Chemical composition of natural waters of contaminated area: The case for the Imandra Lake catchment (the Kola Peninsula)

Z A Evtyugina[1,2], N V Guseva[3], J G Kopylova[4], D A Vorobeva[5]

[1] Apatity branch of «Murmansk State Technical University», Russia
[2] Kola branch of Geophysical Survey of RAS, Apatity, Russia
[3, 4, 5] National Research Tomsk Polytechnic University, Tomsk, Russia

E-mail: [1]zina_evt@mail.ru, [3] guseva24@yandex.ru

Abstract. The study of the current chemical composition of natural waters in the eastern and western parts of the Imandra Lake catchment was performed using ion chromatography, potentiometry and inductively coupled plasma mass spectrometry. It was found that the content of trace elements in the surface water is considerably higher than that in the groundwater. The nickel and copper concentrations exceed the background levels over 19 and 2 times respectively in groundwater, and 175 and 61 times in the surface waters. These data show that the Severonikel influences negatively air and surface water.

1. Introduction

The Kola Peninsula is one of the regions of Russia with the most unfavorable ecological situation. A large number of mining and metallurgical enterprises is located here. The enterprises of the Kola Mining and Metallurgical Company have polluted the atmosphere with sulfur compounds, copper, nickel for many years. This led to degradation of forest landscapes until complete destruction of the forests and the formation of anthropogenic wasteland [4].

The impact of anthropogenic factors leads to a change of all landscape elements, including deterioration of natural water quality. The water bodies in Arctic zone reveal a low ability for self-purification, but they are often used as drinking water sources for the local population. Therefore, the chemical composition of subarctic lakes is studied clearly in the following aspects: anthropogenic impact, mechanisms of chemical element accumulation in water and bottom sediments, transformation of aquatic ecosystems [11, 12].

In 1992-1996 an ecogeochemical project was implemented in the territory of Russia (north of the Kola Peninsula) and neighboring areas of Finland and Norway. The project objectives were to study catchments, the regional geochemical mapping, to research the sources and migration of chemical elements [6, 7]. The parts of the project such as the description of the content and source of chemical elements (Cu, Ni, isotopes of S etc.) were published in the article [7]. In Finland, the composition of the aerosols, the solubility of elements of anthropogenic origin and their sources were studied [8].

The Kola Peninsula is not the only region in the Arctic territory of Russia where the anthropogenic influence is so significant. The Norilsk industrial complex in the Taimyr Peninsula is also mining and processing of copper-nickel ore. In this region the concentration of heavy metals (Cu, Ni, Zn, Hg, Cd and Hg) and sulfate ion in the ecosystems was studied taking into account the orography and the wind rose [10].

At the same time, soil, as a landscape element, is a biogeochemical barrier for chemical elements input to ecosystems from the polluted atmosphere. Soil degradation leads to decrease in their sorption capacity and, consequently, to groundwater contamination with heavy metals. According to the Central Kola Expedition study in 2008-2010, in the territory with the local impact of «Severonikel» plant where soils are undestroyed, the groundwater is protected from aerotechnogenic input of copper and nickel [2].

Nickel, copper and SO_2 emissions from the «Severonikel» plant decreased from 287 thousand tons in 1990 to 45.8 thousand in 1999 and to 36.6 thousand tons in 2013 [5]. This led to the reduction of anthropogenic impact on the environment, including natural water.

The aim of this research is to study the current chemical composition of natural waters in the lake Imandra catchment, exposed to significant anthropogenic impact.

2. Methods

The studied area is located in the south-western part of the Kola Peninsula in the western and eastern part of the Lake Imandra catchment (Figure 1). Aluminosilicate rocks are widely spread in the studied area. In the western part of the lake catchment geological structure is represented by acidic and basic metavolcanics of the Upper Archean and peridotites, pyroxene, gabbronorites, basalt porphyrites, diorites of the Early Proterozoic age. Vendian deposits composed of arcosic and polymictic sandstones, siltstones, argillites are locally spread. In the eastern part of the Lake Imandra catchment near Kirovsk city the Devonian-age rocks such as alkaline ultramafic, nepheline syenite, carbonatite predominate.

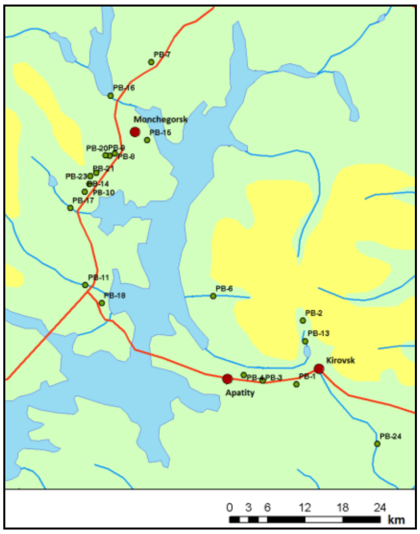

Figure 1. Map of the studied area and sampling points.

In July 2014, 24 samples of surface water and groundwater were taken (Figure 1). In the east of the lake Imandra catchment 3 springs: Prihibinskij (PB-1), Molodezhnyj (PB-3), Poddorozhnyj (PB-4), 3 rivers: Malaya Belaya (PB-6), Vudyavrjok (PB-13), Ajkuajvenjok (PB-14) and Lake Malay Vudyavr (PB-2) were sampled. In the western part of the lake Imandra catchment 5 springs : Bolotnyj (PB-7), Sportivnyj (PB-15), Kislaya Guba (PB-18), Dorozhnyj (PB-9(19)) and Gornyj (RV-10(22); 6 surface water points: the River Kurka (PB-11), the River Moncha (PB-16), the river that flows into the lake Sopchyavr (PB-21), a stream 7 kilometers from the plant (PB-14 (23)), drainage lake of the River Vita – Devichya Lambina (PB-17) and the lake near spring Dorozhnyj (PB-8(20)) were sampled.

The samples were taken in 0.5 liter plastic bottles for the major element analysis and two 50 ml vials for the trace element analysis. The temperature, pH, Eh were measured in situ. The water chemical composition was studied using ion chromatography, potentiometry and inductively coupled plasma mass spectrometry in the laboratory of the Research and Development Center «Voda», Institute of Natural Resources, TPU.

3. Results and discussion

Taking into account the peculiarities of the water chemical composition, geological structure and the degree of anthropogenic impacts, two principally different areas were identified. The first area is the Khibiny massif area (the eastern part of the lake Imandra catchment) and the second one is area exposed to anthropogenic impact of «Severonikel» plant (the western part of the lake Imandra catchment).

The groundwater of the Khibiny massif area is slightly alkaline HCO_3 and SO_4-HCO_3 Ca and Na-Ca composition. The TDS value is 111-201 mg/l. The high TDS value and SO_4-HCO_3 Na-Ca composition is in alkaline groundwater of the spring PB-4. In this point the nitrate ion concentration is 33 mg/l. Features of anthropogenic contamination are detected in the spring PB-1, where the potassium and nitrate ion concentrations are high. The high concentration of chlorine ion and the TDS value of 115 mg/l are observed in the spring PB-3.

In this groundwater the calcium concentration is higher than the concentration of sodium and silicon, which significantly exceeds the concentration of potassium and magnesium (Table 1). This is the main cationic composition peculiarity of the groundwater of the Khibiny massif area. In the studied groundwater the concentration of such trace elements as lithium, titanium, nickel, copper, strontium, yttrium, molybdenum, antimony, barium, lanthanum, cerium, rhenium and bismuth is high. This association of chemical elements reflects the geochemical peculiarities of alkaline rocks.

In surface waters of this area the sodium and potassium content exceeds the concentration of calcium and magnesium at TDS 27 mg/l and the silicon concentration is 3.5 mg/l. It is also explained by the influence of alkaline rocks rich in sodium and potassium. As compared with the background concentrations in the groundwater, in the surface water of the Khibiny massif twice or more times as many excess is observed for magnesium (7 times), for aluminum (2.4 times), for calcium (9.9 times), for manganese (3.3 times), for zinc (3 times), for gallium (19 times), for arsenic (2.8 times), for rubidium (4.2 times), for zirconium (4.6 times), for niobium (2.8 times), for molybdenum (twice), for cesium (3.2 times), for cerium (4.9 times), for hafnium (2.8 times), for tungsten (13 times), for iridium (twice), for platinum (2 times), and for lead (twice).

In the area exposed to anthropogenic impact of «Severonikel» plant, the chemical composition of groundwater varies depending on the degradation degree of soil and vegetation layer. In the area with forest cover, groundwater (springs PB-15 and PB-18) is neutral HCO_3 Mg-Ca and contains sulfate ion of 7.6-11.0 mg/l, TDS 67-87 mg/l. In the spring PB-7 (TDS 63 mg/l) pH decreases with increase of free carbon dioxide concentrations to 22 mg/l. The high concentration of free carbon dioxide is conditioned by the mineralization of organic matter.

In the area with disturbed soil and vegetation layer, groundwater (springsPB-9(19), PB-10 (22)) is slightly acidic. The TDS value is 30-39 mg/l and free carbon dioxide concentration is 16-25 mg/l. The recharge of this groundwater occurs by rainfall, which infiltrate through destroyed vegetation and soil layer in the technogenic wasteland [1]. This peculiarity of groundwater formation influences the trace element composition of water. In comparison with the groundwater of the Khibiny massif, the excess of trace elements in these groundwater is observed for boron (5 times), for manganese (7 times), for iron (2.5 times), for gallium (4.3 times), for bromine (5.9 times), for rubidium (2.6 times), for rhodium (4 times), for palladium (3 times), for hafnium (4.3 times), for tantalum (5.6 times), for tungsten (3.9 times), for iridium (4.1 times), for aurum (2.5 times), for uranium (10 times). The nickel and copper concentrations are 0.0065 mg/l and 0.001 mg/l, respectively, in the spring PB-9(19), 0.003 mg/l and 0.00013 mg/l, respectively, in the spring PB-10(22).

Table 1. The chemical composition of waters in the Lake Imandra catchment area, mg/l

Element	Background water of the Khibiny massif (eastern part of the lake Imandra catchment)		Water exposed to anthropogenic impact of «Severonikel» plant (western part of the lake Imandra catchment)		
	Surface water (N=4)	Groundwater (N=3)	Groundwater in an undisturbed landscape (N=3)	Groundwater in a disturbed landscape (N=4)	Surface water (N=5)
pH	7.09	7.46	6.67	5.84	6.4
HCO_3	17.4	77	39.4	12.2	12
SO_4	1.7	19	10.7	10.3	5.36
Cl	0.63	5.2	2.46	1.77	1.24

NO_3	0.13	12	0.65	1.42	0.1
Total hardness	0.09	1.5	0.74	0.36	0.3
Ca	1.33	27	9.8	5.31	4.69
Mg	0.23	1.7	3.1	1.17	0.86
Na	3.68	9.5	3.07	1.77	1.4
K	1.09	2.6	1.43	0.41	0.33
TDS	26.1	142	70	32.9	25.5
Li	0.000016	0.00011	0.001	0.00004	0.00012
Be	0.000015	<0.000003	<0.000003	0.0000342	<0.000003
B	0.00012	0.0062	0.0013	0.002	0.0021
Al	0.039	0.0085	0.016	0.01	0.03
Si	2.68	5.46	7.30	4.00	2.81
P	0.0081	0.0095	0.014	0.006	0.014
Sc	0.00011	0.00027	0.00026	0.00014	0.0001
Ti	0.00023	0.00019	0.00074	0.00012	0.00067
V	0.00012	0.00041	0.00061	0.0002	0.001
Cr	0.00013	0.00055	0.00054	0.0003	0.00028
Mn	0.00047	0.00102	0.00014	0.0004	0.0025
Fe	0.007	0.019	0.0077	0.0075	0.0037
Co	0.0000051	0.000024	0.000015	0.00004	0.0004
Ni	0.00012	0.0000198	0.00051	**0.0049**	**0.046**
Cu	0.00029	0.00013	0.00041	**0.00056**	**0.017**
Zn	0.00085	0.00038	0.00028	**0.0004**	**0.002**
Ga	0.00016	0.000035	0.0000082	0.000004	0.00001
Ge	0.0000053	0.0000037	0.0000039	0.000004	0.0000086
As	0.000082	0.00014	0.000029	0.00004	**0.00042**
Se	0.00032	0.0004	0.00034	0.00026	0.0004
Br	0.0058	0.08	0.014	0.007	0.011
Rb	0.0019	0.0012	0.00045	0.0009	0.0006
Sr	0.064	0.013	0.032	0.019	0.016
Y	0.000022	0.000027	0.000059	0.00004	0.000019
Zr	0.000061	0.000011	0.000013	0.0000035	0.000009
Nb	0.000011	0.0000025	0.0000039	0.0000021	0.0000025
Mo	0.0014	0.00028	0.00063	0.00003	0.000089
Ru	0.000012	0.000021	0.000015	0.0000008	0.0000056
Rh	0.000001	0.0000032	0.0000008	0.0000007	0.0000012
Pd	0.0000024	0.0000075	0.0000025	0.0000019	0.0000030
Ag	0.0000025	0.0000015	0.000002	0.000002	**0.000029**
Cd	0.0000029	0.000003	0.0000017	0.0000016	**0.000023**
Sn	0.0000041	0.000002	0.0000068	0.0000039	0.0000062
Sb	0.000015	0.000011	0.000029	0.00001	0.000034
Te	0.0000033	0.0000183	0.0000120	<0.000005	0.0000390
Cs	0.0000104	0.0000018	0.0000032	0.0000016	0.0000034
Ba	0.0112	0.0129	0.0273	0.013	0.0139
La	0.00008	0.000022	0.00008	0.00004	0.00005
Ce	0.000082	0.0000064	0.00002	0.000009	0.000052
Pr	0.000014	0.0000048	0.00019	0.000014	0.00001
Nd	0.000039	0.000018	0.000078	0.00006	0.000039
Sm	0.0000054	0.0000027	0.000014	0.000009	0.0000062
Eu	0.0000023	0.0000024	0.0000054	0.0000034	0.0000027
Gd	0.0000049	0.0000029	0.000011	0.000008	0.0000049
Tb	0.0000005	0.0000004	0.0000017	0.0000011	0.0000006
Dy	0.0000033	0.0000022	0.0000055	0.000005	0.0000021
Ho	0.0000008	0.0000005	0.0000016	0.0000010	0.0000007
Er	0.0000011	0.0000011	0.0000039	0.0000012	0.000001
Tm	0.0000003	0.0000003	0.0000008	0.0000006	0.0000004
Yb	0.0000008	0.0000012	0.0000015	0.0000022	0.0000005
Lu	0.0000002	0.0000005	0.0000008	0.0000006	0.0000003
Hf	0.0000017	0.0000026	0.0000006	0.0000004	0.0000012
Ta	0.000001	0.0000062	0.0000011	0.0000006	0.0000011
W	0.0000323	0.0000095	0.0000024	0.0000022	0.000031

Re	0.0000004	0.0000036	0.000011	0.0000057	0.0000059
Ir	0.000033	0.000067	0.000016	0.0000010	0.000014
Pt	0.0000004	0.0000003	0.0000002	0.0000004	0.0000012
Au	0.0000055	0.000013	0.0000054	0.000004	0.0000039
Hg	0.0000019	<0.00005	0.0000049	<0.00005	0.0000068
Tl	0.0000007	0.0000014	0.0000021	0.0000026	0.0000035
Pb	0.000031	0.0000091	0.000015	0.0000190	**0.00014**
Bi	0.0000008	0.0000004	0.0000045	0.000001	0.0000033
Th	0.0000025	0.0000013	0.0000019	0.0000016	0.0000032
U	0.000019	0.00013	0.000013	0.0000024	0.0000069

In the area exposed to anthropogenic impact, the river water is neutral, the TDS value is 19-28 mg/l. The pH value decreases with TDS increase up to 40 mg/l. Bicarbonate is a predominant anion in the studied area, but the content of sulfate ion is 8-27 %-eq and the content of chloride ions varies from 5 to 10 %-eq. The concentration of free carbon dioxide increases in the Lake Dorozhnoe (PB-8(20)) and the River Kurka (PB-11). The pH value increases due to organic matter mineralization. The cationic composition of the studied surface water (point PB-17, PB-11, PB-16, PB-14 (23)) is Na-Mg-Ca, the content of silicon is 2.4-2.7 mg/l. The silicon content in the stream PB-14(23) is 4.4 mg/l.

As the results of the previous studies [3], high nickel and copper concentrations were found in the stream PB-14(23). This microstream drains the destroyed forest landscape (technogenic woodlands). Over the past period, technogenic woodlands changed radically. Many conifer trees had been killed, but the ratio of deciduous trees and shrubs increased. The ground cover transformed - the area uncovered by vegetation increased and the soil was destroyed until the mineral horizon.

Reduction of anthropogenic impact on the environment has shown a positive trend in changing abundances of chemical elements in natural waters due to an increase of natural carbon compounds and cations in the water. In July 2014 in the stream PB-14(23), the content of sulfate ion (the main air pollutant sulfur compounds) was less than the minimum concentration in comparison with the sampling period 1987–1990. The hydrocarbonate ion concentration in the water increased by 1,5 times, the concentration of calcium and magnesium is close to the maximum value of the previous period. The content of copper and nickel in the stream PB-14(23) has not changed and corresponds to the previous study [3].

The highest nickel content 0.0269 and 0.0649 mg/l was found in the Dorozhnoe Lake (PB-8(20)). The copper content in this point is 0.0152 and 0.0211mg/l. The nickel concentration (0.0045 mg/l) in the waters of the river (PB-21), the River Kurka (PB-11) and the River Vita (PB-17) are nearly the same as that in the springs Gornyj and Dorozhnyj (0.0049 mg / l nickel), but higher than the nickel content in the water of the stream PB-14(23), and in the Moncha River PB-16.

Table 1 shows that, in addition to nickel and copper, in surface waters the high concentration of trace elements is observed. As compared with background concentrations of groundwater, a wide range of chemicals is observed in the surface waters of the Severonikel area. There is an excess for Mn (40 times), for Fe (6.7 times), for Co in 27 times, for Ni (89 times), for Cu (41 times), for Zn (7 times), for Ga (2.4 times), for Ge (2.2 times), for As (15 times), for Ag (14 times), for Cd (13 times), for Te (3 times), for Ce (5 times), for Yb (twice), for Hf (twice), for W (13 times), for U (twice).

4. Conclusions

The chemical composition of waters in the lake Imandra catchment is various. Taking into account the peculiarities of the water chemical composition, geological structure, and the degree of anthropogenic impacts, the two principally different areas were identified. The first area is the Khibiny massif area (the eastern part of the lake Imandra catchment) and the second one is area exposed to anthropogenic impact of «Severonikel» plant (the western part of the lake Imandra catchment). The chemical composition in both areas differs in pH and TDS values, the concentration of trace elements.

Moreover, the groundwater chemical composition differs markedly from the surface water chemical composition. Groundwater is characterized by the high concentrations of sulfate ion, calcium, magnesium and silicon. Nevertheless, the concentration of sodium, potassium, and chloride ion is the same in surface and groundwater. However, the trace element concentration in surface water is significantly higher than that in groundwater. In the surface waters, excess over background concentrations in groundwater reaches for Ni 175 times, for Cu 61 times, for Co 20 times, for Ag 15 times, for Pb 14 times, for Cd 8 times, for Pt 6 times, for As 5 times, for W 5 times, for Te 4 times, for Al 3 times, for V, Ge, Sn, Sb, Tl, Bi, Th 2 times.

These data allow us to recognize the negative impact of «Severonikel» plant firstly on the atmosphere and surface water. The degree of groundwater contamination depends on soil condition. If the soil is destroyed, the groundwater is polluted. If there is ground cover and soil, the groundwater is not significantly affected by anthropogenic activity. Thus, the main negative impact is referred to the top of biosphere that implies the development of measures for protecting groundwater from pollution.

Acknowledgements
This work was supported under the state assignment of the Ministry of Education and Science of Russia "Nauka".

References
[1] Ananev V N 2010 *Rodniki Murmanskoy oblasti spravochnik (*Murmansk) p 88 [in Russian]
[2] Ananev V N, Karpova R V and Sycheva L B *Poiski podzemnyh vod dlya obespecheniya hozyaystvenno-pitevogo vodosnabzheniya Monchegorska Murmanskoy oblasti* Otchet za 2008-2010 gody. Gos. registracionnyy № 47-08-16b Monchegorsk, fondy CKE 2011 [in Russian]
[3] Evtyugina Z A and Nikonov V V 1990 Osobennosti migracii medi i nikelya po profilyu podzolistyh pochv v usloviyah aehrotekhnogennogo zagryazneniya // Issledovanie pochv na Evropeyskom Severe: *Cbornik materialov nauchnoy sessii posvyashchennoy 130 letiyu so dnya rozhdeniya N.M. Sibirceva (13-15 fevralya 1990) (Arhangelsk)* 107–106 [in Russian]
[4] Evtyugina Z A and Asming V EH 2013 Osobennosti formirovaniya sostava infiltracionnyh vod v usloviyah aehrotekhnogennogo zagryazneniya // *Vestnik MGTU: trudy Murmanskogo gosudarstvennogo tekhnicheskogo universiteta* **16** 73–80 [in Russian]
[5] Norilsk Nickel URL:http://www.kolagmk.ru/rus/ecology/
[6] de Caritat P, Reimann C, Ayras M and et al. 1996 Stream Water Geochemistry from Selected Catchments on the Kola Peninsula (NW Russia) and in Neighbouring Areas of Finland and Norway: 1 Element Levels and Sources *Aquati. Geochem.* **2** 149–168
[7] de Caritat P, Krouse H R and Hutcheon I 1997 Sulphur isotope composition of streamwater, moss and humus from eight arctic catchments in the Kola Peninsula region (NW Russia, N Finland, NE Norway) *Water, Air, and Soil Pollution* **94** 191–208
[8] Laing J R, Hopke P K, Hopke E F and et al. 2014 Long-term particle measurements in Finnish Arctic: Part I - Chemical composition and trace metal solubility *Atmospheric. Environ.* **88** 275–284
[9] Motuzova G V, Lukina N V, Nikonov V V and et al. 2004 Effect of Natural and Anthropogenic Factors on Soils, Soil Water, and Subsoil Water in Kola Peninsula *Water Resources* **31** 297–302
[10] Zhulidov A V, Robarts R D, Pavlov D F and et al. 2011 Long-term changes of heavy metal and sulphur concentrations in ecosystems of the Taymyr Peninsula (Russian Federation) North of the Norilsk Industrial Complex *Environ. Monit Assess* **181** 539–553
[11] Moiseenko T I, Gashkina N A, Sharov A N and et al. 2009 Anthropogenic Transformations of the Arctic Ecosystem of Lake Imandra: Tendencies for Recovery after Long Period of Pollution *Water Resources* **36** 296–309
[12] Moiseenko T I, Gashkina NA, Dinu M I and et al. 2013 Aquatic Geochemistry of Small Lakes: Effects of Environment Changes *Geochem. Int.* **51** 1031–1148