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METALS AND METALLOIDS IN THE NATURAL WATER OF THE KOLA PENINSULA AND THEIR ENVIRONMENTAL DANGER

SUMMARY. This article presents the results of the research on dangerous elements in the lake water of the Kola Peninsula (the Murmansk region). The study has revealed some differences in the distribution of elements according to the landscape and geochemical characteristics of the region and the distance from the source of pollution. The higher concentrations of Ni, Cu, Se, and Ti in the lake water are observed near anthropogenic sources of pollution. The concentration of the trace elements in the lake water reflects the processes that can explain the peculiarities in the distribution and variability of the elements in the sub-regions. In general, we observe the process of adding the elements like Re, In, Se, As, Mo, Sb, Cd, Ag, Sc, Ni into the lake water of the Kola Peninsula. The coefficient of water migration is calculated as the ratio of the element concentration in the mineral balance of water to its concentration in rocks or soil (or to the lithosphere clarke). In the selected sub-regions such elements as Se, Re, Bi, Mo, Sb, U, Cd have a high coefficient of water migration. Increasing concentration of metals and metalloids in the natural water as a result of local and regional anthropogenic loads can lead to the changes in geochemical cycles and to the formation of ecotoxic conditions for water habitats.

KEY WORDS. Dangerous elements; addition of elements; dispersion.

Introduction

Rapid industrial development that leads to population growth, vast exploitation of mineral resources, climate change and acid precipitation negatively influences the environment. Vladimir I. Vernadsky noted that the increasing role of technical progress in the world could be compared to a geological catastrophe. The concept of "stable development" similar to Vernadsky's idea of noosphere, presupposes, on the one hand, that all the environment protection measures should be respected and, on the other hand, that the economy should ensure stable development of the society.

In today's situation of heavy anthropogenic loads, discharging dangerous substances (such as metals and metalloids) into natural waters seems an acute problem. Metals get into the atmosphere and water because of natural and anthropogenic processes that occur both on the Earth's surface and its interior. Among the natural processes we can name chemical weathering and volcanic activity. The anthropogenic processes include human economic activities, e.g. various types of industrial production, mining operations, firing, etc. It has been proved that for the recent century the anthropogenic role in releasing elements into the environment has dramatically increased due to more intensive mining of metals and their dispersion in the environment ([2], [3]).

The highest concentration of metals is found in stack emissions of nonferrous metal processing plants and battery manufacturing plants. Concerning the Kola Peninsula there are three centers of technogenic (and aerotechnogenic) pollution. Firstly, it is the north-west center where nonferrous metal processing plants are located. The biggest contaminating plant is the Pechenga Nickel Plant (located in the towns of Nikel and Zapolyarniy). The meridional center includes the valleys of the Kola and the Niva rivers and Lake Imandra. The territory is used by chemical and mining enterprises as well as by ferrous and nonferrous industries. The region is vulnerable to technogenic pollution mostly because the enterprises of Olenegorsk, Monchegorsk, Kirovsk, Apatity and Kandalaksha (such as Severonickel Mining and Metal-smelting Company, OJSC Apatit, Olkon, Kola Nuclear Power Plant, Lovozersky Mining and Concentrating Plant, Kandalaksha Aluminium Smelter) are located there. The south-west center includes iron-mining and other enterprises of the Kovdor industrial hub which also add to the aerotechnogenical pollution of the territory. Metals concentrated in the smoke emissions can be found in the forms of dust particles and aerosols.

The aim of the research was, firstly, to reveal the level of chemical pollution in natural waters depending on the landscape and geochemical peculiarities of the region and on how far the source of pollution is; secondly, to calculate water migration coefficients in different sub-regions of the Kola Peninsula.

Materials and methods

The information the research was based upon was the statistics on the chemical composition of 21 lakes of the Kola Peninsula.

The lakes were divided into several groups according to their landscape and geochemical peculiarities: the first group (I) consists of the lakes located in the zone affected by the Kola copper nickel smelting plants (base rocks); the second group (II) includes the anthropogenically acidified lakes of the tundra-taiga zone (acidic rocks – granite and quartz sand); and the third group (III) consists of naturally acidified lakes of the wetlands (mainly acidic rock – granite). It should be mentioned that within the territory of the Kola Peninsula there is a number of deposits of rare-earth metals; the central part (the Khibiny and the Lovozero mountains) is made of alkalaine massifs with high phosphorus content – the apatite-nepheline syenite.

The concentration of the elements (over 60) was measured by applying the method of inductively coupled plasma mass spectrometry, using a Plasma Quad-3 mass-spectrometer (Fisons Instruments Elemental Analysis, UK) [4]. The substances with the average values below the analytical detection limit were not included in the analysis: Te, Hg (detection limit <0,05 μg/L), Ge, Ru, Pd, Hf, Os, Ir, Pt, Au, Sm, Eu, Dy, Er, Yb, Lu (detection limit <0,02 μg/L), Rh, Ta, Tl, Tb, Ho, Tm (detection limit <0,01 μg/L) according to the measurements made for this region. The sum total of all the elements, contained in the lake waters and studied in the research is 38 trace elements (metals and metalloids).

Results and discussion

Table 1 shows the mean values and the limits of variation for trace element concentrations in the three sub-regions of the Kola Peninsula named above.

The lakes near the copper nickel plants are characterized by the higher concentration of Ni, Cu, Se and Ti – these substances spread with smoke emissions and are leached by acid precipitation. The anthropogenically acidified lakes of tundra and taiga dwell upon acid granite rock and quartz sand. Unlike base rock, granite is less affected by acid leaching. The acidic environment, with high concentration of Al and Fe, provides higher concentration of such elements as Ni, Zn, Sr, Li, Cs, Bi.

The naturally acidified lakes of the wetlands are characterized by peat and bog soils that enrich the water with humic substances and contribute to the active migration of Al, Fe, Mn and Ba into the lake water. The concentration of Al and Fe in the lakes of this area is ten times higher than in the other sub-regions mentioned above (table 1). As a result of the high level of biogenic migration, the lake water receives Mn and B. The high concentration of La, Ce, Nb can be explained by their high mobility in the natural water and by the great number of alkaline-earth elements.

Table 1

Median (50%) values and the limits of variation for the elemental composition of the lake water (μg/L) in different sub-regions of the Kola Peninsula

Element	I near the smelters (basalt and gabbro), n=4	II anthropogenically acidified lakes (quartz sand and granite), n=11	III naturally acidified lakes of the wetlands, n=6
1	2	3	4
Al	27,4 (16,3-29,7)	35,3 (10,0-160,)	387 (202-808)
Fe	31,1 (22,3-102,0)	44 (4,8-225,0)	278 (81-472)
Cu	4,97 (1,56-8,85)	0,84 (0,40-1,94)	1,42 (0,70-2,69)
Ni	5,6 (2,7-28,7)	1,20 (0,60-4,10)	2,15 (1,0-4,4)
Co	0,05 (0,05-0,20)	0,05 (0,05-0,50)	0,40 (0,40-0,60)
Zn	2,0 (1,0-4,0)	2,70 (1,6-3,1)	3,30 (2,10-3,80)
Mn	3,9 (2,2-5,5)	8,1 (1,3-11,8)	13,3 (3,3-23,7)
Sr	0,1 (5,9-10,7)	4,7 (2,0-23,4)	0,13 (6,7-15,0)
Pb	0,20 (0,10-0,30)	0,30 (0,10-0,80)	0,25 (0,10-0,70)
Cr	0,3 (0,2-0,4)	0,20 (0,10-0,40)	0,65 (0,50-0,90)
Cd	0,07 (0,04-0,08)	0,07 (0,05-0,12)	0,08 (0,02-0,16)
As	0,50 (0,35-0,64)	0,27 (0,05-0,55)	0,38 (0,24-0,67)
Li	0,86 (0,11-1,22)	1,15 (0,18-3,01)	1,13 (0,34-1,94)
Se	1,44 (0,86-1,60)	0,80 (0,42-1,44)	0,96 (0,64-1,12)
Mo	0,27 (0,19-0,30)	0,08 (0,01-0,29)	0,06 (0,03-0,07)
U	0,05 (0,01-0,06)	0,01 (0,01-0,03)	0,04 (0,01-0,25)
Rb	0,01 (0,42-0,94)	1,01 (0,67-22,99)	0,01 (0,46-7,92)
Sb	0,05 (0,03-0,11)	0,08 (0,03-0,24)	0,09 (0,04-0,31)
Ba	6,45 (1,48-7,33)	3,35 (1,06-7,86)	11,56 (4,83-27,19)
Be	0,01 (0,01-0,02)	0,02 (0,01-0,07)	0,03 (0,02-0,03)
B	1,5 (1,0-2,0)	1,5 (0,9-2,9)	1,3 (1,0-1,9)

1	2	3	4
Sc	0,61 (0,27-0,91)	0,17 (0,13-0,34)	0,59 (0,20-1,48)
Ti	1,72 (0,70-2,37)	1,24 (0,45-2,54)	2,91 (1,39-4,98)
V	0,57 (0,28-0,65)	0,31 (0,15-0,77)	0,70 (0,62-1,12)
Re	0,01 (0,01-0,02)	0,01 (0,01-0,02)	0,01 (0,01-0,03)
Sn	0,11 (0,05-0,31)	0,15 (0,05-0,29)	0,11 (0,09-0,43)
Ga	0,03 (0,02-0,05)	0,01 (0,01-0,03)	0,03 (0,02-0,07)
Y	0,05 (0,01-0,06)	0,02 (0,02-0,03)	0,31 (0,10-1,54)
Zr	0,07 (0,04-0,08)	0,08 (0,02-0,14)	0,13 (0,03-0,25)
Nb	0,01 (0,01-0,01)	0,01 (0,01-0,03)	0,02 (0,01-0,03)
Cs	1,42 (1,00-1,46)	2,70 (1,44-3,72)	1,60 (1,23-3,35)
W	0,03 (0,01-0,04)	0,03 (0,02-0,07)	0,04 (0,02-0,05)
Bi	0,53 (0,39-1,12)	1,05 (0,42-2,03)	1,04 (0,69-1,19)
La	0,40 (0,23-2,88)	0,57 (0,12-6,68)	1,13 (0,40-3,00)
Ce	0,35 (0,25-4,69)	0,61 (0,13-8,06)	2,32 (0,51-3,67)
Pr	0,04 (0,02-0,20)	0,04 (0,01-0,46)	0,37 (0,06-0,71)
Nd	0,14 (0,04-0,18)	0,07 (0,06-0,47)	1,19 (0,13-2,34)
Th	0,01 (0,01-0,01)	0,01 (0,01-0,04)	0,08 (0,01-0,13)

The comparative analysis of the element concentrations in these sub-regions has revealed the main differences (pic. 1). The lakes located in the industrial zone are characterized by the high concentration of Cu, Ni, Mn, Se, Ti, due to the direct impact of smoke emissions from copper nickel plants. On the other hand, a large group of elements is characterized by their low concentration in the lake water because the base rock helps the elements accumulate in the catchment area and prevents them from migrating and therefore getting into the natural water.

The anthropogenically acidified lakes are also characterized by low concentration of elements in the water. It is well-known that acid precipitation contributes to the chemical weathering of the rocks that make up the Earth's crust. The acid lakes have high concentration of As, La, Bi, V. At the same time, granite is resistant to leaching, that is why the concentration of a large group of other elements is low.

The naturally acidified lakes are characterized by higher concentration of elements such as Co, Zn, Mn, Cr, Li, Ba, Ti, Nb, Bi, La, Ce, Pr, Nd. This fact can be proved by the presence of the elements that are not very common for the Earth's crust, which can be explained, first of all, by the diversity of rocks determining the variability of the chemical composition in the lakes and by the development of the wetlands near the catchment areas (the elements can migrate from the wetlands into the lakes). The concentration of Al and Fe was up to 400 and 300 (μg/L) respectively – ten times more than the concentration of these elements in the anthropogenically acidified lakes of tundra, where the soil layer is thin and the substrate consists of granite. Thus, the landscape and geochemical peculiarities of the catchment area influence the migration of the element.

Migration of elements and their anthropogenic addition into the natural water

Alexandre I. Perelman [5] put forward an idea of estimating the water migration of the chemical elements by the coefficient defined as the ratio of the concentration of an element in the mineral residue of water to its concentration in rocks or soils (or to lithosphere clarkes). The coefficient shows the intensity of water migration depending on the properties of the element and on the level of its concentration or dispersion in the surface water. The coefficients of water migration of the elements were calculated only for the clarkes of the rocks related to the lakes, which allowed to get more accurate regional characteristics and to find out some common patterns. Table 2 shows the calculated coefficients of migration for metals and metalloids in the lakes of different sub-regions of the Kola Peninsula. The data from the research of the whole region of European Russia have been given for the sake of comparison [4].

The analysis of the coefficients of the water migration of the elements has revealed the main differences in the migration intensity (table 2). In general the selected regions are characterized by the high migration coefficients for Se, Re, Bi and increased coefficients for Mo, Cd, Sb, U. The concentration of these elements in the Earth's crust is extremely low, that is why we can assume that their migration into the water has been caused by some technogenic factors and correlates with the level of anthropogenic loads in the region. It should be mentioned that the water in European Russia also received a large group of elements as a result of pollution in central and southern regions.

The increased concentration of Se, Bi, Re, Cs can be explained by the peculiarities of the geological structure (the apatite-nepheline syenite), while the high concentration of Cu, Ni, Mo, Cd, Sb in the lake water is a result of smoke emissions and acid leaching.

The dispersion intensity of the elements most common for the Earth's crust (Fe, Al, Ti, Mn) in the sub-regions has the following features: the concentration of Fe, Al and Ti near the smelting plants is lower than in the tundra or taiga. The developing wetlands help the elements get into the water bodies. The concentration of Mn is also higher in the taiga because of the increasing biogenic migration. Besides Mn, the three regions are characterized by the rising concentration of Cu, Zn and Cd.

Table 2. The intensity of water migration (concentration and dispersion) of the elements in the lakes of different sub-regions of the Kola Peninsula and in European Russia, in general (depending on the type of the rock forming the Earth's crust). The elements in bold are the rare elements the high concentration of which has mainly resulted from anthropogenic influence, a dash means that there are no elements with such coefficient of migration.

The intensity of water migration (concentration and dispersion)	The coefficient of water migration (concentration and dispersion)	Lakes near the smelters (basalt, gabbro), n=4	Anthropogenically acidified lakes (quartz sand and granite), n=11	Naturally acidified lakes of the wetlands (granite), n=6	European Russia in general [4]
1	2	3	4	5	6
Very high	> 100	**Se**, Cs, **Bi, Re**	Ni, **Se, Re, Bi**	**Se, Re, Bi**	**Re**
High	1 — 100	Ba, Ni, Cu, Zn, B, Li, Sc, V, La, Ce, **Mo**, Pb, Sn, **Cd, Sb, As, U**, Ag, W, Be	Cu, Co, Zn, Sr, Pb, Mn, **Cd**, Li, **Mo, Sb, As**, Be, B, Sc, Sn, Cs, V, Ag, W	Cu, Ni, Co, Zn, Sr, Pb, Cd, Cr, Li, **Mo, U, Sb, As**, Be, B, Sc, V, Ag, Cs, La, Ge, Gd, Pr, Nd	**Se**, Cd, B, Cs, **Bi, Mo, As**, Sr, **Sb**, Li, **U**, Rb

1	2	3	4	5	6
Average	0.05 — 1	Mn, Pr, Nd, Cr, Ga, Th, Co, Gd	Cr, U, Fe, Rb, Ba, Ti, Ga, Y, Nb, La, Ce, Gd, Pr, Nd, Th	Al, Fe, Mn, Cr, Rb, Ba, Sn, Y, W, Th	Sc, Sn, Zn, Ba, Cu, Ni, Mn, W, La, Cr, Fe
Low	0.001 – 0.05	Fe, Al, Ti, Sr, Zr, Nb	Al, Zr	Ti, Ga, Zr, Nb	Be, Ce, Pr, Co, Y, Nd, Gd, Pb, Ti, Al, Th, V, Zr, Ga, Nb
Very low	< 0.001	-	-	-	-

The group of lanthanides (La, Ce, Pr, Nd) along with the accompanying elements (Al, Fe, Be) are characterized by high ability to migrate. However in the anthropogenically acidified lakes these elements are less active in the migrating process because the acidified lakes are located close to the granite rocks. The elements U and Re are characterized by the high level of migration and accumulate in great quantities in the lakes located near the sources of aerotechnogenic pollution and wetlands. In the area affected by the smelters the water receives Ni and Cu and sometimes Co. Ba is less free to move, that is why its concentration within the territories is less considerable.

Ecological threat of metals and metalloids

Accumulating in natural areas many metals can participate in biogeochemical cycles and accumulate in the living organisms; they can also have direct toxic effects and long-term negative consequences [3]. The elements are divided into essential (biophil) and non-essential (toxic). The first group includes such metals as Fe, Co, Cu, Cr, Mn, Zn, etc. Low concentrations of these elements do not have toxic effects on living organisms; on the contrary, they are necessary for the normal functioning of the organisms. The ecotoxic properties of the elements depend on the forms these elements take. This is an important feature of metals as polluting elements: after getting into the environment their toxicity and bioavailability greatly depend on the form they take. In recent years at the global (and regional) level we can observe a tendency of adding into the lake water such dangerous elements as Pb, Cd, Al, Cr, etc [3]. Humic substances consentrated in natural water play the main role in the inactivation of metals. It is well-known that anthropogenic acidification of water contributes to the increase in the toxicity of metals, because in such environment metals mostly take ionic forms. For example, the concentration of Al (in 30 μg/L) in transparent acidic water can kill the fauna of the lakes, whereas 400 μg/L in coloured humus enriched water did not have any toxic effects [3]. In order to evaluate the consequences of element dispersion for the environment, it is necessary to take into account not only the concentration of these elements in the water, but also the chemical composition of natural water, especially the concentration of calcium and humic substances [4]. Despite the fact that in our research the concentration of many elements was higher in the naturally acidified water with high concentration of humus than in the anthropogenically acidified lakes, the latter are more exposed to the ecological threat of increasing concentration of the elements.

In recent years, scientists are especially concerned with the increasing concentration of Hg, Cd and Pb in the environment. Our research has revealed the increased concentration of Cu, Ni, Cd, Vi, Mo, Cr, Se, Re. Briefly we will dwell upon the ecotoxic properties of these elements.

It has been experimentally proved that in the acidified environment water organisms suffer from the increased accumulation of such dangerous elements as Hg, Cd, Zn, Pb, etc, which can be explained by the extremely low concentration of calcium in the water. Cadmium is a toxic and rather labile element; in recent decades cases of its active migration into the water bodies have been observed (the migration was caused by acid precipitation). Cadmium also gets into the environment with fertilizers. Many scientific works state its high concentration in water bodies and, as a result, in living organisms. Cadmium can substitute calcium in the metabolic process; its negative impact causes the inhibition of calcium-transport proteins ([2]; [3]; [6]).

Plumbum is a high-toxic element that gradually accumulates in natural water, negatively influencing the living organisms. The accumulation of Pb in the organisms leads to the destruction of cellular organelles as a result of decreasing intensity of protein synthesis [3]. The signs of lead intoxication in fish can be blackening of distal kidneys, scoliosis, lordosis, necrosis of the lateral line sensory cells [2].

Increased concentration of nickel in natural water leads to heart and lever involvement, the involvement of organs of vision; nickel has some cancerogenic properties [7]. Bismuth is a moderately toxic element and is less poisonous than plumbum. Despite this fact, when combined with salts its effect on the living organisms can be compared to that of mercury ([8]; [9]; [10]). Increased concentration of molybdenum in natural water is a result of aerotechnogenic dispersion from industrial enterprises and can lead to cardiovascular diseases and podagra [11]. Accumulation of chromium in organisms results in a number of diseases, including oncological ones. Low concentration of Se in natural water is essential for normal functioning of living organisms. It increases due to the anthropogenic activity and can have a strong toxic effect as a cancerogenic element ([12]; [13]).

In our research we have not come across any concentration of metals that would exceed the TLV, however metals can influence simultaneously and their synergetic effect may create toxic environment for the water habitats. Special attention should be paid to the fact that increased concentrations of metals act in low-mineralized and acidified water. Such conditions are favourable for the penetrating power and toxic influence of metals to increase manifold [3].

Conclusion

The lakes of the Kola Peninsula can provide significant information on the formation of their chemical composition as well as the level of regional anthropogenic pollution. Some elements can be added into the water because of the anthropogenic dispersion of elements and leaching by acid precipitation. The lakes located close to the source of pollution are characterized by the increased concentration of Al, Fe,Cu, Ni and Mn, due to smoke emissions and leaching by acid precipitation. The anthropogenically acidified lakes of the tundra-taiga region are characterized by the increased concentration of Al, Fe and Mn, as a result of spreading wetlands and As, La, Bi, V as a result of anthropogenic loads on the water catchments. The lakes near the wetlands are characterized by the increased concentration of Fe, Al and Mn (because of the increasing biogenic migration of this element). Increasing concentration of lanthanides is caused by their high migration activity.

Increasing concentrations of dangerous elements in the environment and natural water can have a negative impact on water ecosystems and on human's health. The increased concentrations of a large group of elements, studied in the research, can have synergetic effects on living organisms.

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