laboratory of JSC “Kola Geological Information Laboratory Centre”, Apatuty: pH values, hardness, ion composition (Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4\)\(^+\), HCO\(_3\)\(^-\), SO\(_4\)\(^{2-}\), Cl\(^-\), HCO\(_3\)\(^-\), F\(^-\)), trace elements (Al, Fe, Mn, Sr, Cu, Zn, Ni, Co, Cr, Cd, Pb, Mo, Hg, B, Be, Ba) were determined. The analysis of the chemical composition dynamics of the water of Lake Komarinoe before and during the development of the apatite-nepheline deposit was carried out.

Lake Komarinoe (catchment of the Umba River) is located in the southeast of the Khibiny Alkaline Massif, 8.9 km northeast of the settlement Koashva, Murmansk Region (figure 1). The coordinates of the lake are 67°40′49.93″ N, 34°16′28.47″ E. It is small (lake area is 0.66 km\(^2\)), oval in shape, the lake of glacial origin, the maximum long is 1.53 km, the greatest width is 0.65 km, and altitude is 174 m. The catchment area by type of landscape belongs to the forest-tundra zone with heights up to 600 m. The shores of the lake are high and rocky. Birch and pine forests were common in the catchment area prior the development of the apatite-nepheline deposit Oleniy Ruchey [8].

![Figure 1. Satellite image of the location of Komarinoe and Umbzero lakes and the Oleniy Ruchey mine of SZFK JSC (https://yandex.ru/maps)](https://example.com/image)

3. Results and discussion
Prior to the development of the Oleniy Ruchey deposit, water in Lake Komarinoe was neutral and was characterized by low values of total mineralization (average 36 mg/L) and alkalinity (average 350 μeq/L). The lake was characterized by low concentrations of basic ions, among which sodium (on average 6.5 mg/L) and hydrocarbonates (on average 22 mg/L) prevailed [8]. The content and ratio of
the forms of nutrients varied depending on the season, and their dynamics was largely determined by the level of development of production processes and, consequently, the trophicity of the reservoir. The concentration of total phosphorus in the lake averaged 3 μgP/L. The concentration of total nitrogen averaged 142 μgN/L. According to the content of nutrients, the lake was characterized as oligotrophic. The water content of bioavailable forms of nutrients (NO₃⁻), which determine the productivity of the lake, was on average 60 μg/L. Low values of color, organic matter (on average 4.4 mg/L) and Fe content (on average 11 μg/L) prevailed [8].

Changes in the hydrochemical composition of water of Lake Komarinoe can be traced by the ratio of the basic ions. Prior to the development of the apatite-nepheline deposit, the formula (Kurlova) for the ionic composition of water of Lake Komarinoe is looked as follows [8]:

\[
M_{0.036} \ pH_{7.22} \ HCO_{3}^{-} 72 \ SO_{4}^{2-} 21 \ Cl^{-} 21 \ NO_{3}^{-} 1 \ Na_{62} \ Ca_{23} \ K_{10} \ Mg_{4} \\
\]

where M – the mineralization of water in g/L, pH – the value of the hydrogen index, the fraction numerator shows the percentage of the basic anions in terms of the equivalent content, and the denominator – the basic cations. The basic ions are in order of decreasing their content.

In 2011, i.e. at the beginning of the activities of SZFK JSC, the Kurlov water formula of Lake Komarinoe remained practically unchanged:

\[
M_{0.040} \ pH_{7.3} \ HCO_{3}^{-} 76 \ SO_{4}^{2-} 18 \ Cl^{-} 15 \ NO_{3}^{-} 2 \ Na_{60} \ Ca_{20} \ K_{12} \ Mg_{8} \\
\]

In 2019, a decade after the beginning of deposit development, this formula has undergone significant changes:

\[
M_{0.181} \ pH_{8.1} \ HCO_{3}^{-} 44 \ SO_{4}^{2-} 27 \ NO_{3}^{-} 22 \ Cl^{-} 15 \ F^{-} 1 \ Na_{50} \ Ca_{36} \ K_{11} \ Mg_{2} \\
\]

After the beginning of the activities of SZFK JSC, the chemical composition of the water of Lake Komarinoe significantly changed. The content of basic ions increases, as well as the water mineralization (figures 2–4). The chemical composition of the water of Lake Komarinoe, like all natural waters of the Khibiny Alkaline Massif [5], is characterized by the prevailing position of the Na⁺ cation, as well as an increased relative content of the K⁺ cation, which is comparable in concentration with the Ca²⁺ cation (figure 2), while the natural waters of the plain territories of the Murmansk Region that do not receive direct pollution of industrial enterprises is characterized by a hydrocarbonate class and a calcium group, and the K⁺ cation, as a rule, is in last place among the basic cations [9–11]. A significant tendency to increase the content of basic ions and mineralization has been recorded over the entire period of hydrochemical monitoring of Lake Komarinoe (figures 2–4), which is associated with the extraction of apatite-nepheline ores, weathering of alkaline rocks and the entry of its products into natural waters. Hydrocarbonate anion is the predominant anion in the water of Lake Komarinoe, sulfate anion is in the second place, nitrate anion is in the third place, which in recent years has been comparable in content with sulfate anion and considerably exceeds chloride anion (figure 3), i.e. the anionic composition of the water of Lake Komarinoe differs from the “classical” distribution characteristic of the unpolluted surface waters of the Murmansk Region – HCO₃⁻ > SO₄²⁻ > Cl⁻ [8], [10].

Nitrogen-containing blasting explosives are used by SZFK JSC during the mining operations of apatite-nepheline ores that significantly increase the content of nitrogen compounds in surface waters. The content of nitrate anion NO₃⁻ has risen by two orders of magnitude compared to the period before the start of mining of apatite-nepheline ores and has recently been increasing in an exponential progression, as well as of the basic ions, reaching the maximum permissible concentration for water of fishery reservoirs MPCₙₗₕ = 40 mg/L (figure 3). According to the content of nutrients, the lake is characterized at the present time as eutrophic. The sharp increase in the content of compounds of the biogenic element (nitrogen) can lead to the bloom development of potentially toxic algae and cyanobacteria, as happened in Lake Imandra (the largest reservoir in the Murmansk Region) and other
reservoirs of the Murmansk region polluted by sewage of industrial enterprises and domestic waste [4], [12], [13].

**Figure 2.** Dynamics of basic cations in the water of Lake Komarinoe in 2011–2019
A significant increase in pH value over the observation period occurs in the water of Lake Komarinoe (figure 4), which is associated with an increase in the influence of deposit development and an increase in the depth of mine workings. The pH value should not go beyond the values of 6.5-8.5 in accordance with the requirements for the composition and properties of the water of fishery reservoirs. The maximum pH values of the water of Lake Komarinoe have recently approached a critical value of 8.5 (figure 4), which corresponds to the boundary value between weakly alkaline and alkaline waters according to the pH classification. The increase in pH value is associated with the contacting of water with alkaline rocks containing alkaline and alkaline earth metals [5]. An increase in the content of alkaline earth metals (Ca and Mg) has led to an increase in water hardness of Lake Komarinoe (figure 4).

The main ore mineral of the Oleniy Ruchey deposit is fluorapatite (Ca$_5$(PO$_4$)$_3$F), which during weathering supplies F to natural waters. Elevated F contents were noted in the natural waters of the territories affected by the development of apatite-nepheline deposits [5, 8, 11]. The content of F came close to the MPC$_{fish}$ value (0.75 mg/L) in the water of Lake Komarinoe (figure 4).
Figure 4. Dynamics of pH values, hardness, mineralization and F content in the water of Lake Komarinoe in 2011–2019

The mineral Mo molybdenite MoS$_2$ is widespread in the Khibiny massif [14]. The conditions for the presence of molybdenite are described in detail by A.N. Labuntsov, who discovered the Tahtarvumchorr molybdenite deposit in 1927 [15]. The presence of Mo was found in amounts significantly exceeding MPC$_{\text{fish}}$ in natural waters, confined to the areas of development of the Khibiny apatite-nepheline deposits [5], [11], [14], [16]. The Mo content has increased in recent years and exceeds the MPC$_{\text{fish}}$ (0.001 mg/L) up to 11 times in the water of Lake Komarinoe (figure 5).

Strontium is a tautomorphic element for nepheline syenites of the Khibiny massif [17]. Significant increase in the Sr content was found in the water of Lake Komarinoe during hydrochemical monitoring and in recent years it exceeds the MPC$_{\text{fish}}$ value (0.4 mg/L) (figure 5). Elevated Sr contents were noted in the water and sediments of Imandra and Bolshoi Vudyavr lakes, as well as other lakes and groundwater of the Khibiny alkaline massif, polluted by effluents of apatite-nepheline production [3–5, 11]. An increase in the Cu content was also recorded in the water of Komarinoe Lake, exceeding the MPC$_{\text{fish}}$ value (0.001 mg/L) up to 14 times.
4. Conclusion

Thus, as a result of a ten-year monitoring study of the chemical composition of the water of Lake Komarinoe from the beginning of the development of the apatite-nepheline deposit Oleniy Ruchey, significant tendency has been revealed towards an increase in pH value, mineralization, content of basic ions, nitrate ion NO₃⁻, as well as concentrations of a number of trace elements (Sr, Cu, Mo, F), which are several times higher than the MPCₑvelop value. The sharp increase in the content of nutrient element (nitrogen) compounds, i.e. development of the eutrophication process, can lead to the bloom development of potentially toxic algae and cyanobacteria in Lake Komarinoe, as well as in Lake Umbozero, the second largest lake in the Murmansk Region. Lake Umbozero is fishery lake, and it is also threatened by environmental degradation as the result of the influx of pollutants from the Lake Komarinoe connected with Lake Umbozero.

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