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Original Research

Biomonitoring Air Pollution Using Moss in Georgia

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Abstract

The results of atmospheric deposition of trace elements in a 2015 moss survey in Georgia are reported. The 36 moss samples were collected in different regions of the Caucasus in compliance with the UNECE ICP Vegetation guidelines. Elemental determination was carried out by epithermal neutron activation analysis (ENAA). For the first time, 47 elements were determined for the sampled areas. The scanning electron microscopy with x-ray energy-dispersive analysis was applied to examine the origin of atmospheric particles accumulated by mosses. Microanalysis of moss samples collected in the highlands of Georgia showed the presence of clastic, anthropogenic, and cosmic dust particles. Comparison of the determined values with corresponding data from a pristine area of Norway was carried out. Multivariate statistical analysis of the results obtained was used to identify and characterize pollution sources in the sampled areas of Georgia. Elevated levels of heavy metals were revealed in Western Georgia, where many industrial mining enterprises and high-traffic roads are located.

Keywords: Georgia, moss biomonitoring, heavy metals, neutron activation analysis, scanning electron microscopy

Introduction

Since 2014 Georgia has participated in the moss biomonotoring program of UNECE ICP Vegetation in the framework of the Convention on Long-Range Transboundary Air Pollution in Europe (CLRTAP) [1]. Presently a wide range of atmospheric quality monitoring methods exists. One of these directions is the study of atmospheric deposition of heavy metals by means of moss biomonitors. The most commonly used moss species in air pollution biomonitoring are *Hylocomium splendens* (Hedw.) (Schimp.), *Pleurozium schreberi* (Mitt.) (Brid.), and *Hypnum cupressiforme* (Hedw.) [2-4].

Georgia is a mountainous country in the Caucasus with specific geographic conditions and climate, characterized by high-level anthropogenic pollution

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in some districts, namely Lower Svaneti, Kutaisi, Zestafoni, and others [5-9]. In 2014 a preliminary collection of Georgian moss (16 samples from different sites around the country) was investigated in collaboration with JINR [10]. It was the first time for the western Caucasus, when the moss biomonitoring method of atmospheric deposition of trace elements was used. The investigation showed that this method is an efficient technique for studying the environmental situation in a country with a unique geographical location. In 2015 the research was continued and moss samples were collected on a larger territory of Georgia.

Materials and Methods

Study Area and Sampling

The sampling of the 2015 collection was carried out according to the standard procedure described in the Moss Manual of the ICP Vegetation 2015 [11]. The vertical altitudes of sampling range of 161 m to 2,052 m a.s.l. Seventeen samples were taken in southern Georgia (mostly from Meskheti). The climate in this part of Georgia is mild and moderately humid. Eight samples were collected from eastern Georgia, the majority from Khevsureti. The climate in this mountain region is cold and temperate. Sample Nos. 18 and 19 were taken near Stepantsminda in Dariali gorge, near a Georgian Military Road. Seven samples were taken from northwestern Georgia, mainly from Svaneti. Here several areas are contaminated by arsenic extraction, which was performed until 1990 (Ailama, Koruldashi). The landscape of this region is dominated by mountains and deep gorges that separate them. Two samples were taken in western Georgia in Imereti. One was taken near Rikoti Pass, which passes a highway that connects two main cities of Georgia (Tbilisi and Kutaisi), and the other one is not far from Kutaisi. The main environmental pollution sources in sampled regions are transportation, mining of manganese, metallurgy, machinery, human waste, and burials of old industrial waste from Soviet times [5-9].

A total of 36 samples of three moss species (*Hylocomium splendens* (Hedw.) (Schimp.) – 13, *Pleurozium schreberi* (Mitt.) (Brid.) – 8, and *Hypnum cupressiforme* (Hedw.) – 15) growing on organic top-soils in forests, covering foothills, subalpine, and alpine belts and other natural environments were collected during summer 2015. For each sampling site no fewer than 10 sub-samples were taken in the area of 50 x 50 m and combined into one collective sample. Descriptions of all sites have been recorded along with geographical coordinates determined by GPS. The sampling map is shown in Fig. 1.

Sample Preparation

NAA

The preparation of samples for NAA was performed in the chemical laboratory. Only the green and green-brown shoots from the last three years' growth were taken for analysis. Each sample was cleaned from extraneous materials like soil particles, leaves, needles, etc. To prevent contamination of the material we used plastic tweezers and disposable polyethylene gloves. The samples were not washed and not homogenized [12], they were dried to constant weight at 30-40ºC for 48 hours. About 0.3 g of mosses were pelletized in press-forms. Then the samples were precisely weighed. Moss samples for short-term irradiation were heat-sealed in polyethylene foil bags, while the samples for long-term irradiation were packed in aluminum cups.

SEM

To increase the probabilities of seeing micro particles, which are expected to be in a small quantity (like cosmic dust), two moss samples (No. 8 Lesser

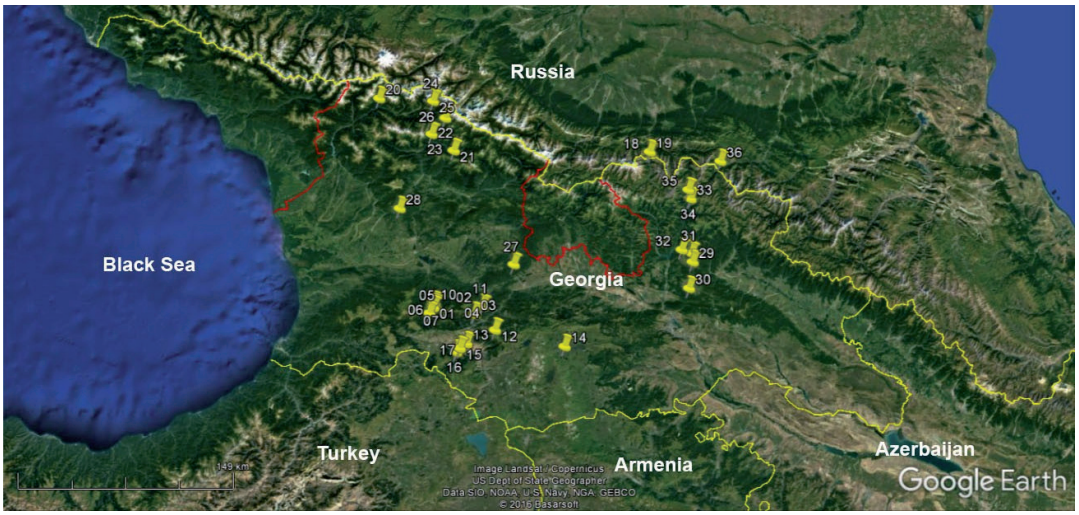

Fig. 1. Area of study showing sampling locations.

Table 1. Concentrations of elements (mg/kg) determined by NAA for Georgia and Norway.

Element	Isotope	Half life	Gamma peak energies (keV)	Georgia 2014		Georgia 2015		Norway	
				n = 16		n = 36		n = 100	
				Median	Range	Median	Range	Median	Range
Na	^{24}Na	14.7 h	1,368.55	721	268-1990	338.5	101-2,080	nd	nd
Mg	^{27}Mg	9.5 m	1,014.44	4410	2720-11600	2,380	1,380-6,300	1730	940-2370
Al	^{28}Al	2.2 m	1,778.9	5195	2450-20800	2,955	759-12,600	200	67-820
Cl	^{38}Cl	37.2 m	2,167.68	225	140-465	149.5	57.3-333	nd	nd
K	^{42}K	12.4 h	1,524.6	5875	3080-9040	4,610	2,030-8,360	nd	nd
Ca	^{49}Ca	8.7 m	3,084.4	11800	7140-15300	6,530	4,880-10,900	2820	1680-5490
V	^{52}V	3.8 m	1,434.4	11.8	6.2-54.0	5.575	1.71-18.9	0.92	0.39-5.1
Mn	^{56}Mn	2.6 h	1,810.7	158	70-592	109	21.7-525	256	22-750
Fe	^{59}Fe	44.5 d	1,099.1	3935	1640-14700	2,000	404-11100	209	77-1370
Zn	^{65}Zn	244.0 d	1,116.0	38.1	17.3-68.7	20.4	7.15-48.4	26.5	7.9-173
As	^{76}As	26.3 h	559.1	0.88	0.33-2.87	0.6935	0.176-7.55	0.093	0.020-0.505
Br	^{82}Br	35.3 h	554.3	4.545	2.3-9.8	5.145	2.33-7.45	4.5	1.4-20.3
Mo	^{99}Mo	66.0 h	140.5	0.35	0.24-0.77	0.286	0.174-0.894	0.135	0.065-0.70
Cd	^{115}Cd	53.5 h	527.6	0.25	0.12-0.56	0.175	0.0317-0.791	0.058	0.025-0.171
I	^{128}I	25.0 m	442.9	2.795	1.3-5.1	1.29	0.577-2.79	2.5	0.6-41.7
La	^{140}La	40.2 h	1,596.2	2.13	0.92-6.28	1.615	0.342-12	0.189	045-2.56
Sm	^{153}Sm	46.7 h	103.2	0.43	0.03-0.94	0.182	0.0402-1.86	0.33	0.05-1.34
W	^{187}W	23.9 h	685.7	0.13	0.06-0.27	0.10405	0.0485-0.597	0.127	0.009-1.23
Au	^{198}Au	2.7 d	411.8	0.00091	0.00031-0.00225	0.0000403	0.00000602-0.000267	nd	nd
U	^{239}Np	2.4 d	228.2	0.19	0.08-0.50	0.1075	0.0207-0.752	0.015	0.001-0.138

Caucasus, Mescheti and No. 25 Greater Caucasus, Lower Svaneti) were specially prepared for scanning electron microscopy with energy-dispersive x-ray spectroscopy (SEM/EDX). To increase the amount of micro particles, moss samples were ground into fine powders in an agate mortar, then subjected to ultrasonic dispersing in a beaker. On the bottom of the beaker a powerful neodymium magnet of 35 mm diameter was attached to avoid the loss of magnetic particles. Afterward the particles were mounted on a double-sided adhesive coal tape.

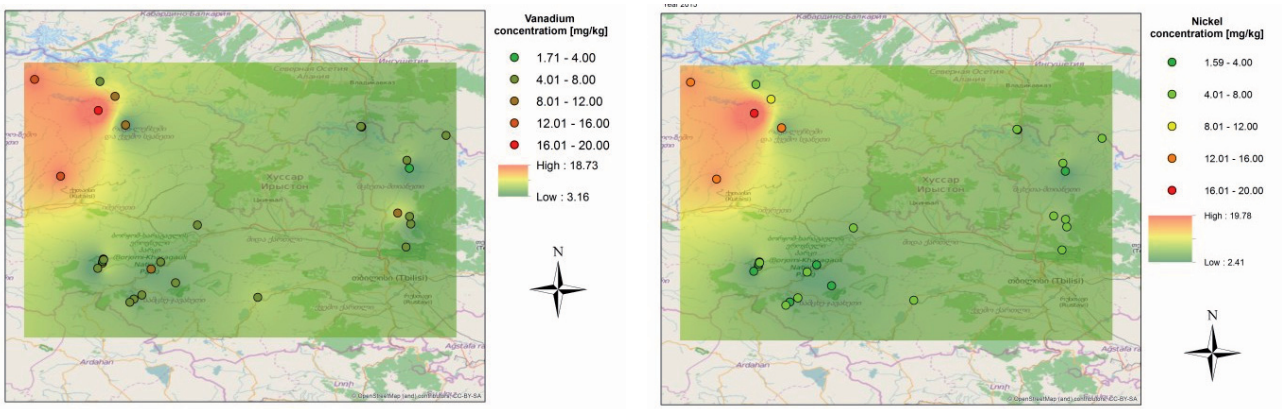

Fig. 2. Maps of the spatial distribution of concentrations of some heavy metals.

Table 2. Matrix of rotated factor loadings (n = 36, 20 selected elements).

	Factor 1	Factor 2	Factor 3	Factor 4
Ti	**0.70**	0.08	**0.55**	0.26
V	**0.83**	0.12	0.44	0.17
Cr	**0.95**	0.08	0.17	0.15
Mn	0.38	0.12	0.02	0.49
Fe	**0.94**	0.15	0.22	0.17
Ni	**0.90**	0.15	0.33	0.15
Co	**0.95**	0.13	0.14	0.17
Zn	0.48	**0.63**	-0.14	0.37
As	**0.95**	0.11	-0.07	0.01
Br	0.31	0.03	-0.32	**0.72**
Mo	**0.71**	0.25	0.06	0.51
Ag	0.22	0.00	**0.84**	0.01
Cd	0.27	**0.57**	-0.46	0.22
In	0.02	**0.77**	0.12	0.02
Sb	**0.84**	0.37	-0.09	0.10
I	-0.14	0.26	-0.03	**0.85**
Au	0.29	**0.79**	-0.04	0.22
Hg	0.15	-0.01	**0.77**	-0.25
Th	**0.97**	0.14	0.01	0.07
U	**0.97**	0.15	0.02	0.11
Exp. variance	**14.65**	**2.47**	**2.66**	**2.60**
Prp. Total	**0.54**	**0.09**	**0.10**	**0.10**

Analysis

NAA

ENAA of moss samples was carried out at the IBR-2 pulsed fast reactor (JINR, Dubna) as described elsewhere [13]. Concentrations of elements based on short-lived radionuclides were determined by irradiation for 30 min. Gamma spectra of induced activity were measured twice, for 5 min after 5-7 min of decay. For determining the long-lived isotopes the samples were irradiated for 4 hours, repacked and then measured after 4-5 days of decay during 45 min. The concentrations of 47 elements (Na, Mg, Al, Si, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Zn, As, Br, Rb, Sr, Zr, Mo, Ag, Cd, In, Sb, I, Ba, Cs, La, Ce, Nd, Sm, Eu, Tb, Dy, Tm, Yb, Lu, Hf, Ta, W, Au, Hg, Th, and U) were determined based on relative method using the certified reference materials: trace elements in pine needles-1575a (NIST), trace elements in coal-1632c (NIST), Montana soil-2710 (NIST), and BCR-667 (Belgium).

Table 3. Factor scores.

Sampling sites	Factor 1	Factor 2	Factor 3	Factor 4
1	-0.27	-0.19	**1.43**	-0.96
2	-0.72	0.28	0.82	-0.44
3	-0.45	-0.14	-0.36	-0.99
4	0.03	0.44	**1.71**	-1.66
5	-0.49	-0.63	**0.99**	-0.72
6	-0.67	-0.43	**1.06**	**0.64**
7	-0.72	-0.62	0.39	-1.60
8	-0.51	0.24	-0.24	**0.99**
9	-0.66	-0.24	**1.24**	-0.24
10	-0.44	-0.51	-0.56	0.38
11	-0.50	-0.51	-0.79	-0.11
12	-0.61	-0.39	-0.83	**0.72**
13	-0.40	-0.38	-0.41	-0.63
14	0.17	-0.22	0.03	0.36
15	-0.19	-0.94	-0.74	-1.16
16	0.05	-0.56	-0.55	-0.25
17	-0.11	-1.27	-0.33	-0.07
18	-0.77	**4.06**	-0.16	-1.53
19	0.22	0.72	-1.46	-0.32
20	2.51	-0.18	-0.28	-0.49
21	-0.10	-0.54	-0.89	-0.58
22	4.22	0.42	0.43	0.60
23	2.13	0.02	-0.93	-0.46
24	0.14	**1.13**	0.24	-0.64
25	-0.25	0.85	-0.11	0.49
26	0.88	0.05	0.43	-1.35
27	-0.49	**2.68**	-1.44	**2.22**
28	0.11	0.23	**3.83**	**1.88**
29	-0.37	-0.21	0.08	-0.05
30	-0.36	0.15	-0.08	**1.10**
31	-0.50	-0.05	0.12	**1.41**
32	0.19	-0.58	0.17	**1.93**
33	-0.42	-0.86	-0.64	-0.12
34	-0.35	-1.21	-1.16	0.40
35	-0.07	-0.71	-0.42	**1.18**
36	-0.22	0.10	-0.33	0.07

For measuring sample activity in laboratory of NAA at IBR-2 reactor the automated registration and data processing system of gamma-ray spectra was

used to conduct analysis of large sets of samples, to process large amounts of data, to increase productivity of analysis, to improve quality of results, to decrease the number of human errors, and to minimize human involvement in routine operations [14]. The system includes three high-purity Ge detectors, three sample changers, and control software with a database and processing programs.

SEM

The composition and morphology of the two samples from the 2015 collection (No. 8 Lesser Caucasus, Mescheti and No. 25 Greater Caucasus, Lower Svaneti) from the mountainous regions of Caucasus was examined using a Tescan Vega II scanning electron microscope with an energy-dispersive Drycool spectrometer at the Borok Geophysical Observatory (a branch of the Schmidt Institute of Physics of the Earth of the Russian Academy of Sciences). The separated mineral particles from samples dispersed by ultrasound were deposited on two-sided coal scotch. The investigations were carried out at an accelerating voltage of 20 Kv and a current of 200 Pa (200 picoamperes, or 0.2 nanoamperes).

Results and Discussion

The results of the descriptive statistics are presented in Table 1 along with data on the Georgian collection of 2014 [10] and data on Norway [15], which is considered to be a pristine area of Europe. The comparison of results for 2014 and 2015 mosses shows that the median concentrations of most elements decreased in 2015, which may be attributed to a larger number of averaging samples taken from points with different levels of contamination. A comparison of moss concentrations from Georgia and Norway showed increased values for most heavy metals (Mg, Al, V, Fe, As, Mo, Cd, La, and U) in the studied samples, which is due to the state of the industrial sector of Georgia. In mosses of Georgia the highest concentrations of arsenic were observed,

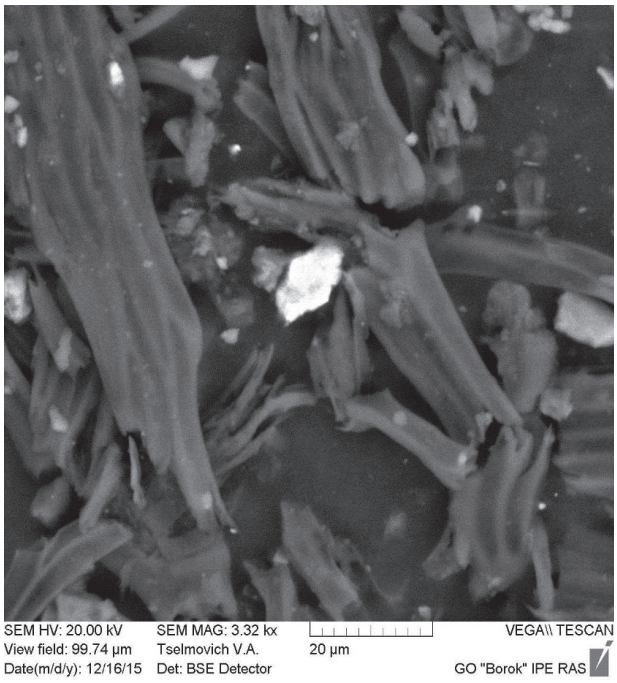

Fig. 4. The terrigenous particle of titanomagnetite, sample 8.

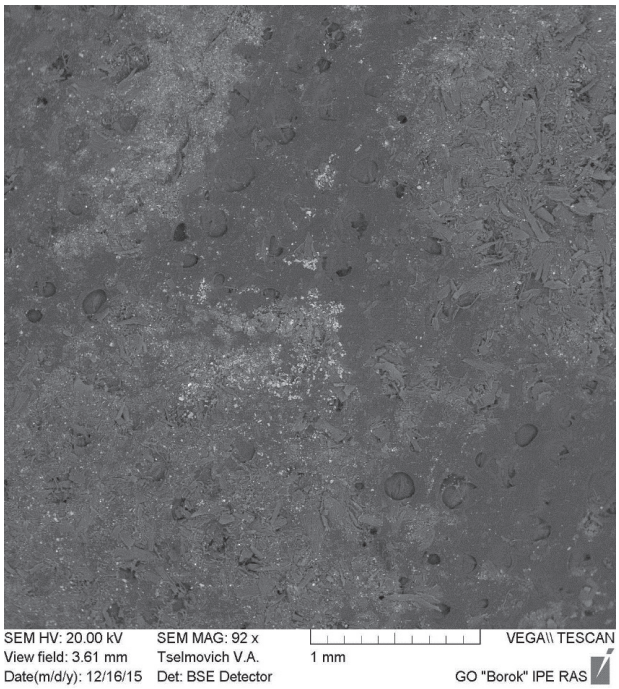

Fig. 3. Group of magnetic and paramagnetic particles, sample 8.

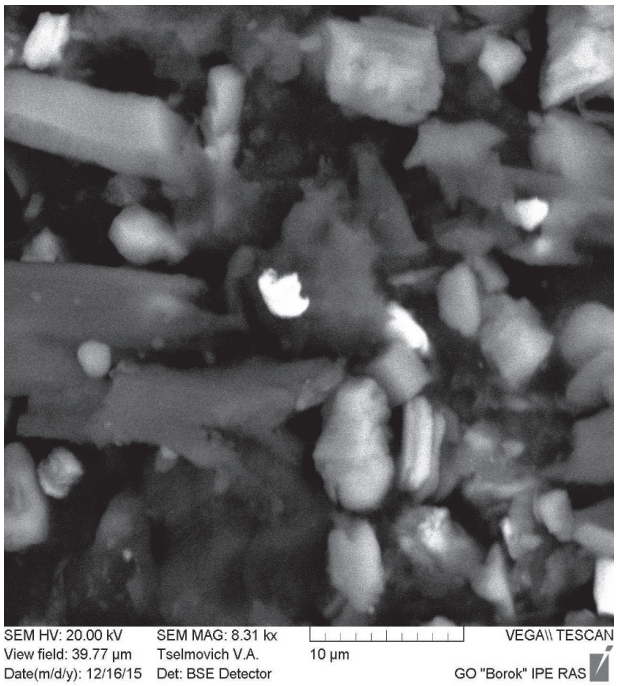

Fig. 5. Particles of native iron, size 3x3 µm, sample 25.

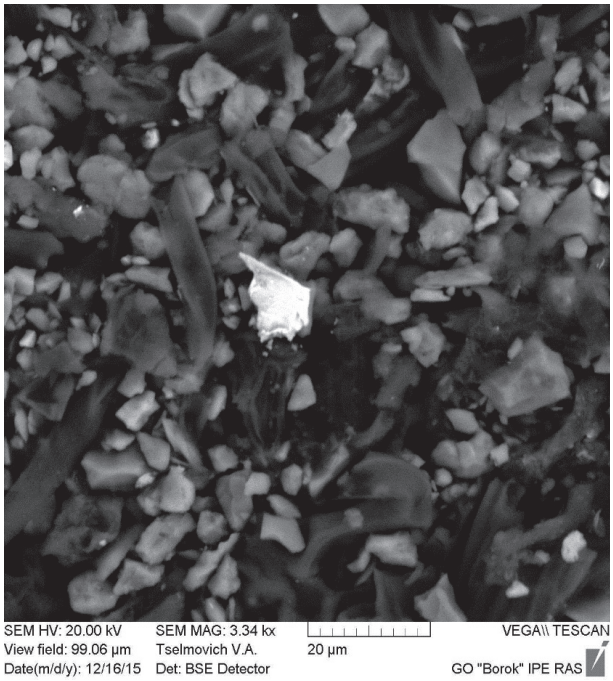

Fig. 6. FeCr alloy particle (intermetallic compound), size 10 x12 µm, sample 25.

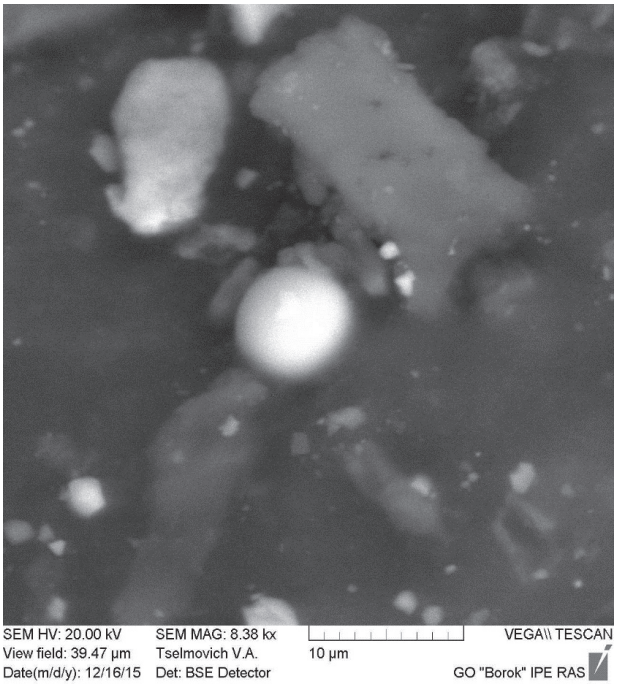

Fig. 8. Aluminosilicate microsphere, presumably cosmic dust, diameter 6 µm, sample 8.

which is apparently due to the poor condition of the old ore deposits of shut-down plants [5-7]. The higher concentrations of I and Br in moss from Norway are due to the proximity of the sea in this country, whereas moss in Georgia was mostly collected in the mountains.

Using the results of analysis of moss from the 2015 collection, we created maps of the spatial distribution of concentrations of some heavy metals. The examples for vanadium (V) and nickel (Ni) are given in Fig. 2. As can be seen from these results, the northwest region of Georgia is characterized by a high level of pollution as the majority of metallurgical and mining industry enterprises – like the machine-building factory in Kutaisi, Zestaponi Ferroalloy Plant, and old mining of arsenic performed until 1990 (Ailama, Koruldashi) – the Chiatura mine complex and others are located there. For characterization of the pollution sources, the results were subjected to multivariate statistical analysis (factor analysis) using STATISTICA 12.6 softaware. To simplify the interpretation of the results, the rotation method of Varimax with Kaiser normalization was applied. The initial number of variables was reduced to four factors (Tables 2 and 3) [16].

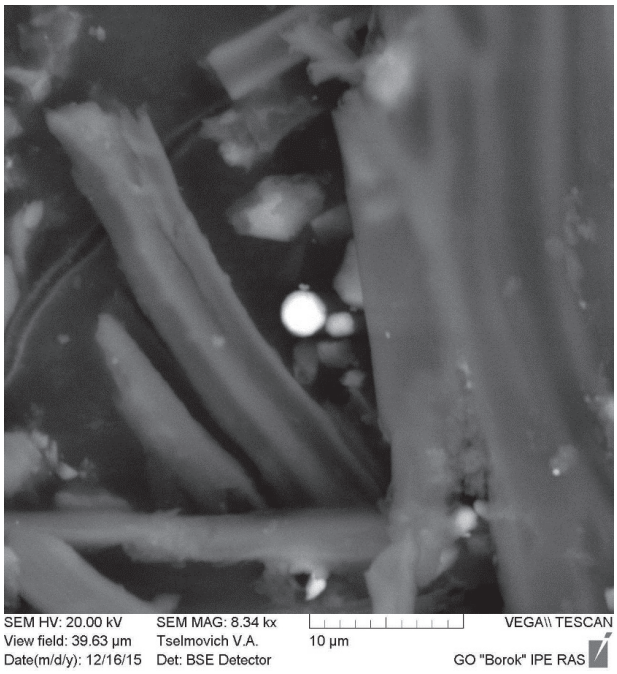

Fig. 7. Magnetite microsphere of cosmic dust, diameter 3 µm, sample 8.

- Factor 1: these elements obviously belong to light (Ti (0.70), V (0.83), Cr (0.95)), and heavy (Fe (0.94), Ni (0.90), Co (0.95), As (0.95), Mo (0.71), Sb (0.84), Th (0.97), U (0.97)) crust components.
- Factor 2: Zn (0.63), Cd (0,57), In (0.77), and Au (0.79) associated with maximal factor scores for sampling sites 18, 24, and 27 could be attributed to contamination from the road (18), Kutaisi metallurgical enterprises (24), and Zestaponi Ferroalloy Plant (27).
- Factor 3: Ti (0.55), Ag (0.85), and Hg (0.77) associated with maximal factor scores for sampling sites 1, 4, 5, 6, 9, and 28 most probably reflects contamination by local industrial enterprises.
- Factor 4: Br (0.72) and I (0.85) associated with sampling sites 6, 8, and 12 (western slopes of the Lesser Caucasus mountain range) and 27, 28, 30, 31, 32, and 35 (eastern slopes of the Greater Caucasus) is definite-

ly a marine factor due to the influence of their source – the Black Sea in the west and the Caspian Sea in the east.

Correlation analyses revealed most noticeable positive correlations of geochemically bounded elements such as Al and V (r = 0.94); Mg and V (r = 0.89); Ti and Al (r = 0.89); Fe and Cr (r = 0.97); W and Fe (r = 0.89); As and Sb (r = 0.85); and Th and U (r = 0.99).

Figs 3-6, which were taken using the SEM technique, show terrigenous and anthropogenic particles. Fig. 3 shows many particles of magnetic and paramagnetic origin in light color while the silicate particles are grey. In images of sample No. 25 (Figs 5-6) FeCr alloy and native iron particles are observed. These particles can be characterized as cosmic dust. Diagnostics of cosmic particles against terrigenous and anthropogenic particles by composition and morphology is a rather complicated procedure due to the fact that particles of different origins can have a similar chemical composition and similar morphology. However, this has been worked out by many authors [17-20], whose experience and achievements have been used by us. In images of sample No. 8 (Figs 3-4) clastic titanomagnetite particles of volcanic origin are observed. Figs 7-8 demonstrate inclusion of beads of magnetite and aluminosilicate particles, presumably of cosmic origin.

Conclusions

The performed investigations show that moss biomonitoring of atmospheric deposition of heavy metals is an efficient technique for studying the environmental situation in Georgia. Elevated concentrations of heavy metals in comparison with the similar data for Norway are mainly characteristic of western regions of Georgia, where the main industrial enterprises and high-traffic roads are located. The results of multivariate statistical analysis confirm this conclusion. Microanalysis of moss samples shows the presence of particles of various origins: clastic, anthropogenic, and cosmogenic (cosmic dust).

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