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HEAVY METAL ATMOSPHERIC DEPOSITION STUDY IN AZERBAIJAN BASED ON MOSS TECHNIQUE AND NEUTRON ACTIVATION ANALYSIS

Abstract: The results of this investigation show that Azerbaijan industries and agricultural sector provide considerable anthropogenic impact on the environment of Caucasus. The use of moss biomonitoring technique and neutron activation analysis (NAA) is a first attempt to study heavy metal atmospheric deposition in Azerbaijan, a country different relief and climate. The study was undertaken in the summer of 2015 of atmospheric deposition of man-made heavy metal pollutants in the area of mining and processing plant in Gadabay and Dashkasan mininig district. At the same time samples were collected from the Goygol State Reserve in the Lesser Caucasus not far from the city of Ganja. A total 85 moss samples (predominantly *Pleurozium schreberi*) collected in both environmentally contrast area. Elemental determination was carried out by epithermal neutron activation analysis (ENAA) at the reactor IBR-2 of Joint Institute for Nuclear Research (FLNP JINR). For the first time 44 elemental concentrations were determined (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). Multivariate statistical analysis of the analytical results obtained will make it possible to identify the main sources of pollution and to assess the role of long-range transport of pollutants.

Keywords: trace elements, factor analysis, neutron activation analysis, atmospheric deposition, moss biomonitoring

Introduction

The moss technique is widely used to monitor atmospheric deposition of heavy metals in many countries in Europe, whereas this technique is newly used in Asia. To implement this international reliable and cost-effective methodology in the Asian countries, it is necessary to find proper moss types typical for the Asian environmental and suitable for the biomonitoring purposes. State of the environmental and thus the health of the population largely depend on the state of the earth's atmosphere. The atmosphere basically consists of a mixture of natural gases [1]. In addition, the air can contain pollutant gases, as well as suspensions of liquid or solid particulates. The particulates pass into the air either from

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natural sources (soil, rocks, water bodies and living organisms) or as a result of anthropogenic activity (industry, transport, fuel, human waste, etc.). Essentially, atmosphere is an aerosol system where solid particulates are dispersed in a mixture gases. Among the various types pollutions, the most hazardous are heavy metals. In practice, air pollution monitoring is a multifaceted problem. It is necessary to reveal sources of various pollutants and their emission, select appropriate analytical techniques for quantitative determination of concentrations of particular elements with a required accuracy, and assess the degree of risk associated with the effect of individual pollutants on the environment and human health with due regard for environmental aspects [2, 3]. Investigation of atmospheric deposition of trace elements using special aerosol filters is a classic line of research in this field. The aspiration sampling method requires special devices called samplers. In the samplers large volumes of air are passed through various filters [4, 5]. The method is difficult and not productive for investigations of large territories. Since the early nineties in individual countries and on the international scale the intensive research to develop new modern methods of assessing air pollution were carried out. One of these directions is the study of atmospheric deposition of heavy metals and other toxic elements with the air of biomonitors [6, 7]. According to the definitions, biomonitors are living organisms that serve to describe the state of environment quantitatively. Lichens, mosses, ferns, grass, bark and leaves of trees, conifer needles, etc., are used as biomonitors [8-10]. The moss technique first introduced Scandinavia more than four decades ago, and has shown to be very suitable for studying the atmospheric deposition of trace elements [11, 12]. Moss biomonitoring has been developing as a method for studying atmospheric deposition of heavy metals since 1960 [13-15]. Mosses have a rudimentary root system and readily take up elements from atmosphere. The advantage of the method is in the simplicity of sample collection, although the determination of the species needs an experienced hand.

Data from existing surveys of heavy metals concentrations in mosses is an invaluable resource for international negotiations on heavy metal pollution. The data from moss surveys allow examination of both spatial and temporal trends in heavy metal deposition, and identification of areas where there is high deposition of heavy metals from long-range atmospheric transport and local sources. Mosses effectively concentrate most heavy metals and other microelements from the air and precipitation. Mosses are usually tolerant to even a high pollution level. The most commonly used moss species in air pollution biomonitoring are *Hylocomium splendens* (Hedw.) (Scimp.), *Pleurozium schreberi* (Mitt.) (Brid.), and *Hypnum cupressiforme* (Hedw.) [16-18]. It is easy to collect samples, and instrumental analysis of mosses is simpler than analysis of precipitation: the exposure period is easy to determine (3 year growth segments of mosses are usually taken for analysis) they can also be employed for studying temporal trends [19-21]. The moss biomonitor method in combination with nuclear physics analysis techniques has been regularly used for the past three decades in Western Europe and in Asia as well. Thirty four countries signed the United Nations Convention for control of emissions of heavy metals in the air using biomonitoring (the Aarhus Protocol), Denmark in 1998 (as of 2004, it had 36 signatories). The United Nations Organization established a special economic Commission for Europe intended for shaping the scientific policy of the countries that signed the UN Convention in the field of research on the critical ozone levels and evaluation of atmospheric heavy metal deposition in Europe by the method based on the collection and analysis of moss biomonitors [22].

The Joint Institute for Nuclear Research (JINR, Dubna, Russian Federation) using neutron activation analysis (NAA) at pulsed fast reactor IBR-2 has been contributing to the European Program "Atmospheric Heavy Metal Deposition in Europe - Estimation based on Moss Analysis" by submitting the results of moss analysis to the UNECE ICP Vegetation [23, 24], since 1995. The contribution of JINR to the UNECE ICP Vegetation has been indicated in many publications (for example [25]).

Environmental pollution is one of the largest problems the world faces today. Sources of elements in air can be both natural and anthropogenic, and they may include industrial processes, power plants, transplantation, and mining, burning of solid waste, fires, and volcanoes. Azerbaijan is the largest agro-industrial country of the Caucasus with an extensively developed industry and a large agricultural sector with a dynamically developing economy, providing significant human impact on the environment. Moreover, in the territory of Azerbaijan over more than 300 mud volcanoes are present, making Azerbaijan top in the world in the number of mud volcanoes characterised by exceptionally high natural radioactivity [26]. Those deposits in the Caucasus and Trans Caspian are associated with large deposits of uranium and rare earth metals. The national policy of Azerbaijan for protection of the environment is compliance with requirements of the International Conventions ratified by the Republic Azerbaijan. The use of moss biomonitoring technique and NAA is a first attempt to study heavy metal atmospheric deposition in Azerbaijan, a country different relief and climate.

Given the importance and actuality of this work, it is planned to study atmospheric deposition of heavy metals and radionuclides by means of moss biomonitoring in most of Azerbaijan (about 60 % of the territory where proper moss species grow). New data on Azerbaijan will make a great contribution to the scientific understanding of the current environmental condition of the country and serving as an enrichment of the scientific methodology of biomonitoring using mosses in a subtropical zone (out of 11 possible climate types in the area, 9 occur within the relatively small territory of Azerbaijan).

Materials and methods

Study area and sampling

The mosses two types *Pleurozium schreberi* and *Hylocomium splendens* were taken for atmospheric deposition study of major and trace elements in Azerbaijan. The sampling was carried out at different vertical altitudes during vegetation periods in late summer (August) and beginning in autumn (September) 2015. Samples were collected at a distance of at least 300 m from main roads, at least 100 m from roads and at least 200 m from village, in forest glades or in open heath to reduce through-fall effects from the forest canopy. In order to make the moss samples representative for a reasonably large area, each sample was composed of four to six sub-samples collected within an area 10 m x 10 m. Collected samples were stored in paper bags. A separate set of disposable polyethylene gloves was used for collection of each sample. The coordinates of the sampling sites were determined using GPS [27-30]. The sampling map is shown in Figure 1. A total of 85 moss samples, predominantly *Pleurozium schreberi* (*Pleurozium schreberi* - 65, *Hylocomium splendens* - 20) have been collected along altitudinal gradients in the Gadabay (30 samples) and Dashkasan (5 samples) mining district, where the plant for the production of cold (as well as silver and copper), Anglo Asian Mining PLC. The company is located in the north-west of city of Gadabay. Dashkasan district is located in north-western Azerbaijan, on

north-eastern edge Lesser Caucasus rising 1600 m - 1800 m above sea level. Starting from Soviet times, the region was one of the strategic centers for mining iron ore, aluminium, cobalt, and marble. At the moment, gold, copper, cobalt, iron ore, marble are being mined. At the same time 50 samples were collected from the Goygol State Reserve ten kilometers from the Ganja, the second city of Azerbaijan. Ganja is one of the industrial cities of Azerbaijan. There are plants, factories and other more industrial companies located in the city of Ganja. Ganja is one of the industrial cities of Azerbaijan. There are plants, factories and other industrial companies located in Ganja. These plants, factories and industrial companies produce products of bauxite and alunite ore, alumina (clay-soil), primary aluminium and semi-finished products (aluminium vodka - in the form of rolls and boards, both painted sheets and boards), polypropylene, which is the leading branch of non-ferrous metallurgy manufacture of pipes, metal structures and apparatus for the construction industry, smelting of non-ferrous metals, wine, cotton threads and fabrics, etc. are produced. The Goygol State Reserve is intended to protect the natural ecosystem of the subalpine zones of the northern slopes of the Lesser Caucasus. Sampling area covering foothill, mixed forest, subalpine belt in the range of altitudes from 600 m to 1800 m.

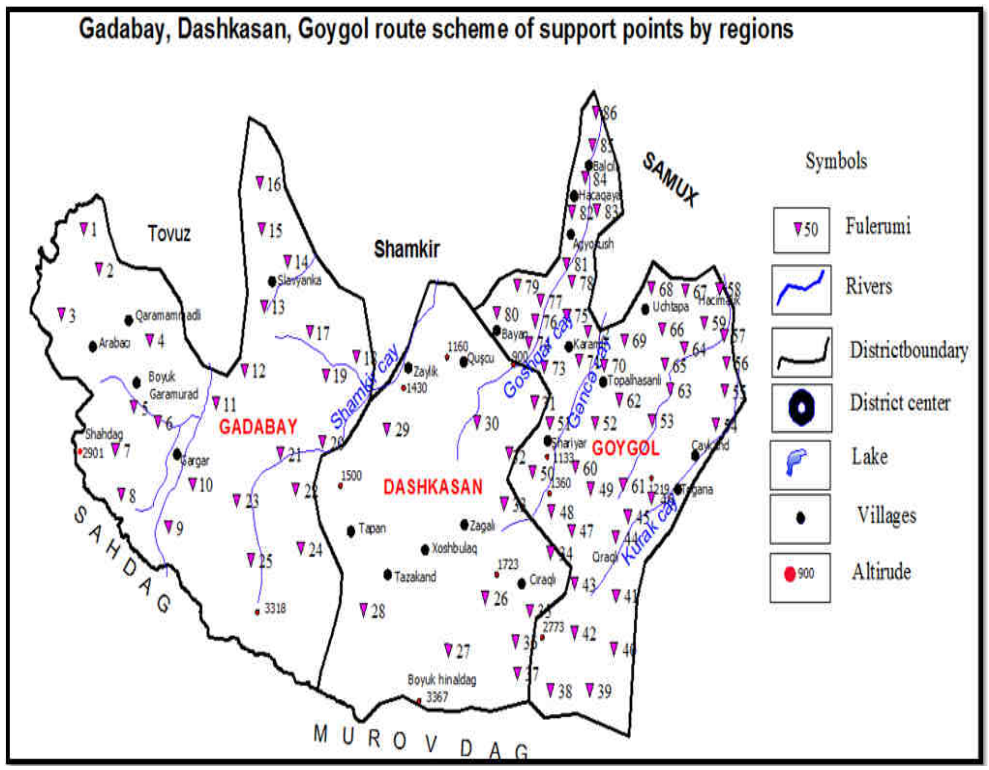


Fig. 1. The sampling map (map scale 1: 500)

The preparation of moss samples was performed in the chemical laboratory. Each sample was cleaned from extraneous materials like soil particles, dry leaves, needles, sticks,

etc., and dried to constant weight at 30 °C - 40 °C for 48 hours. To prevent contamination of the material, plastic tweezers and disposable polyethylene gloves were used during all handling of the samples. Only the green and green-brown shoots from the last three years growth were taken for analysis. Previous experience from the use of neutron activation analysis (NAA) in moss biomonitoring has shown that samples of 0.3 g of mosses are sufficiently large to be used without homogenization [31]. After cleaning about 0.3 g of mosses were pelletised in press-forms. Then the samples were precisely weighed. Moss samples for short-term irradiation were packed heat-sealed in polyethylene foil bags, while the sample for long-tern irradiation were packed in aluminium cups.

Neutron activation analysis

Neutron activation analysis of moss samples was carried out at the IBR - 2 pulsed fast reactor in the Frank Laboratory of Neutron Physics (FLNP, JINR, Dubna) as described elsewhere [32, 33]. Concentrations of elements based on short-lived radionuclides were determined by irradiation for 3 min under a thermal neutron fluency rate of approximately $1.3 \cdot 10^{12}$ n cm^{-2} s^{-1} was used. Gamma spectra of induced activity were measured twice, for 3 min after (5-7) minutes of decay. For determination the long-lived isotopes a cadmium - screened irradiation channel under a resonance neutron fluency rate of approximately $1.6 \cdot 10^{12}$ n cm^{-2} s^{-1} was used. Samples were irradiation for 89 h - 90 h, repacked and then measured after 4 d - 5 d of decay during 45 m. Induced gamma activity was measured by a Canberra Ge (HP) detector with the resolution of 1.9 keV for the ^{60}Co 1332 keV gamma line. A Software package developed at the JINR [34, 35] was used to process gamma spectra and calculate concentrations of elements based on relative method using the certified reference materials: Trace Elements in Pine Needles - 1575a (NIST), Trace Elements in Coal - 1632b (NIST), Montana Soil - 2710 (NIST) and BCR - 667 (Belgium). The gamma-spectra of the induced activites were analysed using software developed at the FLNP [36]. To evidence any association of chemical elements as well as to decrease the number of variables for the obtained data, factor analysis (FA) was used. All statistical analysis were performed using Stat-Soft™ Statistica 9 (StatSoft, Tulsa, OK, USA).

Results and discussions

The concentrations of 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 were determined. Median values and ranges for the elements studied are presented in Table 1, along with corresponding data from similar studies in the neighbouring Georgian collections of 2014 [36] and 2015 [37], for comparison with a pristine territory corresponding data for the Northern Norway [38]. A comparison of moss concentrations Azerbaijan-Norway showed the increased values for most of heavy metals (Mg, Al, V, Fe, As, Mo, Cd, La, and U) in the studied samples that are due to the state of the industrial sector of study area [39, 40]. It can be assumed that the main potential sources of air pollution from the industrial sector of this areas are the plant for the production of gold, as well as silver and copper, mining iron ore, aluminium, cobalt, and marble, non-ferrous industry (melting non-ferrous metals), the production of metal structures and hardware for the construction industry etc. [41, 42].

Table 1

Comparison of the results obtained in the present study [mg/kg] with Georgia and Norway

List of selected peak energies for NAA				Azerbaijan 2015 (this study)		Georgia 2014 [36]	
				n = 85		*n* = 16	
Element	**Isotope**	**Half life**	**Gamma peak [keV]**	**Median**	**Range**	**Median**	**Range**
Na	^{24}Na	14.7 hour	1368.55	512.5	207-1370	721	268-1990
Mg	^{27}Mg	9.5 minute	1014.44	3670	2540-6780	4410	2720-11600
Al	^{28}Al	2.2 minute	1778.9	3870	1070-1120	5195	2450-20800
Cl	^{38}Cl	37.2 minute	2167.68	134	48-585	225	140-465
K	^{42}K	12.4 hour	1524.6	5380	3040-11000	5875	3080-9040
Ca	^{49}Ca	8.7 minute	3084.4	9750	7670-13300	11800	7140-15300
V	^{52}V	3.8 minute	1434.4	1.075	0.4-2.1	42593	6.2-54.0
Mn	^{56}Mn	2.6 hour	1810.7	145	10-335	158	70-592
Fe	^{59}Fe	44.5 day	1099.1	2845	921-5870	3935	1640-14700
Zn	^{65}Zn	244 day	1116	26.15	12.9-40.6	38.1	17.3-68.7
As	^{76}As	26.3 hour	559.1	1.015	0.44-1.86	0.88	0.33-2.87
Br	^{82}Br	35.3 hour	554.3	5.325	2.33-16.6	42494	2.3-9.8
Mo	^{99}Mo	66 hour	140.5	0.4435	0.228-0.761	0.35	0.24-0.77
Cd	^{115}Cd	53.5 hour	527.6	0.308	0.12-1.15	0.25	0.12-0.56
I	^{128}I	25 minute	442.9	3.63	1.65-9.91	42584	1.3-5.1
La	^{140}La	40.2 hour	1596.2	1.745	0.65-4.90	41306	0.92-6.28
Sm	^{153}Sm	46.7 hour	103.2	0.29	0.123-0.727	0.43	0.03-0.94
W	^{187}W	23.9 hour	685.7	0.07575	0.035-0.199	0.13	0.06-0.27
Au	^{198}Au	2.7 day	411.8	0.00171	0.00048-0.00681	0.00091	0.00031-0.00225
U	^{239}Np	2.4 day	228.2	0.1455	0.03-0.33	0.19	0.08-0.50

List of selected peak energies for NAA				Georgia 2015 [37]		Norway [38]	
				n = 36		*n* = 100	
Element	**Isotope**	**Half life**	**Gamma peak [keV]**	**Median**	**Range**	**Median**	**Range**
Na	^{24}Na	14.7 hour	1368.55	338.5	101-2080	n.d.	n.d.
Mg	^{27}Mg	9.5 minute	1014.44	2380	1380-6300	1730	940-2370
Al	^{28}Al	2.2 minute	1778.9	2955	759-12600	200	67-820
Cl	^{38}Cl	37.2 minute	2167.68	149.5	57,3-333	n.d.	n.d.
K	^{42}K	12.4 hour	1524.6	4610	2030-8360	n.d.	n.d.
Ca	^{49}Ca	8.7 minute	3084.4	6530	4880-10900	2820	1680-5490
V	^{52}V	3.8 minute	1434.4	5.575	1.71-18.9	0.92	0.39-5.1
Mn	^{56}Mn	2.6 hour	1810.7	109	21,7-525	256	22-750
Fe	^{59}Fe	44.5 day	1099.1	2000	404-11100	209	77-1370
Zn	^{65}Zn	244 day	1116	20.4	7.15-48.4	26.5	7.9-173
As	^{76}As	26.3 hour	559.1	0.6935	0.176-7.55	0.093	0.020-0.505
Br	^{82}Br	35.3 hour	554.3	5.145	2.33-7.45	42494	1.4-20.3
Mo	^{99}Mo	66 hour	140.5	0.286	0.174-0.894	0.135	0.065-0.70
Cd	^{115}Cd	53.5 hour	527.6	0.175	0.0317-0.791	0.058	0.025-0.171
I	^{128}I	25 minute	442.9	1.29	0.577-2.79	42492	0.6-41.7
La	^{140}La	40.2 hour	1596.2	1.615	0,342-12	0.189	045-2.56
Sm	^{153}Sm	46.7 hour	103.2	0.182	0.0402-1.86	0.33	0.05-1.34
W	^{187}W	23.9 hour	685.7	0.10405	0.0485-0.597	0.127	0.009-1.23
Au	^{198}Au	2.7 day	411.8	0.0000403	0.00000602-0.000267	n.d.	n.d.
U	^{239}Np	2.4 day	228.2	0.1075	0.0207-0.752	0.015	0.001-0.138

n.d. - not determined

Multivariate statistical analysis (FA) was used to identify and characterise different pollution sources and to point out the most polluted areas. FA is a multivariate technique for reducing matrices of data to their lowest dimensionality by the use of orthogonal factor space and transformations that yield predictions and/or recognizable factor. Values of the four factors are given in Table 2. Four identified factors are interpreted as follows:

Table 2

Matrix of rotated factor loadings selected thirty elements

Elements	Factor 1	Factor 2	Factor 3	Factor 4
Na	**0.79**	0.26	–0.03	0.29
Mg	0.55	**0.62**	0.01	0.10
Al	**0.82**	0.45	0.15	–0.06
Cl	–0.01	0.01	–0.02	**0.89**
K	0.03	–0.01	–0.15	**0.86**
Sc	**0.90**	0.35	0.04	0.09
Ti	**0.66**	0.52	0.37	–0.10
V	0.54	**0.69**	0.33	0.01
Cr	0.55	**0.63**	0.26	0.18
Mn	**0.69**	0.11	0.19	–0.09
Fe	**0.80**	0.53	0.17	0.11
Co	**0.70**	0.55	0.15	0.18
Ni	0.44	**0.63**	0.43	0.11
Cu	0.20	0.11	**0.63**	–0.24
Zn	0.18	0.44	–0.09	**0.64**
As	0.18	**0.75**	–0.25	–0.04
Rb	0.53	0.17	**0.55**	0.20
Cd	–0.09	–0.16	**0.59**	0.02
Cs	**0.93**	0.16	–0.06	0.07
Ba	**0.72**	–0.02	0.32	0.10
La	**0.61**	**0.69**	0.14	0.07
Ce	**0.75**	0.53	0.25	0.02
Nd	**0.73**	0.06	–0.14	–0.09
Sm	**0.80**	0.47	0.05	–0.01
Eu	**0.61**	0.17	0.19	0.02
Tb	**0.94**	0.31	0.02	0.03
Tm	**0.90**	0.17	–0.03	0.04
Yb	**0.91**	0.09	0.08	0.02
Hf	**0.86**	0.42	0.16	0.05
Ta	0.66	**0.62**	0.25	0.03
Au	0.04	0.14	**0.69**	–0.01
Th	0.53	**0.61**	0.33	0.01
U	0.54	**0.72**	0.19	0.14
Explaining variance	**14.31**	**7.56**	**3.09**	**2.85**
Total variance	**0.34**	**0.18**	**0.08**	**0.07**

Factor 1 has particularly high of Cs (0.93), Sc (0.90), Hf (0.86), Al (0.82), Fe (0.80), Na (0.79), Ba (0.72), Co (0.70), Mn (0.69), Ti (0.66), and rare-earth elements (REEs) as Tb (0.94), Yb (0.91), Tm (0.90), Sm (0.80), Ce (0.75), Nd (0.73), La (0.61), Eu (0.61). Most of these elements are typical for crustal material, and most probably this component at least partly reflects the contamination of moss samples with soil particles. Another possible

source could be fly-ash particles resulting from high-temperature processes such as coal burning, which may have a major element composition similar to crustal material.

Factor 2 has high values for As (0.73), Ni (0.63), Cr (0.62), Mg (0.62), Th (0.61), and U (0.72). The elevated concentrations of As - toxic and carcinogenic element are mainly related to the copper and gold mines, as well as to coal combustion. Ni and Cr - these elements in the present samples are of the same order as those found in neighbouring areas in Georgia. For the crust components U and Th - the highest values were observed at four sampling sites located in the vicinity of the plant for the production of gold (as well as silver and copper). The main source of high pollution in this region is mining iron ore, aluminium, cobalt, and marble. As well as, gold, copper, cobalt, iron ore, marble are being mined. On the count of Mg we can say that, in many cases, this characteristic is generally ascribed to a number of chemical edaphic factors, especially the (usually) contents of nickel, and chromium and the low contents of available calcium, potassium, and molybdenum.

Factor 3 has high levels of Cu (0.63), Rb (0.55), Cd (0.59), and Au (0.69). These elements may be associated with emissions from metallurgical industry in Ganja city. In the main from plants, factories and other more industrial companies located in the city of Ganja: Ganja steel factory; leading group of companies in the sphere of Azerbaijan Republic non-ferrous industry (that produce aluminium oxide (alumina), primary aluminium and semi-final aluminium products (such as aluminium sheet - in list and roll forms, both) sides painted sheet and lists) of bauxite and alunite ore).

Table 3

A correlation matrix for the elements

Elements	Na	Mg	Al	Cl	K	Sc	Ti	V	Cr	Fe	Co	Ni	Cu	Zn	As	Cs	La	Ce	Sm	Tb	Tm	Hf	Ta	Th	U
Na	1.00																								
Mg	**0.81**	1.00																							
Al	**0.88**	**0.89**	1.00																						
Cl	–0.02	0.24	0.11	1.00																					
K	0.12	0.21	0.24	**0.64**	1.00																				
Sc	**0.91**	**0.82**	**0.89**	0.08	0.10	1.00																			
Ti	**0.90**	**0.87**	**0.97**	0.00	0.18	**0.89**	1.00																		
V	**0.85**	**0.89**	**0.96**	0.14	0.16	**0.91**	**0.94**	1.00																	
Cr	**0.85**	**0.82**	**0.86**	–0.04	0.10	**0.88**	**0.85**	**0.85**	1.00																
Fe	**0.90**	**0.84**	**0.91**	0.10	0.14	**0.99**	**0.91**	**0.93**	**0.90**	1.00															
Co	**0.89**	0.78	**0.87**	0.00	0.07	**0.97**	**0.89**	**0.89**	**0.90**	**0.96**	1.00														
Ni	0.64	0.74	0.74	–0.02	0.11	0.76	0.74	0.77	**0.82**	**0.81**	0.75	1.00													
Cu	0.47	0.62	0.57	0.04	–0.02	0.48	0.57	0.65	0.51	0.49	0.47	0.47	1.00												
Zn	0.66	0.65	0.73	0.32	0.38	0.79	0.71	0.78	0.68	**0.83**	0.79	0.70	0.48	1.00											
As	0.78	0.77	**0.80**	0.05	0.01	**0.89**	0.78	**0.84**	**0.87**	**0.92**	**0.88**	**0.83**	0.42	0.76	1.00										
Cs	**0.82**	**0.81**	**0.91**	0.16	0.30	**0.85**	**0.87**	**0.88**	**0.84**	**0.89**	**0.80**	**0.80**	0.47	0.75	**0.85**	1.00									
La	**0.85**	**0.81**	**0.94**	0.02	0.19	**0.89**	**0.93**	**0.89**	**0.87**	**0.90**	**0.87**	0.78	0.44	0.69	**0.81**	**0.91**	1.00								
Ce	**0.84**	0.76	**0.89**	–0.03	0.14	**0.88**	**0.89**	**0.82**	**0.88**	**0.87**	**0.92**	0.66	0.36	0.65	**0.80**	**0.81**	**0.91**	1.00							
Sm	**0.86**	**0.81**	**0.92**	0.02	0.16	**0.90**	**0.91**	**0.88**	**0.87**	**0.91**	**0.88**	0.78	0.42	0.67	**0.81**	**0.89**	**0.99**	**0.91**	1.00						
Tb	**0.87**	**0.81**	**0.92**	0.01	0.14	**0.92**	**0.91**	**0.88**	**0.91**	**0.92**	**0.92**	0.78	0.41	0.68	**0.84**	**0.89**	**0.98**	**0.95**	**0.99**	1.00					
Tm	**0.80**	0.67	0.78	–0.13	–0.01	**0.84**	**0.82**	0.74	0.79	**0.84**	**0.84**	0.71	0.31	0.60	0.79	0.79	**0.86**	**0.83**	**0.88**	**0.89**	1.00				
Hf	**0.93**	**0.80**	**0.94**	–0.04	0.19	**0.91**	**0.94**	**0.88**	**0.90**	**0.92**	**0.91**	0.75	0.44	0.70	**0.82**	**0.89**	**0.96**	**0.93**	**0.95**	**0.96**	**0.87**	1.00			
Ta	**0.89**	**0.83**	**0.94**	–0.02	0.14	**0.91**	**0.94**	**0.92**	**0.90**	**0.94**	**0.89**	**0.82**	0.49	0.74	**0.86**	**0.92**	**0.97**	**0.88**	**0.96**	**0.95**	**0.85**	**0.96**	1.00		
Th	**0.87**	**0.82**	**0.94**	0.04	0.16	**0.92**	**0.92**	**0.92**	**0.89**	**0.94**	**0.90**	**0.83**	0.48	0.76	**0.88**	**0.93**	**0.98**	**0.89**	**0.97**	**0.97**	**0.86**	**0.96**	0.59	1.00	
U	**0.87**	**0.81**	**0.90**	–0.05	0.09	**0.91**	**0.91**	**0.89**	**0.92**	**0.94**	**0.93**	**0.85**	0.46	0.77	**0.92**	**0.89**	**0.92**	**0.90**	**0.92**	**0.93**	**0.88**	**0.93**	**0.96**	**0.96**	1.00

Factor 4 has high values for Cl (0.89), K (0.86) which are associated with the green areas of sampling zone, and Zn (0.64). High value of zinc is observed at two sampling sites: 24 and 10, which is located near the company is engaged in the production of metal structures and hardware for the construction industry and, as well as not far from the

company is engaged in melting non-ferrous metals in Gadabay mining district. Possible factor source could be metal trash.

Data were subjected to simple statistical analysis in order to explore the possible associations existing between different variables (Table 3). The correlation matrix shows that most metals are well-correlated. The most noticeable positive correlations are between Al and V (r = 0.96); Al and Ti (r = 0.97); Ti and V (r = 0.94); Fe and Co (r = 0.96); Cr and Fe (r = 0.90); Cr and Co (r = 0.90); Sc and Fe (r = 0.99); Sc and Co (r = 0.97); Sc and V (r = 0.91); Mg and Al (r = 0.89); Mg and Ti (r = 0.87); Al and Sc (r = 0.89); Al and Cs (r = 0.91). There are significant correlations also between Na and Al (r = 0.88); Na and most transition metals (Sc, Ti, V, Cr, Fe, Co, Hf, and Ta r = 0.91; 0.90; 0.85; 0.85; 0.90; 0.93; and 0.89 respectively); also between Na and rare-earth elements (La, Ce, Sm, Tb, and Tm r is equal to: 0.85; 0.84; 0.86; 0.87, and 0.80, respectively). In general correlation matrix shows that rare earth elements are well-correlated between themselves, at the same time with Mg and Al, as well as with transit metals. There are also significant correlations between Th and U (r = 0.96), Ta and U (r = 0.96), V and Th (r = 0.92), U and Hf (r = 0.93), also Hf and Th (r = 0.96).

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. 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 performed preliminary investigation shows that the moss biomonitoring of atmospheric deposition of heavy metals is an efficient technique to study the environmental situation in the Azerbaijan mountainous regions characterised by mining and industrial enterprises. The experience of this study can be successfully used in the other regions of Republic.

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