Impact of mining activities on the surface water quality (case study of Khibiny mountains, Russia)

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Abstract. The paper deals with present hydrological and hydrochemical regime of southern Khibiny rivers affected by apatite-nepheline mining activity. Changes in water quality resulting from mining activities include increase of water turbidity, concentrations of major ions and trace elements. The impact of mining area can be traced over 34 km downstream. We conclude that existing treatment system is not sufficient to mitigate pollutants loads leading to elevated concentrations of toxic substances in dissolved and suspended modes. The process substances concentration reduction is mainly represented by dilution, since the hydrochemical decrease is insignificant. Using trace elements migration phase distribution, the effect of treatment plants on elements distribution downstream was observed.

1. Introduction

Khibiny mountains are situated in central part of Kola Peninsula in Northern West part of Russia. The mountains have a unique mineral composition. It is mainly represented by alkaline ultrabasic rocks. Khibiny mountains are among the largest phosphate ore deposits in the world. The processes of mining and anthropogenic transformation of natural landscapes of southern part of Khibiny started in 1930. Nowadays, Kirovsk city surroundings represent transformed landscapes with mining infrastructure, hips of empty rock and sedimentation pounds. The long period of excavation and modern trends of increasing mining activity cased significant degradation of water quality in vicinity of mines.

Khibiny mountains are situated in tundra zone. Water bodies of territory in the undisturbed state are characterized by low concentrations of suspended particles, low content of organic matter, slowed down rates of metabolic processes. Also, a long winter low water period, often accompanied by freezing of watercourses, is typical. Under these conditions, the process of transformation of water quality under the influence of production is intensified, and the cleaning process is slowed down.

This study refers to Yuksporiok stream, which drains the “Kirovsky” and “Yukspor” minings, providing large values of suspended matter, and heavy metal contamination. Draining waters from these mines come to lake Big Vudyavr – the largest lake inside Khibiny mountains. This lake contains a specially constructed sedimentation pound for wastewater in shallow northern part, separated from the main part by ground dam. The main part of the lake pollution is formed due to the inflow of mining wastewater, but, municipal sewage of Kirovsk city has an additional effect. Through the Belaya River, water from Big Vudyavr comes to Imandra Lake. In the mouth of river Belaya there is
an apatite-nephelin plant which provides additional pollutants to river. Imandra Lake is the largest lake in Kola peninsula. It is an object of intensive scientific research [3;4;9]. The main factors that effect on its water quality are sewage water from local villages, wastewater from mining areas, wastewater from apatite-nepheline plant and nickel-copper smelter. The largest mining areas are concentrated in upper part of Yuksporiok river basin. The total area of Yukspor mining is about 5.1 km2. It occupies about 14% of the basin of river. During the operation of the mining complex, about 75 million m3 of waste rock was stored in the dumps [6]. An infrastructure for the export of mined ore (by railway and road), and logistics points situates in river basin.

The purpose of investigations is an assumption of effects of mining development on water quality. The issue is fairly well covered, but only a few works refer to the polar regions. It is important to note that a significant part of researches falls on limnological ones, whereas less attention is paid to the river waters of small basins. The main aim of this article is making an assessment of anthropogenic influence on water quality of southern Khibiny river basins. The objectives are: (i) observing of turbidity regime in low water period, (ii) characterizing of formation of pollutant water, it’s chemical composition and fate below mining areas and (iii) making an assessment of the main forms of trace metal migration.

The study of Khibiny massif water quality was carried out during summer low-water period and summer-autumn flood period. During low-water period all streams of the area are characterized by small variability of hydrochemical characteristics. Also, it is easier to detect wastewater discharges from the mining areas, as they stand out from the mean values. During floods, the processes of pollutants transfer from catchment could activate and be significantly detected. Basing on data from previous observations, three main sources of pollution in Khibiny mountains were distinguished: atmospheric transport of pollutants, migration of pollutants from wastewater and leaching of components from waste rock and mine tailings.

2. Site description
The study area is located within Khibiny alkaline massif. It was formed 365 million years ago as a result of a multiphase intrusion of mantle melts. The main rocks of the area are represented by nepheline syenites, meytelgit-urtites and apatite-nepheline rocks. Area soil cover is represented by peaty humus-illuvial soils within the valleys, which are largely transformed, and mountain-tundra soils on the mountain slopes and on the plateaus. The main vegetation types on the mountain slopes are dwarf shrubs, birch, and lichens. Pine and spruce forests dominate the lowland areas close to mountains. The climate of Khibiny is marked by increased humidity. About 900 mm of precipitation falls annually. Snow accounts for about 65%. January temperature is -30°C, and in July it upraises to +200°C. Local rivers have a regime with spring-summer high water period, intermittent summer-autumn low water, floods comparable in height to high water. Channel network of research area is quite large, but there are three main rivers: Vudyavriok, Yuksporiok and Loparskiy. All this rivers are the main tributaries of Big

![Figure 1](image-url) Schematic map of studied area. (I) – All sampling points; (II) – River Yuksporiok basin with discharges, measured on sampling stations.
Vudyavr Lake and Belaya River. The average long-term water discharge this rivers is 1.2-1.6 m³/s. The discharge module varies from 40 (l*s)/km² in the upper reaches of the rivers to 25 (l*s)/km² in lower part. In addition, drainage water from the mines, as well as the water of the sedimentation pounds, flows into river basins increasing their discharges.

3. Materials and Methods

This study base on field campaigns, that took place in summer-autumn low water period (18-29 August 2017) and summer low water period (16-27 July 2018). During these periods, a network of monitoring stations was created, as well as a gauging station on the lower reaches of the river Yuksporik.

The main water chemical characteristics, such as pH, conductivity, alkalinity, dissolved O₂, dissolved organic carbon (DOC), main ions concentrations, nutrient concentrations were measured. Also discharge and turbidity measurements took place. Concentrations of trace metals were measured by method of ICP-MS. Trace elements were separated into solid and liquid phase by filtering of water sample on 0.45 μm Millipore membrane filter. Concentrations of 72 trace elements were detected. Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Sr, Ti, U, V, Zn, Zr were chosen for further analysis, as the most widespread trace elements in research region.

4. Hydrology

Streams in the southern part of Khibiny massif could be divided into background and mine affected. The tributaries of Small Vudyavr Lake and the Vudyavriok River, that flows from it, could be considered as none-transformed water bodies. There are no mining areas in this basins, with the exception of a small open-pit mine for the gravel extraction in upper reaches of the Kukisyok stream. Streams of the upper part of Yuksporik and Vuonnemiok basins could be classified as insignificant human influence. Due to the mountainous landscape, atmospheric transport of pollution is quite low in these areas [3]. The highest rate of contamination was detected in the Loparskiy and Yuksporik rivers, where the drainage waters of Kirovsky and Yukspor mine are discharged.

Figure 2 (I) Grain size distribution in background water and wastewater. (II) Grain size distribution is samples, taken from gauging station (K1). (III) Discharge and turbidity graph from gauging station (K1) (August, 2017).
Turbidity measurements in southern Khibiny river basins showed notable differences correlated with the intensity of human activity. Surface waters of the background areas of the valleys have very low turbidity and a mixed grain size composition. The appearance of particles is connected both with the transfer of material from the catchment area and with the vertical and horizontal channel deformations. More than 50% of the suspended particles belong to medium sand and coarse sand fraction (> 0.25 mm). During summer low water period suspended flow in mine affected watercourses is determined by flushing of waste rock hips and by wastewater discharges. Water turbidity is 100-400 mg/l, from 40 to 70% of suspended particles belong to silt and clay particles (<0.05mm). Concentrations significantly exceed the MPC (35 mg/l). Results of nitric acid digestion reveal that the main portion of metals is in particles 0.001-0.05 mm [3]. Zn and Cr mainly migrate in fractions of 0.0005-0.001 mm. Significant volumes of sediments accumulate in the sedimentation pond in Yuksporiok river mouth, but the finest particles are transported downstream as a result of insufficient purification. The impact of the small fraction is expressed in the calmatation of river channels and absence of benthic organisms. Regime measurements at the gauging station (K1) showed increases in turbidity (up to 600 mg/l) associated with wastewater discharges. With the passage of rain floods (18.08; 25.08), there is a slight increase of the fine sand fraction presence to 20%. In the low-flow period, the distribution of particle size is constant. This can serve as confirmation of the constancy of the chemical composition of water during the observation period.

5. Water chemistry
The study of chemical characteristics of surface waters of the Khibiny massif is important in case of explaining migration processes of such contaminating components as heavy metals (Table 1). In addition, modern field data and it’s comparison with the results of previous studies, makes it possible to trace changes in chemical composition of waters in background and polluted areas. The previously performed hydrochemical zoning of the territory of the massif allowed us to identify 4 districts with background chemical composition of water and one district - with a modified to various degrees [8]. The differences in mineralization and content of the main water ions in background areas are small and related to the composition of the rocks prevailing in river basins and the relief features (in particular, to the depth of river valleys).

Chemical composition of Belaya River water in lower part of the basin has been transformed as a result of mining activities. However, the chemical composition of water in the upper reaches of the Yuksporiok River, Gakman Stream, the Kukisiok River and its tributaries has not changed much in comparison with the data from the 1987-1990 survey, and could be considered as background. These watercourses are characterized by hydrogen carbonate-sodium waters of low salinity (less than 15 mg/l). They have a weakly acidic pH values. In the cationic composition of water, the relative content of Si exceeds the proportion of Ca, K and Mg. Such a ratio is typical for watercourses, which drain the territory, composed of well-washed crystalline rocks, almost devoid of soil cover. There is an additional inflow of silica acid into the Khibiny rivers, due to the good hydraulic connection between surface and ground water which is enriched with Si.

After the confluence of Gakman and Yuksporiok rivers the content of all components of the ion composition increase and there is a sharp change in acidity (Table 1). The transformation continues, due to the inflow of sewage waters from the valley and the direct flow of wastewater from the Yukspor mine (fig. 1). A similar transformation is observed in Loparskii (Saamsky) river, where wastewater from the Kirovsky mine is dumped. Hips of empty rock become thermodynamically unstable and tend to equilibrium with the new environment, as a result of which a significant part of chemical components passes into water, changing the mineralization and hydrochemical type of natural waters. High pH values are probably associated with a high content of fine material and the presence of specially introduced reagents in wastewater.

An additional source of $\text{SO}_4^{2-}$, Cl, $\text{NO}_3^-$, $\text{Na}^+$, $\text{Ca}^{2+}$, $\text{K}^+$ ions is leaching from the rock in hips around the mines, caused by intensive precipitation weathering processes. The equilibrium state between water and rock in summer conditions is achieved the faster, the finer fractions are present in
the hip [2]. As a result, not only absolute but also relative concentrations of main ions change in tributaries of Lake Big Vudyavr. The largest increase is typical for SO$_4^{2-}$, Cl, Na and K ions, and P-PO$_4^{3-}$. Comparing background water with polluted water, the increase by 16-30 times could be observed. This leads to a decrease in the values of the genetic coefficients HCO$_3^{-}$/SO$_4^{2-}$ and HCO$_3^{-}$/Cl in 3-7 times, and to the transition of water from the hydrocarbonate class into mixed. The content of Si varies to a lesser extent, small changes are observed in the content of DOC, which presents in the waters of the Belaya River and its tributaries in small quantities. The waters contain nitrate and nitrite ions, received from the use of explosives in mine area.

The mineralization and concentrations of chemical elements reduce below the Big Vudyavr Lake, downstream from the mine workings, which is facilitated by diffuse runoff and the entry of uncontaminated tributaries. The content of a part of chemical components (Na, K, Si) decreases almost one and a half times, the content of F - three times, and the total mineral almost by an order. However, the concentrations of most anions (SO$_4^{2-}$, NO$_3^{-}$, Cl) and Ca vary very little.

As far as Khibiny mountains have unique mineral composition a wide range of trace metals could be found in surface water. Heavy metals, being one of the most toxic agents, mainly come from human-made sources and by leaching of rock [1]. For the studying metals, a correlation matrix was constructed. Basing on it, two groups of elements were distinguished: Al; As; Cr; Cu; Fe; Mo, Mn and Sr; Ti; U; V; Zn.

| Parameters | Background water | River water before treatment facility | River water after treatment facility |
|------------|------------------|--------------------------------------|-------------------------------------|
| pH         | 6,2-6,9          | 9-10                                 | 8-9                                 |
| Cond       | 7,6              | 349                                  | 224                                 |
| F$^-$      | 0,09±0,04        | 6,6±1,3                              | 2,4±0,97                            |
| Cl$^-$     | 0,38±0,05        | 5,8±1,1                              | 5,9±2,3                             |
| SO$_4^{2-}$| 1,2±0,38         | 38±5,3                               | 33,98±10                            |
| NO$_3^{-}$ | n/d              | 1,1±0,39                             | n/d                                 |
| NO$_2^{-}$ | n/d              | 21±2,4                               | 20±14                               |
| Ca$^{2+}$  | 0,7±0,19         | 8,4±2                                | 9,1±2,1                             |
| Mg$^{2+}$  | 0,074±0,005      | 0,36±0,072                           | 0,61±0,2                            |
| Na$^+$     | 2,3±2,7          | 48±4,4                               | 33±0,9                              |
| K$^+$      | 11,1±3,8         | 15±1,2                               | 10±1,8                              |
| TOC        | 1,1±0,14         | 2,4±0,24                             | 2,3±0,74                            |
| P-PO$_4^{3-}$ | 8±3            | 1341±355                             | 132±67                              |
| Si         | 2076±208         | 4692±226                             | 2970±135                            |
| Al         | 14±4             | 135±26                               | 72±33                               |
| As         | n/d              | 2,7±0,94                             | 1,1±0,22                            |
| Cd         | 0,012±0,002      | 0,01                                 | 0,0099±0,0005                       |
| Cr         | 0,13±0,02        | 0,82±0,20                            | 0,35±0,20                           |
| Cu         | 0,34±0,16        | 3,3±1,1                              | 1,9±0,76                            |
| Fe         | 4,3±1,5          | 23±18                                | 13±10                               |
| Mn         | 0,17±0,13        | 1,6±1,1                              | 2,5±2,2                             |
| Mo         | 0,82±0,26        | 39±9,7                               | 24±7                                |
| Sr         | 209±89           | 147±75                               | 123±88                              |
| Ti         | 2,3±1,2          | 2,8±1,9                              | 1,8±1,2                             |
| U          | 1,7±0,91         | 1,5±0,62                             | 0,98±0,60                           |
| V          | 1,2±1,31         | 1,4±0,94                             | 1,4±1,3                             |
| Zn         | 0,92±0,17        | 0,95±0,35                            | 1±0,35                              |
| Zr         | 0,11±0,07        | 0,18±0,14                            | 0,07±0,03                           |
The metal concentrations distribution in Yuksporiok valley can be traced by drawing (fig 3). In background areas, trace metal concentrations are determined by groundwater flow through fractures in the rock, as well as pressurized artesian water from wells, leaching of rocks, and also by atmospheric aerosols. Elements are in exchangeable and non-exchangeable forms. Low content of organic matter suggests the absence of significant concentrations of chelated complex compounds.

Close to the station U2, wastewater from “Yukspor” mine flows into river Yuksporiok. The drainage channel has a discharge of about 0.5-0.7 m$^3$/s and turbidity values of 150-600 mg/l. For the first group of metals there is a significant increase in concentrations in water. The reason for the increase in concentrations is the migration of elements from the finest particles of suspension to liquid phase as a result of changes in external hydrochemical conditions. Saturated solution of drainage and wastewater entering natural water and enriches them with trace elements. Concentrations of substances do not significantly decrease even in the Big Vudyavr Lake, while for Fe and Mn there is an increase in concentrations as a result of the intra-water processes. Downstream, there is a decrease in the content of metals, as a result of dilution by tributaries, as well as the flow of organic matter (the lower reaches of the rivers are swamped). The second group of metals is characterized by a gradual increase in concentrations downstream of the rivers. Stations in the Gakman valley (G1-G3) have lower concentrations, probably due to precipitation that occurred earlier in the day before measurements. A gradual increase in concentrations is due to the influx of groundwater as well as tributaries. The waters of Lake Big Vudyavr dilute the concentrations of elements of the second group. Downstream (B1-2), they again begin to increase as a result of the flow of water from the catchment.

The solid-solution partitioning of major and trace elements was quantified using the distribution coefficient, Kd (fig.5), expressed as: $K_d = C_{p}/C_{d}$. $C_{p}$ (μg/l) and $C_{d}$ (μg/l) are the contents of any element C in suspended sediments and in the dissolved phase, respectively. Kd depends upon the abundance and speciation of elements in materials. Elevated Kd values reveal that elements have high affinity for solid phases, while elements with low Kd values are more easily weathered, removed in soil solution and/or groundwater and transported in dissolved phases in the river [5].

For the studying territory, the variability of Kd elements in background, waste and transformed waters is rather large. The proportion of elements migrating in the composition of suspended matter in
areas of wastewater discharges increase for 20 times for Zr, Ti, Fe. It remains almost unchanged for Cr, Mo and U. Distributions of Kd below treatment facilities are almost similar to background.

The processes of phase migration of trace elements in the rivers Yuksporiok and Belaya were studied. Substances migrate in dissolved and suspended form. The composition of the dissolved form includes colloidal forms of elements. In the background areas (U1), the majority of elements are characterized by a slight predominance of the suspended form of migration (50-60%) (fig.5). The elements Fe and Mn are mainly in a dissolved state. Such a distribution could be the result of leachate of rock in a catchment area by acid water from precipitation. It is important to note that the absolute concentrations of substances are quite low. In the area of wastewater flow (U2), hydrochemical conditions change dramatically. Up to 98% Al, Fe, Mn migrates in the composition of suspended particles. For other metals, there is also an increase in suspended migration phase. Downstream, as a result of the reach of chemical equilibrium, an increase in the concentration of Cr, Cu, Ti, V, Zn in suspended forms is observed. In the area of the Big Voudyavr Lake there is a sedimentation pound, which facilitates the sedimentation of suspended particles with metals in their structure. The effect of the sedimentation process is particularly noticeable for Al, Fe, Cu, Mn, Zn, which stay in suspended and non-exchangeable phase in wastewater. After purification, only the finest fractions of suspension fall into the lake. Dilution of water occurs, contributing to an increase in the dissolved form of element transport. Multidirectional migration processes occur in the waters of the Belaya River (B1, B2), which are also affected by discharge of treated wastewater from the ore production plant (ANOF-2). Down the valley, the influx of water saturated with organic matter increases, leading to formation of sparingly soluble organic-mineral complexes. Metals Mo, Sr, U have an increased natural background values throughout the study area [7]. Their concentrations depend on the intake with groundwater, as well as on the mineral composition of the suspension. Concentrations of Sr and U in the solution decrease in the area of the lake as a result of dilution of river water. Zr is mainly concentrated in the composition of mineral particles.

![Figure 5](image.png)

**Figure 5** Distribution of trace metal forms of transport in Yuksporiok river basin (August 2017).

Metal concentrations analysis of trace elements distribution in dissolved and suspended forms shows the exceptional role of wastewater discharge for the area. The influence of this factor can be traced for more than 34 km downstream and leads to the accumulation of toxic substances in bottom sediments of Big Vudyavr and Imandra lakes. The accumulation process is particularly intense in the northern part of Big Vudyavr, in the region of the Loparskiy delta. The thickness of bottom sediments there exceeds 1.3 m.

6. Conclusions

The study of water quality in river basins of the southern part of the Khibiny mountains during summer low-water period showed a significant hydrological and hydrochemical heterogeneity of the
As a result, rivers were classified based on degree of human impact and surface water quality.

In natural (baseline) conditions, the main drivers of chemical composition are geological structure, leaching of rocks by atmospheric precipitation, the flow of organic matter from wetlands, and the presence of lakes in a catchment area. Waters are characterized by low values of turbidity, mineralization, content of nutrients and organic substances. High concentrations of Sr, Mo are typical. Up to 50% of heavy metals are transported in suspension.

Waters impacted by mining activities are characterized by shifted chemical composition along middle and lower reaches of rivers, draining apatite-nepheline ore mining. The chemical composition is determined by the volume of wastewater discharged from industrial site. As a result of salvo discharges, the turbidity of water increases 600 times as compared with the background. Concentrations of micro and macro components increase, especially concentrations of Al, Fe, Cu, Mn, and Zn. The pH increases from slightly acid to alkaline (9-10). Most of the elements (70-99%) are transported in suspended sediments. The transformed waters are inherent for the river sections below the treatment plant, as well as the Big Vudyavr Lake and the Belaya river, which flows into Imandra Lake. Water purification helps to reduce turbidity for 100 times. However, most of the suspended particles remain as the finest fractions. Concentrations of macro components slightly exceed the background, the content of organic matter increases. Concentrations of heavy metals gradually decrease as a result of complexation processes with organic matter and sedimentation of particles, but they continue to significantly exceed the background ones.

50-60% of chemical elements are transported in suspended sediments.

Mining is the main driver of pollution in the Khibiny range. The impact of wastewater discharges can be traced 34 km below the discharge point and leads to the accumulation of bottom sediments saturated with heavy metals in the mouths of the Yuksporiok, Loparskiy and Belaya rivers. In this case, an important implication is a development of an effective monitoring system and construction of additional settling ponds with a physico-chemical methods for turbidity lowering.

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