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Study of the Content of Heavy Metals in Atmospheric Precipitation of the Goygol Region of Azerbaijan

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***Abstract* – The increasing content of heavy metals in the soil and atmospheric air can lead to serious consequences and even affect a person. The method of moss biomonitoring was used to define heavy metals in atmospheric depositions. In 2015, the scientists of the Joint Institute for Nuclear Research introduxed moss biomonitoring in Azerbaijan. The first system studies were conducted the same year in the Goygol National Park. Geographical coordinates of the Goygol National Park: 40° 35' northern latitude and 46° 18' east longitude. 50 moss samples were collected (mainly Pleurosium Schreberi), which were studied via neutron activation analysis in the Joint Institute for Nuclear Research in Dubna. In total the content of 44 elements were determined. The concentrations were defined by the instrumental neutron activation analysis (NAA) and atomic-absorption spectroscopy (AAC) in 50 moss samples. Moss species used in the study: Pleurosium Schreberi. The most polluted sites were defined on the basis of the analysis.**

Keywords – biomonitoring; bioindicator; radionuclides; moss; heavy metals.

I. INTRODUCTION

Azerbaijan is located on the border between Europe and Asia and some of its regions belong to Eastern Europe. Mountains occupy half of the territory of Azerbaijan. The area is 86.6 thousand km^2, the most northerly point – 3648 m/41° 54' NL, the most southerly point – 38° 25' NL, the most easterly point – 50° 49' EL, the most westerly point – 44° 46' EL. Azerbaijan is characterized by 9 out of 11 types of climate. The average temperature in winter is +5 in mountainous, and up to 32-35°C in low-land areas (sometimes up to 40°C).

Azerbaijan is industrially agrarian country with developed industry and diversified agriculture. Oil and gas, oil refining, chemical (mineral fertilizers, synthetic rubber, etc.), machine-building, mining, nonferrous metallurgy, food and light industries take the major place in the economy of Azerbaijan.

Agriculture: winegrowing, tobacco growing, vegetable growing.

The samples were collected in the Goygol National Park 40 kilometers from Ganja, the second largest city in Azerbaijan.

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Ganja is one of the industrial cities of the country. Different plants, factories and other industrial enterprises are located ın Ganja. They include the following: Ganja steel works; DET.AL HOLDING – the leading group of companies in nonferrous metallurgy of the Republic of Azerbaijan that produces aluminum oxide (alumina), primary aluminum and aluminum semi-finished products (for example, aluminum sheet in sheets and rolls) from bauxite and alunite ore; Ganja instrument making; Ganja automobile plant; SEMPA Company – production of polypropylene pipes; SEMSAN Company – production of metalwork and hardware for construction industry; ASMET Company – smelting of non-ferrous metals; Ganja Sharab winery; and GENCE TEKSTIL company – production of cotton threads and fabrics, etc.

The Goygol National Park was created in 2008 and is located on northern slopes of the Mount Kyapyaz. The area of the national park is 12.755 hectares.

The Goygol National Park is aimed to protect the natural ecosystem of subalpine zones of northern slopes of Lesser Caucasus.

In the conditions of vigorous human activity, the heavy metals pollution is a priority problem in the world. This problem is complex and diverse. The complexity of this problem is that there are no reliable mechanisms for self-cleaning of heavy metals. Heavy metals migrate from one environment to another thus negatively influencing living organisms. A particular danger of heavy metals is caused by their stability in the environment [1, 2]. According to the study and forecasts they can become more dangerous than nuclear waste. Their main sources of pollution are transport and industrial enterprises. There are different anthropogenic sources of air pollution. At the same time, pilot studies show various biological activity of compounds of one and the same element. The international program for the assessment of vegetation damage by air pollution was established in 1980 to study the impact of air pollution on plants. At present, scientists of more than 40 countries work according to this program (Harmens, 2013) [3-5]. The program is coordinated by the Center for Ecology & Hydrology in Great Britain. Since 2014 the sampling of mosses has been coordinated by the Joint Institute for Nuclear Research in Dubna, Russia. This program is included into activity of group on the Convention on Transboundary Air Pollution. The program is one of the several international programs studying the impact of water and air pollution on human health. This international cooperation is supported by the Convention on Transboundary Air Pollution [6-10].

The increase of heavy metals in air, soil and water slows down the growth of plants and increases the concentration of heavy metals in food, which eventually has a negative impact on healthy people.

II. MATERIALS AND METHODS

There is a simple and cheap technique to determine heavy metals in atmospheric precipitation. Mosses are good biomonitors of atmospheric precipitation of heavy metals.

Since 1990 this method has been used across the whole Europe. The main advantage of this method is that mosses accumulate heavy metals in concentration strongly exceeding that in air and water. The sampling of moss is easy.

50 moss samples were collected in the Goygol National Park of Azerbaijan for analysis. Mainly Pleurozium Schreberi mosses were collected. The sampling was as follows: samples were collected in August – September (it is usually recommended to collect samples from April to October).

The samples were collected at least 300 m from the main roads, villages and industrial enterprises, and at least 100 m from local roads and houses at a distance of not less than 3 m from the nearest trees to reduce the forest influence. Sampling and processing of samples was carried out with polyethylene gloves, the collected material was kept in paper bags.

A)

B)

C)

D)

Fig. 1. Maps of moss sampling

In laboratory the samples were carefully cleaned from needles, leaves and soil particles, after that they were air dried at 30 ÷ 40 °C during 48 hours to their constant weight.

For short-term radiation the 300 mg samples were granulated in simple compression molds.

It shall be noted that the concentration of heavy metals in Pleurozium Schreberi does not change with season. This rule may not be applicable to other moss species.

The coordinates were specified for each point of sampling. 2-6 moss samples were collected from each point.

The complex analytical methods using the most advanced systems was applied to define the metals. The study was conducted via neutron activation analysis on the IBR-2 reactor of the Joint Institute for Nuclear Research.

III. RESULTS AND DISCUSSION

Air pollution with heavy metals and radionuclides is one of the most important problems of the present. Every day they create a big load of the ecosystem and thus present a big danger to living organisms. For this purpose, the study of heavy metals content in atmospheric precipitation began in 2015 in Azerbaijan [9].

50 moss samples (Pleurozium Schreberi) were collected in various points of the Goygol area. The figures illustrate moss samples and a card of their sampling.

Table 1 shows the results of the study.

Fig. 2. Moss samples

Fig. 3. Preparation for analysis

TABLE I. RESULTS OF THE MOSS STUDY

Al	
No.	***mg/kg***
600 m. Goy-gol Ashigli	***4160***
610 m. Goy-gol Ashigli	***2950***
610 m. Goy-gol Ashigli	***6440***
1000 m. Goy-gol Togana	***8630***
1000 m. Goy-gol Togana	***13300***
1000 m. Goy-gol Togana	***3250***
1250 m. Goy-gol	***7440***
1250 m. Goy-gol	***5480***
1250 m. Goy-gol	***5000***
1270 m. Goy-gol	***5450***
Ca	
No.	***mg/kg***
600 m. Goy-gol Ashigli	***14900***
610 m. Goy-gol Ashigli	***10300***
610 m. Goy-gol Ashigli	***9030***
1000 m. Goy-gol Togana	***12200***
1000 m. Goy-gol Togana	***12100***
1000 m. Goy-gol Togana	***11000***
1250 m. Goy-gol	***14900***
1250 m. Goy-gol	***14600***
1250 m. Goy-gol	***14400***
1270 m. Goy-gol	***10700***
Cr	
No.	***mg/kg***
600 m. Goy-gol Ashigli	***11.2***
610 m. Goy-gol Ashigli	***8.03***
610 m. Goy-gol Ashigli	***8.11***
1000 m. Goy-gol Togana	***11.7***
1000 m. Goy-gol Togana	***14.5***
1000 m. Goy-gol Togana	***5.3***
1250 m. Goy-gol	***11.2***
1250 m. Goy-gol	***10.3***
1250 m. Goy-gol	***12.5***
1270 m. Goy-gol	***7.72***
Mn	
No.	***mg/kg***
600 m. Goy-gol Ashigli	***118***
610 m. Goy-gol Ashigli	***102***
610 m. Goy-gol Ashigli	***126***
1000 m. Goy-gol Togana	***820***
1000 m. Goy-gol Togana	***605***
1000 m. Goy-gol Togana	***123***
1250 m. Goy-gol	***132***
1250 m. Goy-gol	***138***
1250 m. Goy-gol	***125***
1270 m. Goy-gol	***113***
Fe	
No.	***mg/kg***
600 m. Goy-gol Ashigli	***3710***
610 m. Goy-gol Ashigli	***2870***
610 m. Goy-gol Ashigli	***4110***
1000 m. Goy-gol Togana	***5380***
1000 m. Goy-gol Togana	***8510***
1000 m. Goy-gol Togana	***2090***
1250 m. Goy-gol	***4020***
1250 m. Goy-gol	***4910***
1250 m. Goy-gol	***4420***
1270 m. Goy-gol	***2910***

Concentration of 44 elements were defined (Na, Mg, Al, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Tm, Yb, Hf, Ta, W, Au, Th, U).

The concentration of elements: Na, Mg, Al, Si, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, CD, In, Sb, I, Cs, Ba, La, Ce, Nd, Sm, EU, Tb, Tm, Yb, Hf, Ta, W, Au, Th, U. Table 2 shows the results of the study. Alongside with the corresponding results of analytical research the study shows the comparative data for Georgia (2014-2016) and uncontaminated territories of northern Norway (2016). The comparison of moss concentration between Azerbaijan and Norway showed increased content in the majority of heavy metals (Mg, Al, V, Fe, As, Mo, Cd, La and U) of the studied samples, which is explained by the condition of industrial production. It can be assumed that the main potential sources of industrial air pollution of these areas are as follows: plant that produce iron ore, aluminum, cobalt and marble, nonferrous metallurgy (melting of non-ferrous metals), production of metalwork and hardware for building industry, etc.

IV. CONCLUSION

The multiparameter statistical analysis of obtained analytical results will allow revealing the main sources of pollution and estimating the role of long-range transport of atmospheric pollutants. Considering the importance and relevance of this work it is planned study the atmospheric precipitation of heavy metals and radionuclides by moss biomonitoring on the most part of the territory of Azerbaijan (about 60% of the territory is covered with mosses). New data will make a big contribution to scientific research of the country's environment and will enrich scientific biomonitoring of mosses in subtropical zone (9 out of 11 possible types of climate). Due to these study Azerbaijan intends to become the participant of the UN program on air pollution in Europe within the Convention on Long-Range Transboundary Air Pollution (CLRTAP). The preliminary study shows that moss biomonitoring of atmospheric precipitation of heavy metals is an efficient method to study the environmental situation in the mountainous areas of Azerbaijan characterized by a variety of mining and metallurgical enterprises. The experience of this study can be successfully used in other regions of Azerbaijan.

TABLE II. COMPARATIVE DATA (MG/KG) FOR GEORGIA AND UNCONTAMINATED TERRITORIES OF NORTHERN NORWAY

List of selected peak energies for NAA				**Azerbaijan 2015 (this study)**		**Georgia 2014[ ]**		**Georgia 2015 [ ]**		**Norway [Ref.]**	
				n=85		***n=16***		***n=36***		***n=100***	
Element	Isotope	Half life	Gamma peak, keV	Median	Range	Median	Range	Median	Range	Median	Range
Na	24Na	14.7 h	1368.55	512.5	207-1370	721	268-1990	338.5	101-2080	nd	nd
Mg	27Mg	9.5 m	1014.44	3670	2540-6780	4410	2720-11600	2380	1380-6300	1730	940-2370
Al	28Al	2.2 m	1778.9	3870	1070-1120	5195	2450-20800	2955	759-12600	200	67-820
Cl	38Cl	37.2 m	2167.68	134	48-585	225	140-465	149.5	57,3-333	nd	nd
K	42K	12.4 h	1524.6	5380	3040-11000	5875	3080-9040	4610	2030-8360	nd	nd
Ca	49Ca	8.7 m	3084.4	9750	7670-13300	11800	7140-15300	6530	4880-10900	2820	1680-5490
V	52V	3.8 m	1434.4	1.075	0,4-2,1	42593	6.2-54.0	5.575	1.71-18.9	0.92	0.39-5.1
Mn	56Mn	2.6 h	1810.7	145	10-335	158	70-592	109	21,7-525	256	22-750
Fe	59Fe	44.5 d	1099.1	2845	921-5870	3935	1640-14700	2000	404-11100	209	77-1370
Zn	65Zn	244 d	1116	26.15	12,9-40,6	38.1	17.3-68.7	20.4	7.15-48.4	26.5	7,9-173
As	76As	26.3 h	559.1	1.015	0,44-1,86	0.88	0.33-2.87	0.6935	0.176-7.55	0.093	0.020-0.505
Br	82Br	35.3 h	554.3	5.325	2,33-16,6	42494	2.3-9.8	5.145	2.33-7.45	42494	1.4-20.3
Mo	99Mo	66 h	140.5	0.4435	0,228-0,761	0.35	0.24-0.77	0.286	0.174-0.894	0.135	0.065-0.70
Cd	115Cd	53.5 h	527.6	0.308	0,12-1,15	0.25	0.12-0.56	0.175	0.0317-0.791	0.058	0.025-0.171
I	128I	25 m	442.9	3.63	1,65-9,91	42584	1.3-5.1	1.29	0.577-2.79	42492	0.6-41.7
La	140La	40.2 h	1596.2	1.745	0,65-4,90	41306	0.92-6.28	1.615	0,342-12	0.189	045-2,56
Sm	153Sm	46.7 h	103.2	0.29	0,123-0,727	0.43	0.03-0.94	0.182	0.0402-1.86	0.33	0.05-1.34
W	187W	23.9 h	685.7	0.07575	0,035-0,199	0.13	0.06-0.27	0.10405	0.0485-0.597	0.127	0.009-1.23
Au	198Au	2.7 d	411.8	0.00171	0,00048-0,00681	0.00091	0.00031-0.00225	0.0000403	0.00000602-0.000267	nd	nd
U	239Np	2.4 d	228.2	0.1455	0,03-0,33	0.19	0.08-0.50	0.1075	0.0207-0.752	0.015	0.001-0.138

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