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First Results on Moss Biomonitoring of Trace Elements in the Central Part of Georgia, Caucasus

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Abstract: The moss biomonitoring technique was used for assessment of air pollution in the central part of Georgia, Caucasus, in the framework of the UNECE ICP Vegetation. A total of 35 major and trace elements were determined by two complementary analytical techniques, epithermal neutron activation analysis (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Se, B, Rb, Sr, Zr, Mo, Sb, I, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, W, Th, and U) and atomic absorption spectrometry (Cu, Cd, and Pb) in the moss samples collected in 2019. Principal Component Analyses was applied to show the association between the elements in the study area. Four factors were determined, of which two are of geogenic origin (Factor 1 including Na, Al, Sc, Ti, V, Cr, Fe, Co, Ni, Th, and U and Factor 3 with As, Sb, and W), mixed geogenic–anthropogenic (Factor 2 with Cl, K, Zn, Se, Br, I, and Cu) and anthropogenic (Factor 4 comprising Ca, Cd, Pb, and Br). Geographic information system (GIS) technologies were used to construct distributions maps of factor scores over the investigated territory. Comparison of the median values with the analogous data of moss biomonitoring in countries with similar climatic conditions was carried out.

Keywords: moss biomonitoring; trace elements; atmospheric deposition; neutron activation analysis; atomic absorption spectrometry; multivariate statistics

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1. Introduction

At present air pollution is recognized as the fifth largest threat to human health [1]. Air pollution and the associated problems are not confined by any geopolitical boundaries. The European Directives on air quality related to particulate matter (PM), heavy metals, and polycyclic aromatic hydrocarbons in ambient air [2,3], define target and limit values in the monitoring and further control of the pollutants. During the last several decades, biomonitoring surveys considering the use of an organism as a monitor of environmental pollution [4] have become a valuable complement to instrumental measurements. Widespread species that reliably reflect air pollution represent a simple and cost-effective alternative for instrumental measurements, thus enabling measurements with much higher spatial resolution. Mosses are recognized as good biomonitors of air pollution due to their specific morpho-physiological features: the lack of a root system, large surface area, and a high cation-exchange capacity of cell membranes, which represent their adaptations to nutrition from the air. Mosses are ubiquitous species and they have been extensively used in large-scale studies for biomonitoring of trans-boundary air pollution [5] known as passive moss biomonitoring [4]. The moss biomonitoring method, in combination with

nuclear and related analytical techniques, has been regularly used for the last 25 years in Western European countries to study atmospheric deposition of heavy metals (HM). Over the past 15 years it has spread to Eastern Europe [5]. The first moss survey in Georgia was undertaken in 2014 [6] and the results included in the Report on the European Moss survey 2015–2016 [5] along with data obtained in the next surveys [7,8]. Rocks of different composition, age and stability are spread on the territory of Georgia. The high degree of the relief-dissection is due to strong tectonic movement and intense erosion processes in the Caucasus region. At certain locations of Georgia the depths of erosion-cuts exceeds 2000 m [9].

There is a need to investigate whether mosses sampled in this region can be used as biomonitors of atmospheric heavy metal deposition given the rather high contribution of mineral particles to the metal concentration in mosses. The present research was carried out by the Georgian and Russian teams aimed to cover white spots in the map of this territory of Caucasus.

2. Experimental

2.1. Study Area

The study area is located in Georgia between coordinates: 42°40′ N latitude and 43°17′ E longitude for the North, 41°22′ N latitude and 43°46′ E longitude for the South, 42°35′ N latitude and 43°13′ E longitude for the West, and 41°40′ N latitude and 44°41′ E longitude for the East. Elevation ranges from 651 to 2132 m a.s.l.

The South Caucasus region is highly prone to natural disasters, and its mountainous regions are particularly high risk areas. Natural phenomena common in the region include landslides and mudflows, floods, flash floods, droughts, avalanches, rainstorms, and earthquakes. The countries are located in a region of moderate to very high seismic activity and are therefore particularly prone to earthquakes, which can have devastating consequences for lives, buildings and infrastructure. This seismic activity can also trigger secondary events such as landslides, avalanches and flash floods in mountainous areas [10].

The mountainous regions of the South Caucasus have a wide range of climatic zones, from cold temperate alpine peaks to temperate, humid and arid landscapes.

The relief of Georgia is characterized by complex hypsometric and morphographic features: heavily dissected mountain slopes, deep erosive gorges, intermountain depressions, flat lowlands, plains, plateaus, and uplands. The most important landforms found in the territory of Georgia are erosive, volcanic, karst, gravitational, and old glacial landforms [11,12].

The climate in the high-mountains contributes to the formation of eternal snows and glaciers. Mountain meadow soils prevail in the highlands, and brown forest soils on the plains. Landscape and ecosystems of each sampling site differ considerably and depend on wind direction. Study area is located outside industrial zones; however, it may experience a long-range transport of pollutants due to resuspension of soil particles.

During the summer season, the main source of air pollution is traffic. It should be noted that as of 2018, 45.5% of vehicles were over 20 years old. Diesel fuel quality and requirements remain a particularly problematic issue in the country [13].

The main industrial activities taking place in the mountainous regions of Central Caucasus are related to the extraction and processing of natural resources. Mining activities alter the structure of the landscape, which can have severe consequences. Mining and processing activities often create toxic waste, which can have adverse impacts on the surrounding environment. In the Ambrolauri region, near village Uravi arsenic mining sites are situated. When the mining sites were abandoned in 1992, approximately 100,000 tons of wastes containing arsenic were left in surface areas. These sites are situated in the basins of the Rioni river, and there was an existing high risk of arsenic leakage [14,15].

2.2. Moss Sampling

Passive moss biomonitoring was performed in compliance with the guidelines of the Convention on Long-Range Transboundary Air Pollution (CLRTAP) and International Cooperative Program on Effects of Air Pollution on Natural Vegetation and Crops monitoring manual Moss Manual 2020 [16]. The following regions are represented: Racha-Lechkhumi and Kvemo Svaneti, Shida Kartli, Mtskheta-Mtianeti, Kvemo Kartli, and Samtskhe-Javakheti. Overall, thirty-five moss samples (*Hylocomium splendens* (Hedw.) Schimp. (4), *Hypnum cupressiforme* Hedw. (12)), *Pleurozium schreberi* (Brid.) Mitt (5), and *Abietinella abietina* (Hedw.) M. Fleisch) (14) were collected during summer 2019. (The number of samples of each type is given in brackets). Three first moss species are recommended for biomonitoring purposes in the Moss Manual-2020 [16], However in some sampling sited the only available species was *Abietinella abietina* (Hedw.) M. Fleisch) which was considered suitable for sampling due to the closeness of its morphological properties with the mosses listed in the Moss Manual. The sampling map is given in Figure 1. From a map Ecosystems of South Caucasus (Figure 2) one can obviously see the variety of ecosystems and climatic zones of the sampled areas.

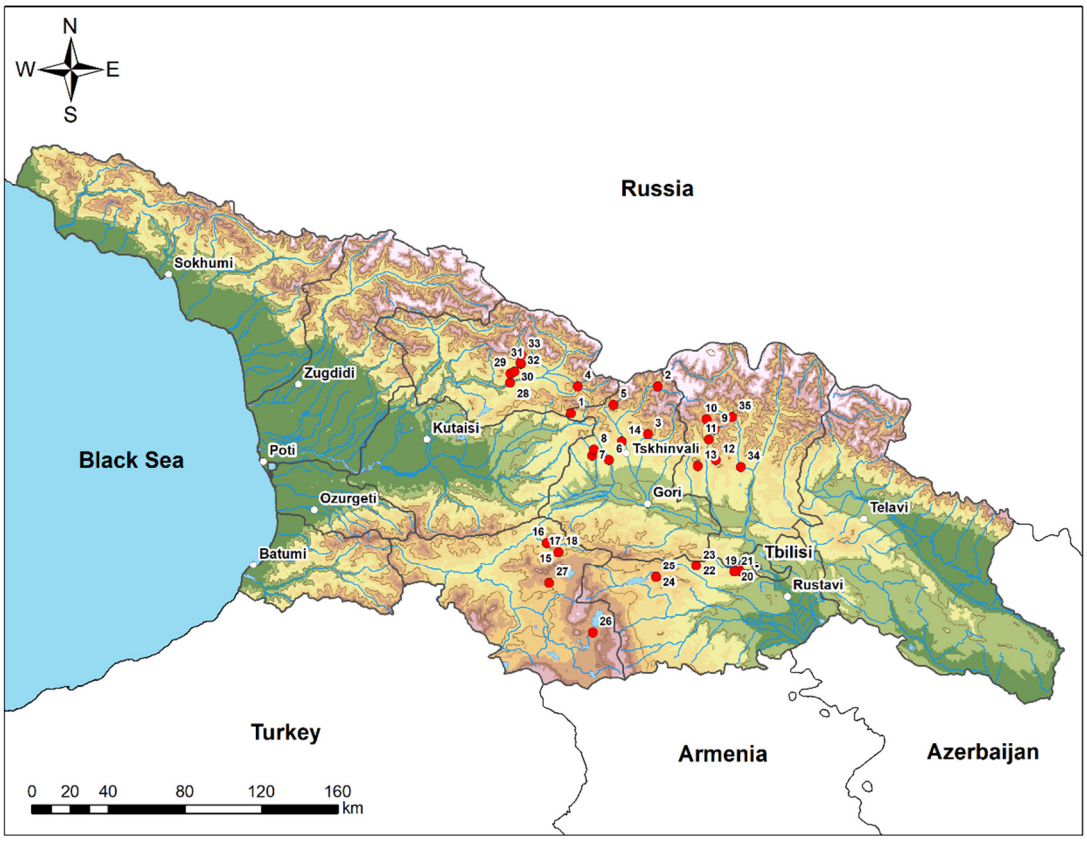

Figure 1. Sampling map.

Samples were collected at least 300 m from the main roads and settlements and at least 100 m away from the side roads, mainly from open areas to avoid the impact of higher vegetation. Longitude, latitude, and elevation were noted for every sampling location using the global positioning system.

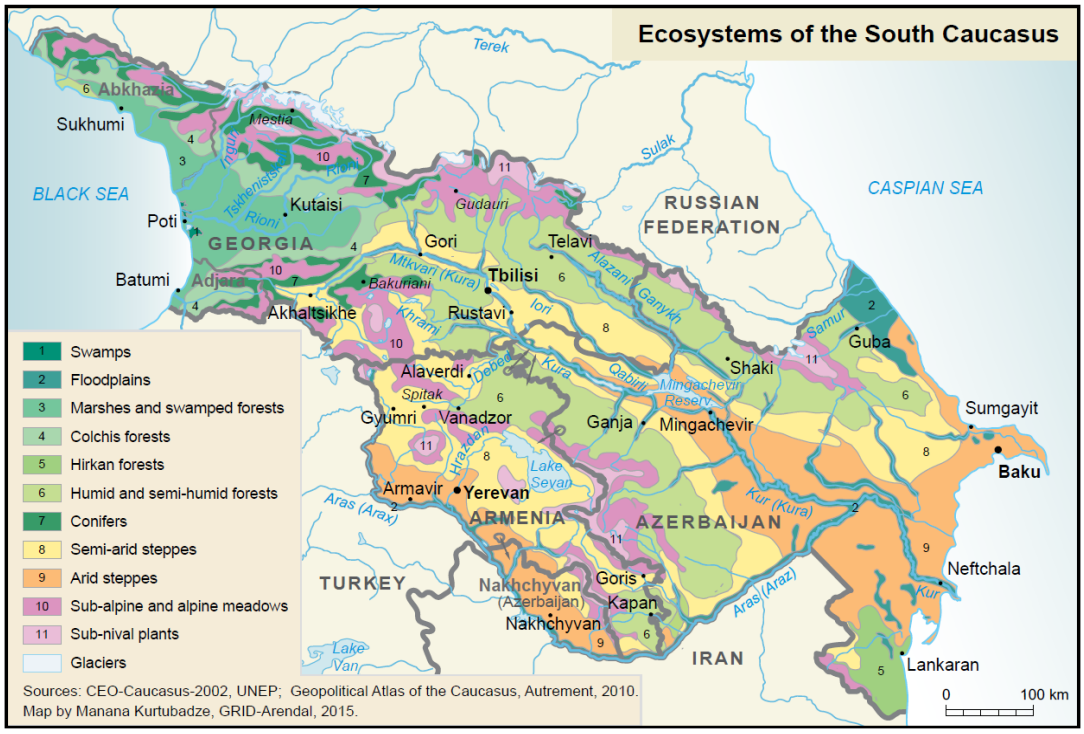

Figure 2. Ecosystems of South Caucasus [15].

For each sampling site, details (date of the sampling, weather condition, nearby vegetation, topography, and land use) were noted. Five to ten sub-samples were collected within an area of 50 m × 50 m and mixed in one composite sample. Samples were stored and transported in tightly closed paper bags. To prevent any contamination of the samples, sampling, and sample handling in the field and in the laboratory were performed using disposable polyethylene gloves (without talc) for each sample.

2.3. Sample Preparation and Elemental Analysis

Each sample was cleaned from extraneous materials in a chemical laboratory. Only green and green-brown shoots were taken and dried to a constant weight at 30–40 °C for 48 h. The elemental analysis of each sample was performed using instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS). The procedure of moss preparation for INAA and AAS is described in our previous study [8].

Moss samples were subjected to INAA at the neutron activation analysis facility REGATA of the IBR-2 reactor of the FLNP, JINR (Dubna, Russia). To determine elements with short lived isotopes (Mg, Al, Cl, Ca, Ti, V, Mn, I) samples were irradiated for 3 min and measured for 20 min. To determine elements with long lived isotopes (Na, K, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Sn, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, W, Au, Th and U) samples were irradiated for 3 days, re-packed, and measured twice using HPGe detectors after 4 and 20 days of decay, respectively. The calculation of element concentrations was performed using software developed at FLNP JINR [17].

The AAS was used to determine amounts of Cu, Cd, and Pb in the moss samples using the iCE 3300 AAS atomic absorption spectrometer with electrothermal (graphite furnace) atomization (Thermo Fisher Scientific, Waltham, MA, USA).

The calibration solutions were prepared from a 1 g/L stock solution (AAS standard solution; Merck, DE).

2.4. Quality Control of ENAA and AAS

In order to evaluate the precision and accuracy of the results, the certified reference materials and standards were used, namely NIST SRM 1575a—Trace Elements in Pine

Needles, NIST SRM 1547—Peach Leaves, NIST SRM 1633b—Constituent Elements in Coal Fly Ash, NIST SRM 1632c—Trace Elements in Coal (Bituminous), IRMM SRM 667—Estuarine Sediment, NIST SRM 2711—Montana Soil, NIST SRM 2710—Montana Soil.

Table 1 shows the differences between certified and calculated values of concentrations, where "SRM" were used as standards for calculations of concentrations for SRMs in the column "Sample". Most differences between certified and obtained values are lower than 2 σ. There are no such data for elements Mo, Sn, W, and Au because their certified values are in the irradiated SRM only.

Table 1. Epithermal Neutron Activation Analysis (ENAA): obtained and certified values of reference materials, mg/kg.

SRM	Sample	Element	Obtained	Certified	SRM	Sample	Element	Obtained	Certified
2709a	FFA1	Na	21,647 ± 1602	21,900 ± 811	FFA1	2709a	Rb	100.4 ± 16.6	99.00 ± 2.97
1547	1575a	Mg	1086.5 ± 59.8	1060 ± 170	FFA1	2709a	Sr	239.8 ± 21.1	239.00 ± 5.98
1632c	1633c	Al	133,841 ± 4016	132,800 ± 6109	2709a	1632c	Zr	18.31 ± 4.86	16.0 ± 4.8
1549	1632c	Cl	1120 ± 77	1139 ± 41	2709a	FFA1	Sb	17.92 ± 3.79	17.6 ± 2.5
2709a	FFA1	K	22,498 ± 1373	22,000 ± 6600	1549	1547	I	0.394 ± 0.099	0.30 ± 0.09
1633c	2709a	Ca	19,711 ± 1814	19,100 ± 898	2709a	667	Cs	7.9 ± 0.3	7.80 ± 0.71
2709a	667	Sc	13.82 ± 0.35	13.7 ± 0.7	2709a	1632c	Ba	41.83 ± 6.03	41.1 ± 1.61
1633c	2710a	Ti	2928 ± 205	3110 ± 72	667	2709a	La	21.26 ± 1.13	21.7 ± 0.4
1633c	1632c	V	22.79 ± 1.03	23.72 ± 0.53	667	2709a	Ce	42.26 ± 2.79	42.00 ± 1.01
FFA1	667	Cr	181.6 ± 11.9	178 ± 16	667	FFA1	Nd	51.44 ± 6.49	56.8 ± 3.7
1575a	1547	Mn	97.83 ± 5.97	98 ± 3	667	1632c	Sm	1.021 ± 0.092	1.078 ± 0.029
FFA1	2709a	Fe	34,306 ± 1784	33,600 ± 706	667	2709a	Eu	0.833 ± 0.067	0.83 ± 0.02
2709a	FFA1	Co	39.87 ± 1.36	39.8 ± 1.7	667	FFA1	Tb	1.285 ± 0.047	1.38 ± 0.14
2709a	1632c	Ni	9.56 ± 0.76	9.32 ± 0.52	FFA1	667	Yb	2.49 ± 0.23	2.200 ± 0.091
2709a	667	Zn	177.11 ± 9.04	175 ± 13	FFA1	1632c	Hf	0.508 ± 0.047	0.585 ± 0.011
FFA1	1632c	As	6.07 ± 0.36	6.18 ± 0.28	667	FFA1	Ta	1.774 ± 0.055	2.11 ± 0.17
1632c	2709a	Se	1.02 ± 0.18	1.5 ± 0.45	FFA1	2709a	Th	10.95 ± 0.43	10.9 ± 0.2
667	1632c	Br	21.08 ± 0.85	18.7 ± 0.4	2709a	1632c	U	0.51 ± 0.03	0.52 ± 0.02

A comparison of heavy metal concentrations obtained using the AAS with the standard values are presented in Table 2. The difference between the certified and measured elements contents of the certified material varied between 1% and 5%.

Table 2. Comparison of the atomic absorption spectrometry (AAS)-obtained heavy metal concentrations with the standard values, mg/kg.

Element	Certified	Obtained
Cd	0.54 ± 0.02	0.54 ± 0.01
Cu	5.0 ± 0.10	4.6 ± 0.3
Pb	0.20 ± 0.06	0.18 ± 0.01

2.5. Data Analysis Using PCA

Principle Component Analysis (PCA) is a special case of factor analysis, which transforms the original set of intercorrelated variables into a set of uncorrelated variables that are linear combinations of the original variables. The first principal component is the linear combination of the variables that accounts for a maximum of the total variability of the data set. The second principal component explains a maximum of the variability not accounted for by the first component, and so on. The objective is to find a minimum number of principal components that explain most of the variance in the data set. The principal components are statistically independent and, typically, the first few components explain almost all the variability of the whole data set. The minor principal components, which explain only a minor part of the data, can be eliminated, thus simplifying the analysis. Further, these minor components contain most of the random error, so eliminating them tends to

remove extraneous variability from the analysis. A wide range in concentrations makes normalization of the data necessary if all the elements are to be given equal weight in the analysis. The values used in the PCA are made dimensionless by this transformation [18]).

2.6. Construction of GIS Maps

The ArcGis 10.6 software (Esri, Redlands, California, USA) was used to build distribution maps of factor scores over the study area. We are using the OpenLayers library and a few backgrounds like "Oceans", "Gray", "World", "OSM", etc., to generate maps.

3. Results and Discussion

A summary of the results from the 2019 moss sampling over the study area is presented in Table 3 along with similar data obtained in previous surveys in Georgia in 2014–2017 [8], North Macedonia [19], Bulgaria [20], and pristine country Norway [21]. Data from North Macedonia and Bulgaria were obtained by INAA in Dubna, at the IBR-2 reactor of FLNP JINR using the same hard- and software, whereas Norwegian data is a result of ICP-MS. The Table 3 contains the medians and the lower and upper concentration quartiles of all components. Variability of elemental concentrations is reflected by the total range, which often spans approximately two to three orders of magnitude. Direct comparison of the medians does not show great difference in the elemental concentrations for Georgia and the Balkan countries, whereas maximal values of such element as As and Mo, both in 2014–2017 and 2019, exceed those for North Macedonia and Bulgaria, and it is five times higher than the maximum in Norway. This phenomenon is easily explained by mining and processing of arsenic and the presence of polymetallic ores abundant in the Caucasian Mountains. To demonstrate special behavior of As, the Summary Results for arsenic, iron, zinc, and nickel are presented in Figure 3 from which a strong local As contamination is evident, whereas Fe shows normal distribution, and the others are close to normal. In comparison with Norway, a country with fewer anthropogenic influences, Georgia has higher median values for the elemental content in mosses for almost all air pollution elements (As, Cd, Co, Cr, Cu, Hg, Ni, and Pb) [21].

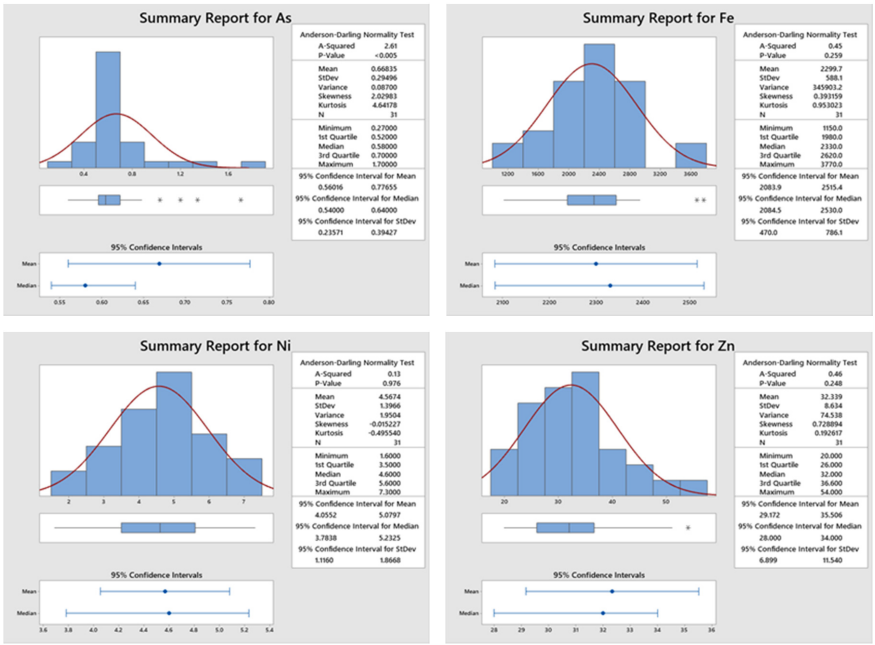

Figure 3. Summary Report for As and some selected elements created byMinitab® 19.

Table 3. Comparison of the results obtained in present study with the countries allocated in relatively the same geographical belt. Norway chosen as a pristine area. Concentration is in mg/kg.

Element	**Georgia, 2019 Present Study**		**Georgia, 2014–2017 [8]**		**North Macedonia, 2015 [19]**		**Bulgaria, 2015/16 [20]**		**Norway, 2015 [21]**	
n—number of samples	n = 35		n = 120		n = 72		n = 115		n = 229	
Element	Median	Range	Median	Range	Median	Range	Median	Range	Median	Range
Na	482	169–1350	581	101–3000	190	140–380	225	79–1560	210	60–800
Mg	2640	1910–4420	3060	1220–11600	1900	1200–3800	2080	514–8550	1350	470–3280
Al	2770	1610–9680	4295	759–24,500	2100	750–7400	2310	569–10,900	460	100–3050
Cl	132	56–635	185	57.3–1080	ND	ND	78.8	16.6–861	ND	ND
K	5930	3970–8860	5935	2030–15,000	6000	3100–14,000	5670	3250–14,200	3560	1770–6400
Ca	8400	5490–12,400	8255	4620–17,100	6900	3500–13,000	6630	606–14,200	3030	1820–7230
Sc	0.8	0.36–2.1	1.11	0.17–6.58	ND	ND	0.41	0.10–3.13	0.09	0.02–1.4
Ti	238	129–596	349.5	68.6–2100	ND	ND	143	46.4–764	24	6–152
V	6.5	3.85–16.2	9.4	1.71–54	3.3	0.47–11	3.89	1.3–22.7	1.2	0.3–14
Cr	6.6	3.14–15.5	7.75	14,337	5.7	11,536.00	2.73	0.219–25	0.7	0.2–17
Mn	142	64–377	141	230,306	160	33–510	180	39–551	400	40–1660
Fe	2410	1150–6110	2725	404–14,100	1700	510–4600	1190	376–7240	310	78–8125
Co	1	0.36–2.6	1.43	0.23–8.12	0.6	0.16–2	0.59	0.197–3.29	0.2	0.06–23
Ni	4.9	1.6–10.8	5.56	1.92–24.2	3.5	0.68–63	2.1	0.45–13.5	1.1	0.4–550
Cu *	8.93	6.58–13.7	5.54	0.13–143	4.6	3.0–8.3	7.36	3.2–46.88	4.2	1.8–370
Zn	32	20–54	28.85	7.15–75.2	30	дек.66	28	9–101	31	8–409
As	0.58	0.27–27.6	1.05	0.18–83.3	0.54	0.13–1.4	0.45	0.20–3.57	0.13	0.04–4.72
Se	0.18	0.09–0.37	0.23	0.068–0.65	ND	ND	0.2	0.008–0.67	0.3	0.009–2
Br	4.4	1.84–8.1	6.31	2.33–25.2	ND	ND	2.8	1.2–9.4	ND	ND
Rb	7.2	4.1–16.4	10.55	2.92–34.2	5.3	02.02.2028	7.38	2.24–50.7	12.4	1.4–81
Sr	37.6	24–68	43.85	17.2–157	25	6.5-220	25	11.3–122	13.6	3.8–60
Zr	9.4	3.5–25	10.55	1.19–67.9	ND	ND	ND	ND	ND	ND
Mo	0.57	0.37–6.3	0.35	0.14–2.1	0.17	0.08–0.51	ND	ND	ND	ND
Cd *	0.12	0.058–0.35	5.57	0.01–0.58	0.23	0.018–0.88	0.1	0.02–1.56	0.08	0.02–1.33
Sb	0.13	0.07–0.72	0.15	0.049–1.36	ND	ND	0.11	0.04–0.51	0.07	0.007–0.38
I	2.04	1.14–4.35	0.16	0.58–11.8	ND	ND	1.28	0.48–2.99	ND	ND
Cs	0.263	0.16–0.97	2.48	0.036–2.67	ND	ND	0.207	0.0716–1.8	0.16	0.02–1.63
Ba	37	17–100	0.42	4.98–365	42	9.7–180	46	14.2–309	25	5.3–130
La	1.57	0.82–6.2	51.3	0.34–12	ND	ND	1.35	0.39–22.6	0.32	0.07–3.5
Ce	2.97	1.38–9.2	2.15	0.31–21.7	ND	ND	2.4	0.5–29.2	0.61	0.10–4.78
Nd	1.73	0.87–7.6	3.75	0.45–10.7	ND	ND	1.3	0.2–24.1	0.23	0.01–2.24
Sm	0.26	0.12–1.17	2.04	0.031–2.7	ND	ND	ND	ND	0.05	0.004–0.38
Eu	0.054	0.02–0.22	0.34	0.023–0.52	ND	ND	0.07	0.009–0.92	0.04	0.01–0.19
Tb	0.04	0.02–0.15	0.1	0.011–0.31	ND	ND	0.03	0.005–0.42	0.01	<0.001–0.09
Yb	0.15	0.054–0.51	0.05	0.022–0.8	ND	ND	0.1	0.03–1.08	0.003	<0.001–0.016
Hf	0.24	0.11–0.76	0.15	0.041–1.81	ND	ND	0.16	0.04–1.44	ND	ND
Ta	0.046	0.02–0.13	0.27	0.0069–0.28	ND	ND	0.04	0.009–0.28	ND	ND
W	0.14	0.04–0.41	0.06	0.026–0.67	ND	ND	0.1	0.02–1.44	ND	ND
Pb *	4.33	2.34–8.21	0.11	0.18–9.1	4.9	2.2–14	10.7	3.72–102.8	0.05	0.001–0.4
Th	0.45	0.18–1.57	0.51	0.063–2.9	ND	ND	0.39	0.09–2.8	0.03	0.007–1.5
U	0.12	0.06–0.34	0.16	0.021–1.25	ND	ND	0.12	0.03–3.2	0.006	0.002–0.08

* Elements determined by AAS marked with asterisks.

It is also clearly confirmed by principal component analysis (PCA) used to classify the elements with respect to contribution sources.

PCA was carried out by using the Statistical Package STATISTICA 13.0 Results of factor analysis are presented in Table 4. Communality values close to 1 suggest that the extracted factors explain much of the variance of the individual variable.

Table 4. Rotated factor loadings for the Central Georgia data set (36 samples). Varimax normalized. Extraction: Principal components (Marked loadings are > 0.6).

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Communality
Na	0.72	0.21	0.53	0.21	0.98
Al	0.82	−0.16	−0.15	−0.43	1.00
Cl	−0.10	0.83	0.04	0.19	0.92
K	−0.08	0.87	0.18	−0.06	0.81
Ca	0.27	0.03	-0.05	−0.80	0.80
Sc	0.93	0.07	0.19	0.14	1.00
Ti	0.93	−0.07	0.21	−0.12	0.98
V	0.86	−0.07	−0.07	−0.30	0.99
Cr	0.90	0.14	0.18	0.19	0.99
Fe	0.94	0.05	0.20	0.11	1.00
Co	0.69	0.01	0.38	0.28	0.94
Ni	0.67	0.34	0.32	0.40	0.97
Zn	0.10	0.78	0.20	−0.12	0.83
As	0.30	0.07	0.89	−0.12	0.97
Se	0.07	0.69	−0.09	0.54	0.92
Br	0.19	0.65	0.00	0.65	0.94
Sb	0.34	0.24	0.85	0.00	0.98
I	0.18	0.74	−0.08	0.54	0.96
Th	0.90	−0.05	0.29	0.06	0.89
U	0.85	0.05	0.41	0.15	1.00
Cd	0.27	0.49	0.10	0.64	1.00
Pb	0.19	0.26	0.12	0.71	0.91
Cu	−0.07	0.80	0.06	0.27	0.92
W	0.26	0.03	0.72	0.32	0.84
Expl.Var	8.39	4.75	3.10	3.49	19.72
Prp.Totl	0.35	0.20	0.13	0.15	0.82

The data set analyzed includes results for 24 trace elements and major components. The PCA indicates four factors, which explain 82% of the total variance.

To visualize the results obtained, the graph on Factor Loadings was built (see Figure 4).

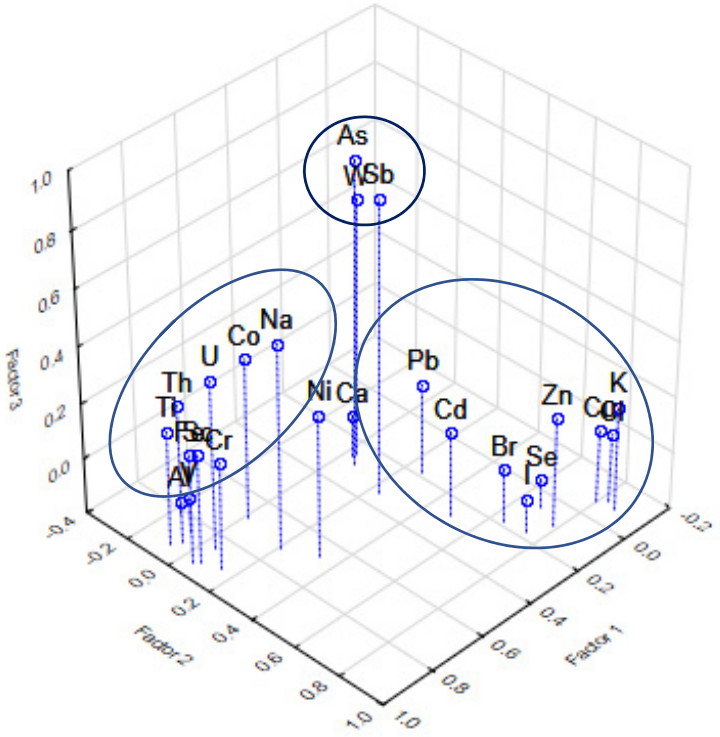

Figure 4. Factor Loadings, Factor 1 vs. Factor 2 vs. Factor 3. Rotation: Varimax normalized. Extraction: Principal components.

The results of factor scores are presented in the form of distribution geographic information system (GIS) maps. See Figure 4.

Factor 1 is loaded with Na, Al, Sc, Ti, V, Cr, Fe, Co, Ni, Th, and U, and represents mainly a combination of light and heavy crust component elements in the form of soil dust. It has almost 35% of the total variability and is the strongest factor (Figure 5). The contents of these elements in the moss samples are significantly influenced by the mineral particles that are carried into the atmosphere by winds, and their spatial distribution mainly depends on urban activities that are not related to industrial activities. High contents of elements of this geochemical association have been found in samples taken from the sampling points 28–29 (Racha-Lechkhumi and Kvemo Svaneti region, Ambrolauri municipality); 4 (Racha-Lechkhumi and Kvemo Svaneti region, Oni municipality); 10 (Mtskheta-Mtianeti region, Akhalgori municipality); 13 (Mtskheta-Mtianeti region, Akhalgori municipality); 22–23 (Kvemo Kartli region, Tetritskaro municipality); and 26 (Samtskhe-Javakheti region, Ninotsminda municipality).

Factor 2 contains Cl, K, Zn, Se, Br, I, and Cu and represents a combination of two sub-factors, a marine one: halogens Cl, Br, I and Se [22], and the second one possibly is due of some local agricultural activity. Zinc, potassium and copper are essential elements for several biochemical processes in plants [23]. The concentrations of heavy metals such as zinc and copper in the environment are currently increasing, due mainly to human activities. Copper is still used for protecting purposes in agriculture: it prevents and cure diseases, which can have adverse effects on crop yields and quality. Factor 3 includes As (0.89), Sb (0.85), and W (0.72) which are characteristic for ores used for arsenic extraction. In particular, in the village of Uravi (Ambrolaur region, Western Georgia) a mining and chemical factory functioned during the Soviet era. Arsenic has been mined and processed there for almost 60 years.

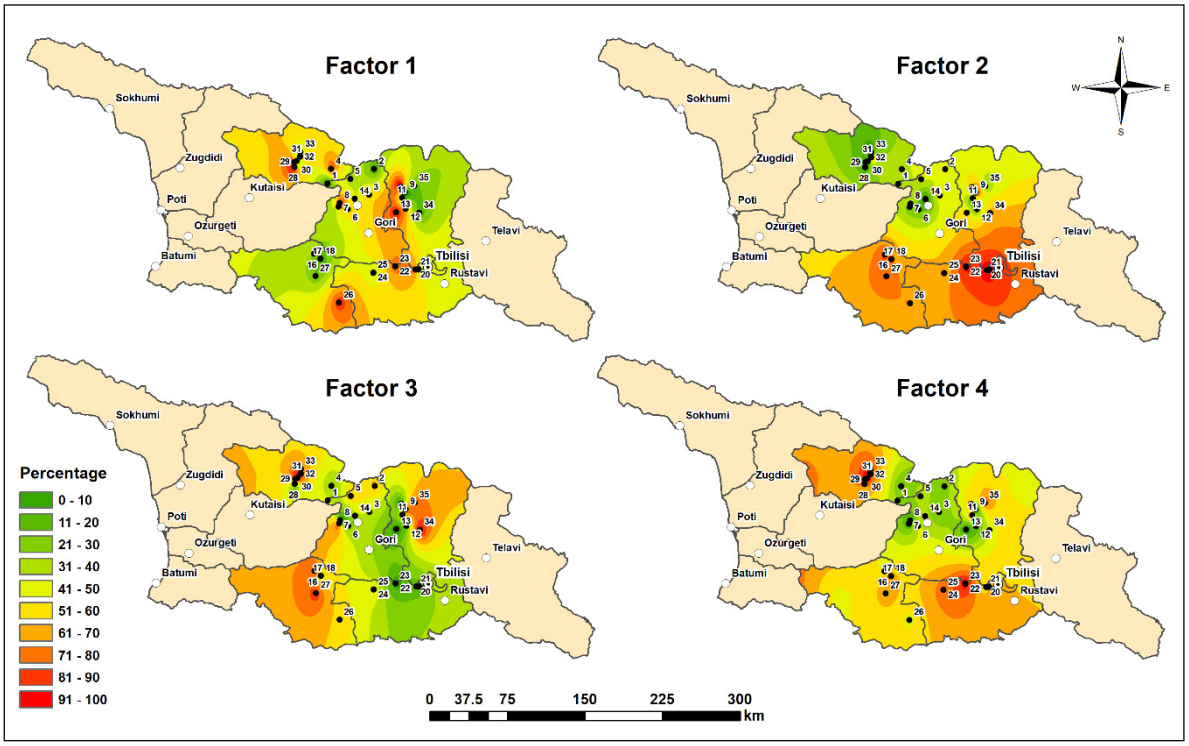

Figure 5. Factor Scores.

Factor 4 is represented by Ca (0,80) Cd (0.64), Pb (0.64), and Br (0.65) of local anthropogenic origin due to closeness to urban areas. Lead and cadmium enter the environment in the form of impurities in fertilizers, halides and oxides of these metals, as well as bromides which are contained in the exhaust gases of cars, as part of the waste generated during the extraction and processing of used batteries [24]. The highest contents of these elements are found in the moss samples collected from the sampling points 28–33 (Racha-Lechkhumi and Kvemo Svaneti region, Ambrolauri municipality); 17–18 (Samtskhe-Javakheti region, Borjomi municipality); 27 (Samtskhe-Javakheti region, Akhalkalaki municipality); 22–23 (Kvemo Kartli region, Tetritskaro municipality); 24–25 (Kvemo Kartli region, Tsalka municipality); 9 (Mtskheta-Mtianeti region, Akhalgori municipality); and 35 (Mtskheta-Mtianeti region, Dusheti municipality).

4. Conclusions

For the first time atmospheric deposition of trace elements using moss biomonitoring technique was studied in Central Georgia in 2019. By the comparison of the obtained values for a broad set of elements (Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Ni, Na, Pb, Rb, Sr, V, Zn, Th, and U) with the data from previous surveys in other parts of Georgia and in the countries of the similar climatic conditions (North Macedonia and Bulgaria) it was shown that air pollution in Central Georgia does not exceed mean values for these European countries, whereas data for potentially toxic elements such as As, Cd, Co, Cr, Cu, Ni, Pb, and Zn exceed the ones in Norway used as an example of a pristine country of Europe. Of the four factors, determined by PCA one factor (F4) is purely anthropogenic (Ca, Cd, Pb, and Br) and it is explained by the relevant high factor scores in the urban areas where they may come from fertilizers, halides, and oxides as well as bromides of these metals, which are contained in the exhaust gases of cars, as part of the waste generated during the extraction and processing of used batteries, etc. High As and W loadings in factor 3 are explained by intense mining activity for more than 60 years of As extraction from ores rich in this element and accompanying elements such as antimony and tungsten. A strong marine component (Cl, Br, I, and Se) in factor 2 is provided by the location of Georgia between two seas—the Black and the Caspian ones. In this factor

2 elements of marine component are mixed with Zn, K, and Cu due to most probably agricultural activity. Factor 1 represents mainly a combination of light and heavy crust component elements in the form of soil dust.

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