Determination of Geochemical Background of Waters of Kola Peninsula in Order to Decrease Anthropogenic Pollution in Analysed Area

Dorota Moroniak-Wawryszuk^{1,5}, Mateusz Wawryszuk¹, Stanisław Chmiel¹, Miłosz Huber², Paweł Kramarz⁴, Lesia Lata³, Sebastian Skupiński³

1. Introduction

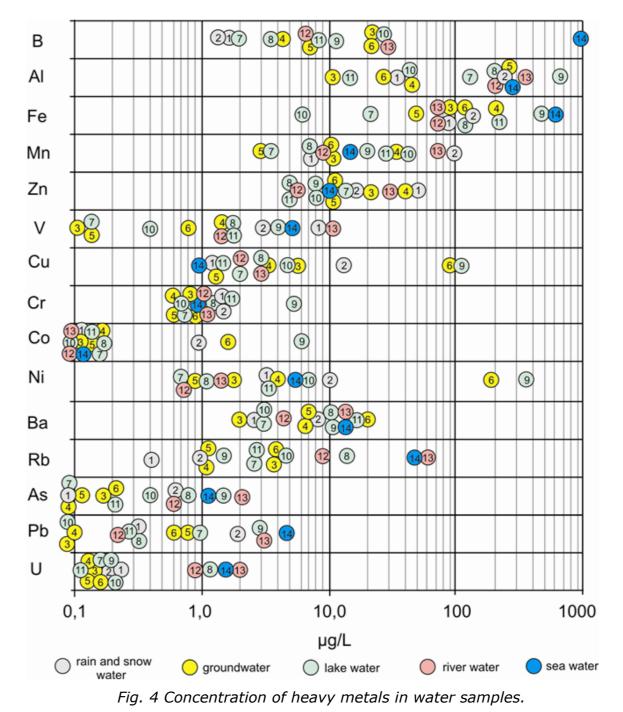
The issue of environmental protection of Kola Peninsula has been taken under consideration at the turn of XXI centaury by Polish and Russian scientists [4, 8, 9, 11]. Furthermore, some of researchers focused on well recognition of water of Imandra Lake located near Monchegorsk and Apatite [5, 6, 7, 15, 16]. We aimed this study to determine the physico-chemical quality of waters and soils of Kola Peninsula in order to define the geochemical background and to examine the anthropogenic impact in selected areas.

2. Material and methods

The study was conducted on 14 water samples from different phases of hydrological cycle- precipitation water, snow-melting water, ground water, river water, lake water, sea water (fig. 1A, B, tab. 1); also 12 samples of rocks and soils were used (fig. 1 C, D, tab. 2). pH of waters, conductivity, isotopic ratio of δ 180 i δ D, concentration of ions (anions and cations) along with metal ions were analysed. For conductivity measure InoLab 1 (WTW) was used, cations and anions were indicated by ions chromatograph (Metrohm MIC 3), metal ions were indicated by spectrometer ICP-MS (Thermo Xseries2). Laser analyzer PICARRO L2130 was used for defining the isotopic ratio of δ 180 i δ D. Soils and rocks samples were analysed using scanning electrone microscope (Hitachi SU6600) with EDS add-on and spectroscope XRF Epsilon 3 (Pananalytical).

Analysis of chemical composition of water samples were held in a specialized program Cs Aspect, wherein the measured absorbance values were read out as the concentration [mg/l], in relation to a calibration curve. The results are shown as the arithmetic mean of obtained values. In the Department of Soil Science additional experiments, concerning isotopic studies, were undertaken. All samples were collected and analysis were conducted in 2013.

Type of water	No.	Sample, (comments)		t) Characteristics of water samples of
Rain	1	Murmansk, rain water, (Lenin region)	Table 2 (rig	ht) Characteristics of soil samples of
Melting snow	2	E slopes of Kukisvumchorr Mt.	No.	Sample, (comments)
	3	Apatyties (Amethyst Hotel), (tap water)	1	Ramzay Pass, (Khibiny)
	4	Murmansk (North West region), (tap water)	2	Malyi Vudyavr, (lake shore)
Ground waters Lakes	5	Kukisvumchorr Mt.		Moraine embankment between Malyi and
	6	Old Cu-Ni sulphide mine no. 5.1	3	Bolshoi Vudyavr Lakes
		in Monchegorsk – ('30 in XX)	4	Botanical Garden of Institute
	7	Malyi Vudyavr Lake	5	River banks, (near Anof)
	8	Bolshoi Vudyavr Lake	6	Bielaya Rieka, (river banks, near Anof)
	9	Sobchijavr lake, (near Monchegorsk)	7	Apatities, (city centre)
	10	Imandra lake, (near road to Apatity)	8	Bolshoi Vudyavr Lake, (lake shore)
	11	Siemonowski lake, (Murmansk)	9	Vicinity of Monchegorsk
	12	White River, (near Anof)	10	Road to Monchegorsk, (1259 km of road)



Heavy metals in the tested waters relatively varied in the range of concentrations (fig. 4). Some of the metals are necessary for the wellbeing of the organisms and the ecosystem (Zn, Ca, Mn), sometimes in trace amounts (Cu, Fe). Although, in significant amounts they are rather harmful than benefical. Same applies to other heavy metals, mostly produced by industry plants like: cadmium (Cd), lead (Pb) or nickel (Ni) [1, 12, 14] . It is noteworthy, that in particular samples (No. 6 and 9), nickel and copper concentration was rather high. In all the analyzed samples with comparatively high concentrations were found in the cases of iron and aluminum source vicinity. Other elements were found in concentrations typical for the polar regions made up of crystalline rocks.

3.2. Soils of Kola Peninsula

Soil samples were collected mostly in Khibiny Massif, Lovoziero Massif and near cities Monchegorsk and Murmansk; all of them were picked from the surface. Soils from Massives had alpine attributes with regolith and scanty layer of organic matter. Near Monchegorsk, it was expected to examine samples related with polymetallic ores mineralization, so the soils were collected in vicinity of closed quarries and the road Murmansk-St. Petersburg. In Murmansk, specimens originated in the city centre with multileveled residential blocks buildings and park with reservoir, both located near active harbour.

XRF analyze of soils samples revealed that in samples 01, 02, 03, 07 occurred mediocre plagioclases and orthoclases, clay materials (same with the 05 sample) and additional compounds and minerals like Ti, S, Cl, P and F (fig. 5). In Khibiny Massif apatite, plagioclases or ilmenite and titanite are common rocks so it is natural that mentioned compounds appeared in examination.Sample 04 contained P, S, Cl, Mn, F and Ti, same with the 06. Soil in 08 in its compostion had acidic plagioclases and a little addition of clay minerals and Sulphur. 09 sample revealed feldspars and clay minerals in the soils albeit also hematite was found (fig. 5). Swatch No. 10 contained acidic plagioclasesand Ti and Ni. Both 11 and 12 were abundant in clay minerals, plagioclases (oligoclases and andesine) with phosphates.

Analysis of chemical composition of soils was also conducted. Results of IPC analysis of soils of Kola Peninsula are showed on fig. 6.



13Zhemchuzhnaya Riverea14Barents sea wharf, (near Murmansk)

- Murmansk (near Memorial of Soldier)
- 12 Aluaiv Mt., (Lovoziero Massif)

11

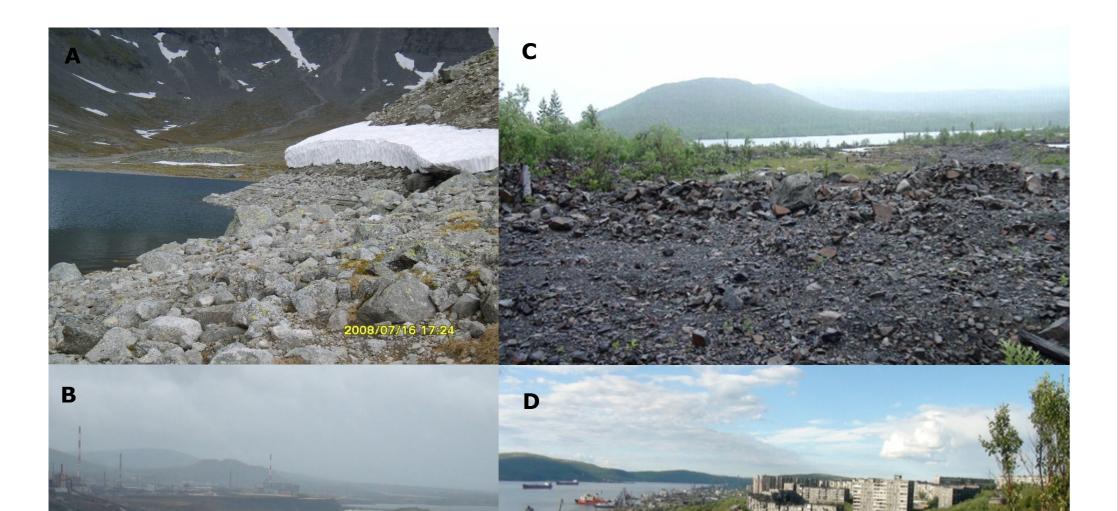


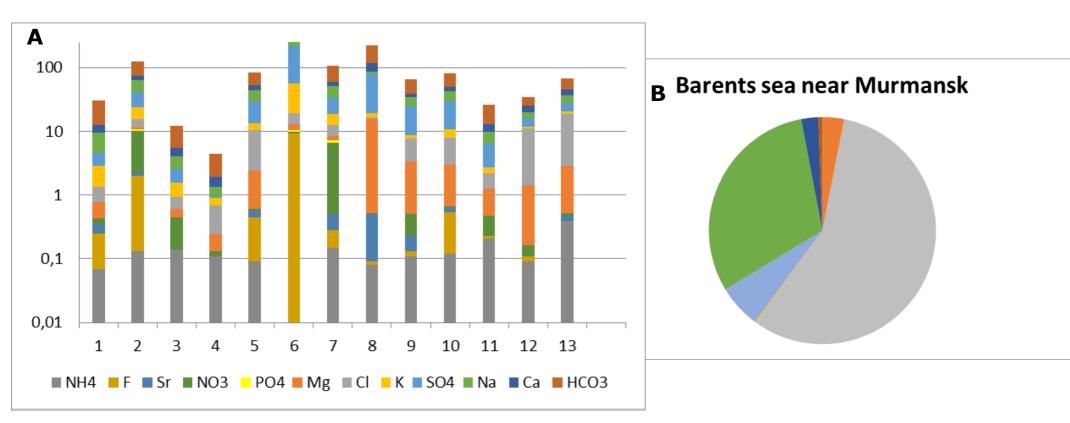


Fig.1 Glacier on the slopes of Kukisvumchorr (khibina Massif)(A), industrial landscape with contaminated lake near Monchegorsk (B), post-industrial soil in closed sulfide ore mine in Monchegorsk (C), Murmansk city by Barents Sea (D).

3. Results

3.1. Waters of Kola Peninsula

In the first place, groundwater, lake and river water were tested. The pH of the water samples was close to neutral, and their mineralization (TDS) ranged within ultra-sweet water (<100 mg/L) in runoff waters and sweet (100 - 500 mg/L) in underground water, rivers and lakes. In the ultra-sweet waters HCO3⁻ anions, SO4²⁻, Cl⁻, cations of Na⁺ and Ca⁺² were dominant while in freshwater highest concentrations were mostly SO4²⁻, HCO3⁻, Na⁺ and Ca²⁺ (fig. 2 A). Some of the samples (Boishoi Vudyavr, White River and Zhemchuzhnaya River) had significant content of F⁻ and PO4³⁻. Ammonium ions reached the value of 0,37 mg/L same with strontium (0,41 mg/L).



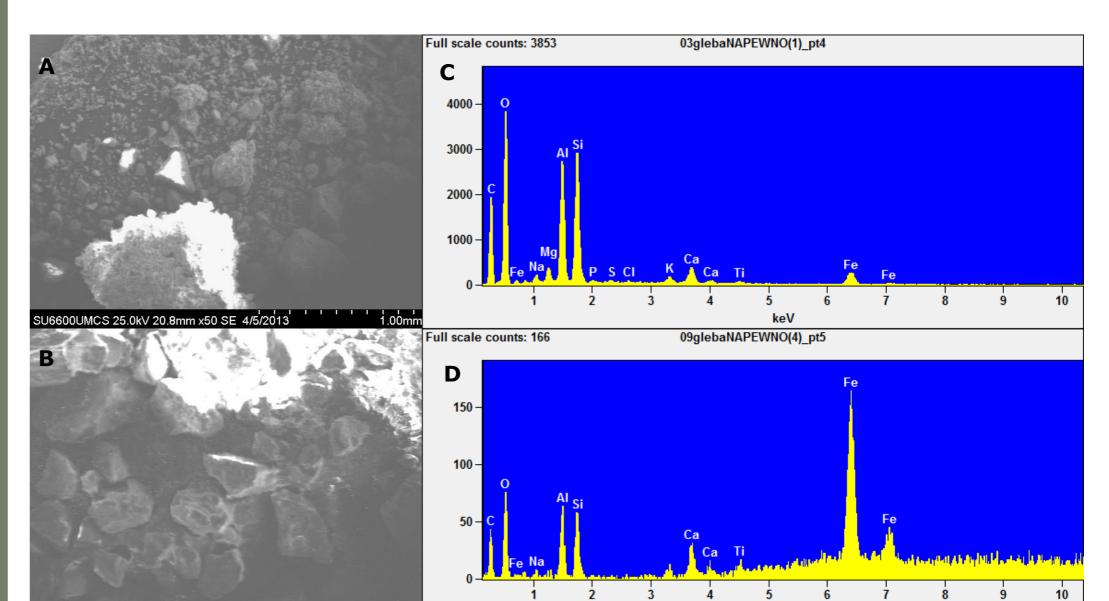


Fig. 5 XRF photo (A,B) and analsis of soil composition in samples 03 (C) and 09 (D).

keV

500um

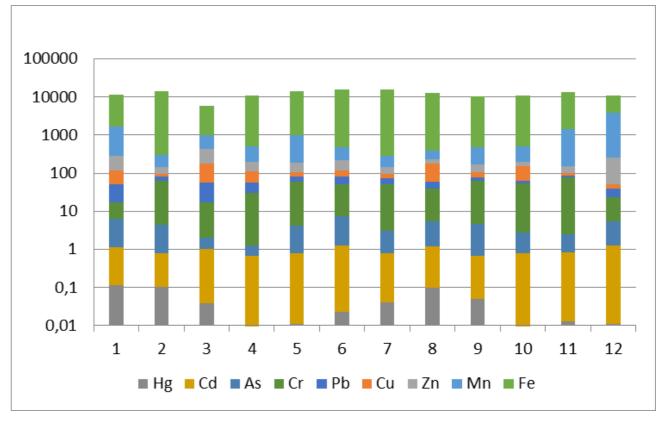


Fig 6. IPC analysis of heavy metals concentrations in soils of Kola Peninsula.

4. Conclusions

6600UMCS 25.0kV 20.8mm x60 SE 4/5/2013

Waters' richness in alkali minerals occured due to alkaline rocks in examined area, i.e. apatite, as a carrier, supplied waters of the rivers in PO4 and F ions. Also water in Monchegorsk was relatively rich in sulphates, because of the presence of sulfide ore in the region. An additional studies of chemical composition and isotope geochemistry of surface water from selected regions of the Kola Peninsula are planned to be assessed in the future. The approach will be extended by a few more elements to examine occurred redox conditions. Examined soil samples varied one from another. Admixture of elements like: P, F, Cl, Ti, Fe, Mn, Cu, Ni, S were mostly related with bedrock. Although, compounds as Zn, Pb or Cr in particulate samples displayed anthropogenic pressure coming especially from cities, watercourses flowing from industry plants or sedimentation tanks. Same thing applies to admixture of P, S or Cd. Coexistence of these elements (Cr/Cd, Fe/Cr, Zn/Pb) were confirmed from graphic analysis of amounts of elements in the samples. Anthropogenic pollution is significant on Kola Peninsula. Over the last 70 years, industry has been greatly expanded with paying little attention to environmental aspects. In example, the vicinity of Monchegorsk is about 5 km in diameter ecological disaster zone- the landscape resembles the surface of the Moon. The signs, warning about an ecological threat, can also be found all around the way from Petersburg to Murmansk. Khibiny Massif does not have any drastic changes in the environment, however, during the expeditions carried out in 2000-2012, authors repeatedly observed increasing amounts of dust aroundindustrial plants in the region. Also broken ships on the shore of lakes and sea were left unattended, corroding, creating the possibility of leakage of fuel and other fluids leading to contamination of waters.

Fig 2. Concentration of ions in freshwater (A) and seawater (B) samples collected in Kola Peninsula.

Seawater was characterized by high TDS value (16 136 mg/L=16,1 g/L). Dominant role in chemical composition of the water had Cl⁻ and Na⁺ ions albeit some other ions had significant values i.e. $SO4^{2-}$ (1 g/L), Mg²⁺ (0,5 g/L) and Ca²⁺ (0,4 g/L) (fig. 2 B).

In the hydrological cycle, stable isotopes of oxygen and hydrogen terrestrial tested water samples were arranged on the world line of precipitation (WMWL) defined by Craig [2]. Due to the climate, the isotopic ratios of oxygen and hydrogen in freshwater showed no crucial influence of water evaporation on its formation of chemical composition (fig. 3). Seawater TDS levels and oxygen/hydrogen ratios indicated the dilution phenomena when freshwaters form the estuary of river flow into the bay. The relatively high content of heavy metals (fig. 4) also pointed to high load of metals delivered from land.

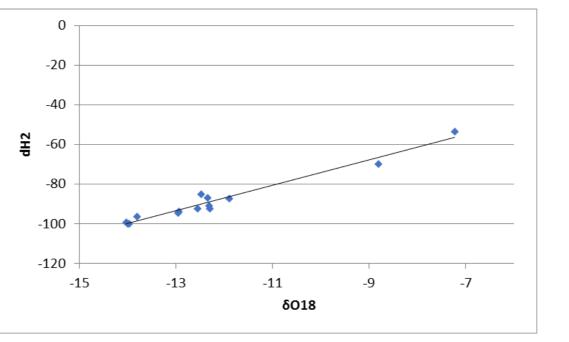


Fig. 3 Isotopic ratios in water samples.

References

[1] Caritat P., Reimann C., Äyräs M., Niskavaara H., Chekushin V.A., Paclov V.A, Stream water geochemistry from selected catchments on the Kola Peninsula (NW Russia) and in neighboring areas of Finland and Norway: 1. Elements levels and sources", Aquat. Geochem, 1996, 2(2) 149-168.[2] Craig H., Isotopic variations in meteoric waters. 1961. Cambridge, pp 133.[3] Dutkiewicz T., Toxicological Chemistry. National Institute of Medical Publishing, Warsaw, 1974, pp. 551[4] Huber, M., Iakovleva O.A., 2009. Problems of existence in the Arctic region Problems of existence in the Arctic region of the Russian Federation: the case of the Kola peninsula (environment protection, pollution, life conditions). Internet publication (https://wiki.oulu.fi/download/attachments/26687142/miloszhuber.pdf?version=1&modificationDate=1334059136000) in the Oulu University materials.[5] Ilyashuk, B.P., 2002. Relict crustaceans under conditions of long-term pollution of subarctic Lake Imandra: Results of observations in 1930-1998. Russian Journal of Ecology 33, 200-204.[6] Ilyashuk, B.P., Ilyashuk, E.A., Dauvalter, V.A., 2003. Chironomid responses to long-term metal contamination: a paleolimnological study in two bays of Lake Imandra, Kola Peninsula, northern Russia. Journal of Paleolimnology 30, 217-230.[7] Ilyashuk, E.A., Ilyashuk, B.P., 2002. Environment reconstructions using chironomid assemblages from sediments. In: Moiseenko T.I. (Eds.). Anthropogenic Modifications of Lake Imandra Ecosystem. Moscow Science, pp. 257-283.[8] Karpioski, T.M., Huber M., 2003. Polar Garden, Kola Peninsula, What blooms on the tundra. Poznaj Świat 1, 82-86 (in Polish).[9] Konstantinova, N.A., 1999. Flora and vegetation of Murmansk Region. Kola Science Centre, RAS, Apatity (in Russian).[10] Konstantinova, N.A., 2001. Bryophytes and vascular plants of the territory of Polar Alpine Botanical Garden (the Khibiny Mountains, Kola Peninsula). Kola Science Centre, RAS, Apatity, pp. 92. (in Russian). [11] Koroleva, N.E. 1994. Phytosociological survey of the tundra vegetation of the Kola Peninsula. J. Veget. Sci. 5: 803-812[12] Mitrofanov A.F., Geological characteristics of Kola Peninsula. Russian Academy of Science, Apatity, 2000, pp. 166.[13] Paczynski B., in The changes of water as a result of natural and anthropogenic processes. Influence of geogenic and anthropogenic groundwater (Eds.: I Dynowska), UJ. Krakow. 1993, pp: 211 - 270.[14] Pekkaa L., J. Ingria, A. Widerlunda, O. Mokrotovarova, M. Riabtsevac, B. Öhlandera, Geochemistry of the Kola River, northwestern Russia, Appl. Geochem. 2004, 19 (12), 1975-1995.[15] Vandysh, O.I., 2000. Zooplankton as indicator for the lake ecosystem condition (in terms of subarctic Imandra lake). Water Resources 27, 364-370 (In Russian).[16] Vandysh, O.I., 2004. Zooplankton as indicator for condition of the Kola Peninsula lake ecosystems under influence of mining-and-metallurgical integrated works. Ecologia 2, 134-140.

Afiliations

¹ Department of Hydrology and Climatology, Maria Skłodowska-Curie University, 2cd Kraśnicka St., 20-718 Lublin, Poland

- ² Department of Geology, Soil Science and Geoinformation, Maria Skłodowska-Curie University, 2cd Kraśnicka St., 20-718 Lublin, Poland
- ³ Institute of Earth and Environmental Sciences, Maria Skłodowska-Curie University, 2cd Kraśnicka St., 20-718 Lublin, Poland
- ⁴ Electrone and Optical Microscopy Laboratory, Department of Geology, Soil Scince Department and Environment Geography, Institute of
- Geography, Pedagogical University of Cracow, ul. Podchorążych 2, 30-084 Kraków, Poland
- ⁵ Polish Society of Geophysics, Department of Lublin, Maria Skłodowska-Curie University, 2cd Kraśnicka St., 20-718 Lublin, Poland

