ANNALI DI BOTANICA
Ann. Bot. (Roma), 2015, 5: 89–95
Journal homepage: http://annalidibotanica.uniroma1.it

PRELIMINARY RESULTS OF ATMOSPHERIC DEPOSITION OF MAJOR AND TRACE ELEMENTS IN THE GREATER AND LESSER CAUCASUS MOUNTAINS STUDIED BY THE MOSS TECHNIQUE AND NEUTRON ACTIVATION ANALYSIS

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(Received 20 March 2015; received in revised form 27 April 2015; accepted 30 April 2015)

Abstract – The method of moss biomonitoring of atmospheric deposition of trace elements was applied for the first time in the western Caucasus Mountains to assess the environmental situation in this region. The sixteen moss samples have been collected in 2014 summer growth period along altitudinal gradients in the range of altitudes from 600 m to 2665 m. Concentrations of Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Fe, Zn, As, Br, Rb, Mo, Cd, I, Sb, Ba, La, Sm, W, Au, and U determined by neutron activation analysis in the moss samples are reported. A comparison with the data for moss collected in Norway (pristine area) was carried out. Multivariate statistical analysis of the results was used for assessment pollution sources in the studied part of the Caucasus. The increase in concentrations of most of elements with rising altitude due to gradually disappearing vegetation cover and wind erosion of soil was observed. A comparison with the available data for moss collected in the Alps at the same altitude (~ 2500 m) was performed.

Keywords: moss biomonitoring, heavy metals, neutron activation analysis, Caucasus mountains

Introduction

The state of the environment 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 (Baumbach et al., 1996). 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 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 of gases. Among the various types of pollutions, the most hazardous are heavy metals.

In practice, air pollutiotn 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 (Markert and Friese, 2000; Wolterbeek and Freitas, 1999; Markert et al., 2008).

Investigation of atmospheric deposition of trace elements

doi: 10.4462/annbotrm-13066

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 (Sampling and Analytical Methodologies IAEA, 1992). The method is difficult and not productive for investigations of large territories. Since the early 90's 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 aid of biomonitors (Wittig, 1993; Markert et al., 1999, 2003, 2004; De Temmerman et al., 2004). 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. The first to use them for biomonitoring purposes were Scandinavian countries, where large scale studies of atmospheric deposition were carried out to evaluate the effect of pollution on the environment (Tyler, 1970; Steinnes, 1977, 1989; Rühling and Tyler, 1971). Moss biomonitoring has been developing as a method for studying atmospheric deposition of heavy metals since 1960 (Rühling et al., 1992; Rühling and Tyler, 1968). Mosses well meet all the requirements imposed on biomonitors. A developed surface of their above ground parts is in good contact with the atmospheric air, and thus deposition and capture of aerosols is quite probable. In this respect moss biomonitors can be thought of as analogues of air filters. Surface properties of moss cuticles facilitate penetration of metal ions into cells and onto the places in which they are bound. Since mosses have an underdeveloped root system, their contact with soil and, thus, intake of metal with substrates can be considered negligibly small. Mosses effectively concentrate most heavy metals and other microelements from the air and precipitation. Mosses are usually tolerant to even a high pollution level. Some types of moss (*Hylocomium splendens* (Hedw.) Schimp., *Pleurozium schreberi* (Willd. ex Brid.) Mitt., *Hypnum cupressiforme* Hedw.) frequently occur in a wide range of moderate climate zones, and their growing part is such that the annular growth segment can be easily identified. 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 (Gydesen et al., 1989; Ross, 1990; Berg and Steinnes, 1977; 1985; Steinnes et al., 1992; 1994).

The moss biomonitor method in combination with nuclear physics analysis techniques has been regularly used for the past three decades in Western Europe to study atmospheric heavy metal deposition, and in the past 20 years it has become widely used in Eastern Europe and in Asia as well.

In 1998, 34 countries signed the United Nations Convention for control of emissions of heavy metals in the air using biomonitoring (the Aarhus Protocol). 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 methods based on the collection and analysis of moss biomonitors (Task Force Meeting of the UNECE ICP Vegetation).

Since 1995, the Joint Institute for Nuclear Research (JINR, Dubna, Russia) 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 (European Atlas, 2003). The contribution of JINR to the UNECE ICP Vegetation has been indicated in many publications (see, for example, (Harmens et al., 2010). Georgian industries and agricultural sector provide considerable anthropogenic impact on the environment of the Caucasus. The use of moss biomonitoring technique and NAA is a first attempt to study heavy metal atmospheric deposition in Georgia, a country different relief and climate.

Materials and Methods

Study area and sampling

The mosses three types *Hylocomium splendens*, *Pleurozium schreberi* and *Hypnum cupressiforme* were taken for atmospheric deposition study of major and trace elements in Georgia. The sampling was carried out at different vertical altitudes during vegetation periods of summer 2014. The coordinates of the sampling sites were determined using GPS. Each sampling site was photographed and archived. The sampling map is shown in Figure 1.

A total of sixteen moss samples (*Hypnum cupressiforme* – 1; *Hylocomium splendens* – 8 and *Pleurozium schreberi* – 7) have been collected along altitudinal gradients in the Caucasus Mountains covering foothill, forest, subalpine and alpine belts in the range of altitudes from 600 m to 2665 m. The 3 year (2011-2014) growth segments of mosses were taken for the analysis.

In the laboratory the moss samples was cleaned from the extraneous material (dry leaves, sticks, etc.) and dried to constant weight at 30–40° C for 48 hours. The samples were not washed and not homogenized (Frontasyeva, 2011).

Figure 1. The sampling map (red dots are the sampling sites for the Greater Caucasus; yellow dots are for the Lesser Caucasus; green dot is for Tbilisi Ridge.

Analysis

NAA of moss samples was carried out at the IBR-2 pulsed fast reactor (JINR, Dubna) as described elsewhere (Frontasyeva, 2011; Frontasyeva and Pavlov, 2000, Dmitriev and Pavlov, 2013). 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}. 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 irradiated for 90 h, repacked and then measured after 4–5 d of decay during 45 m. The results of the second measurement for determination of the rest of long-lived isotopes are not included in this paper.

Induced gamma activity was measured by HP detectors with the resolution of 1.9 keV for the 60Co 1332 keV gamma line. A software package developed at the JINR (Dmitriev and Pavlov, 2013) 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-1632c (NIST), Montana Soil-2710 (NIST) and BCR-667 (Belgium).

Results and Discussion

The concentrations of Na, Mg, Al, Cl, K, Ca, Ti, V, Mn, Fe, Zn, As, Br, Rb, Mo, Cd, I, Sb, Ba, La, Sm, W, Au, and U were determined. The results of the descriptive statistics are presented in Table 1 along with the data on Norway

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

			Georgia n=16		Norway n=100	
Isotope	**Half life**	**Gamma peak, keV**	**Median**	**Range**	**Median**	**Range**
^{24}Na	14.7 h	1368.55	721	268-1990	nd	nd
^{27}Mg	9.5 m	1014.44	4410	2720-11600	1730	940-2370
^{28}Al	2.2 m	1778.9	5195	2450-20800	200	67-820
^{38}Cl	37.2 m	2167.68	225	140-465	nd	nd
^{42}K	12.4 h	1524.6	5875	3080-9040	nd	nd
^{49}Ca	8.7 m	3084.4	11800	7140-15300	2820	1680-5490
^{51}Ti	93.1	320.1	547	216-2070	23.5	12.4-66.4
^{52}V	3.8 m	1434.4	11.8	6.2-54.0	0.92	0.39-5.1
^{56}Mn	2.6 h	1810.7	158	70-592	256	22-750
^{59}Fe	44.5 d	1099.1	3935	1640-14700	209	77-1370
^{65}Zn	244.0 d	1116.0	38.1	17.3-68.7	26.5	7.9-173
^{76}As	26.3 h	559.1	0.88	0.33-2.87	0.093	0.020-0.505
^{82}Br	35.3 h	554.3	4.545	2.3-9.8	4.5	1.4-20.3
^{86}Rb	18.6 d	1076.6	9.705	2.57-22.2	7.7	1.3-51.5
^{99}Mo	66.0 h	140.5	0.35	0.24-0.77	0.135	0.065-0.70
^{115}Cd	53.5 h	527.6	0.25	0.12-0.56	0.058	0.025-0.171
^{128}I	25.0 m	442.9	2.795	1.3-5.1	2.5	0.6-41.7
^{124}Sb	60.2 d	1691.0	0.19	0.095-0.30	0.033	0.004-0.240
^{131}Ba	11.8 d	496.8	59.28	18.8-138	17.1	5.6-50.5
^{140}La	40.2 h	1596.2	2.13	0.92-6.28	0.189	045-2.56
^{153}Sm	46.7 h	103.2	0.43	0.03-0.94	0.33	0.05-1.34
^{187}W	23.9 h	685.7	0.13	0.06-0.27	0.127	0.009-1.23
^{198}Au	2.7 d	411.8	0.00091	0.00031-0.00225	nd	nd
^{239}Np	2.4 d	228.2	0.19	0.08-0.50	0.015	0.001-0.138

considered as a pristine area of Europe.

A comparison of concentrations Georgia-Norway showed the increased values for most of heavy metals (Fe, Mn, Ti, V, As, Mg, Al, Ca, etc) in the studied samples that apparently are due to the state of the industrial sector of Georgia. The main potential sources of air pollution from the industrial sector of Georgia are the cement production in Rustavi and Kaspi, Ferro-alloys production in Zestaphoni, and metallurgical plants in Rustavi and Kutaisi, polymetallic mining in Madneuli, manganese mining in Chiatura, coal mining in Tkibuli etc. Hazard are the arsenic containing waste, accumulated in the Lentekhi and Ambrolauri districts, electricity production in Georgia - JSC ”Energy Invest”, Ltd, ”Mtkvari Energetika” and JSC ”Tbilsresi” and others. The heavy metals associated with these enterprises are obviously present in the studied mosses.

Cluster analysis (Figure 2) clearly revealed the groups of pollutants from manganese, iron-alloys, arsenic and polymetallic industries.

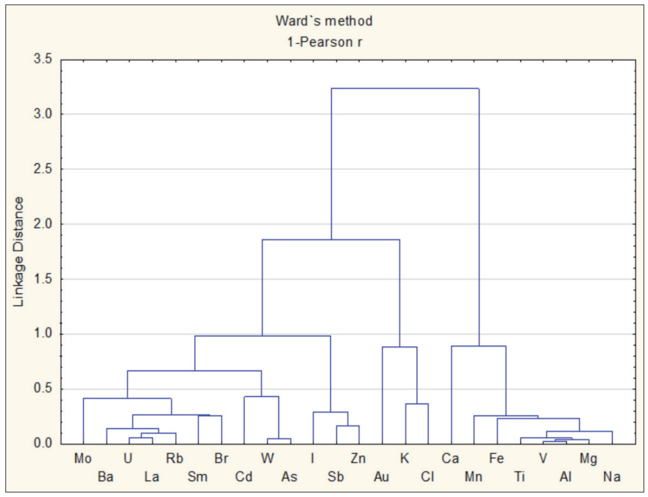

Figure 2. The results of cluster analysis.

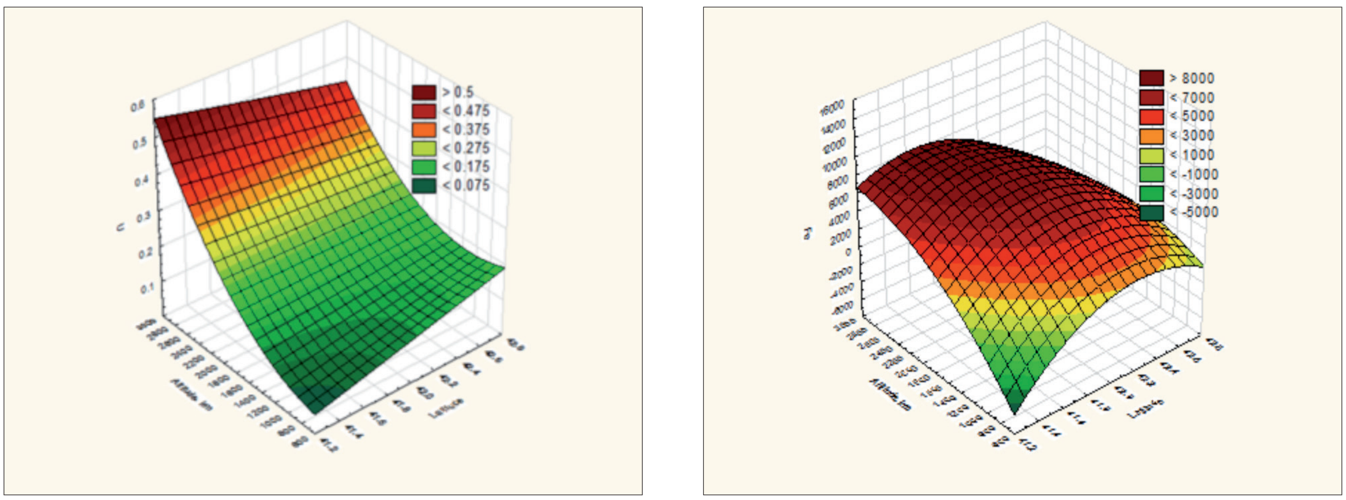

Figure 3. Spatial distribution of U and Fe concentration (mg/kg) versus altitude and longitude (km).

GIS-technology was used to create maps of spatial distribution of the determined elements. Examples for uranium and iron elements are given in Figure 3.

A remarkable increase in concentrations of all elements with rising altitude was observed. The some examples for the samples collected in the Greater Caucasus (Figure 4), Lesser Caucasus (Figure 5) and subalpine and alpine belts (Akhaltsikhe and Ninotsminda districts) (Figure 6) demonstrate the analogous tendencies.

The results obtained shows that dependence of the concentrations on altitude is more pronounced for the light and heavy crust elements. The similar results were obtained in the earlier works for other mountain regions of the world (Steinnes and Jacobsen, 1994; Zechmeister, 1995).

The most obvious explanation of this phenomenon is that the content of mineral soil particles trapped by the moss is increasing with altitude due to gradually disappearing vegetation cover and appearing of barren areas from which soil particles may be released by wind erosion and physically captured on the moss surface. This phenomenon was previously observed in Arctic ecosystems (Steinnes and Jacobsen, 1994). Comparison with the available concentrations of such elements as V, Fe, Zn, As, and Cd for the same altitude (~ 2500 m) in moss collected in the Alps (Zechmeister, 1995) indicates that all sampling sites in that work probably had a sufficient plant cover on the ground to prevent soil erosion.

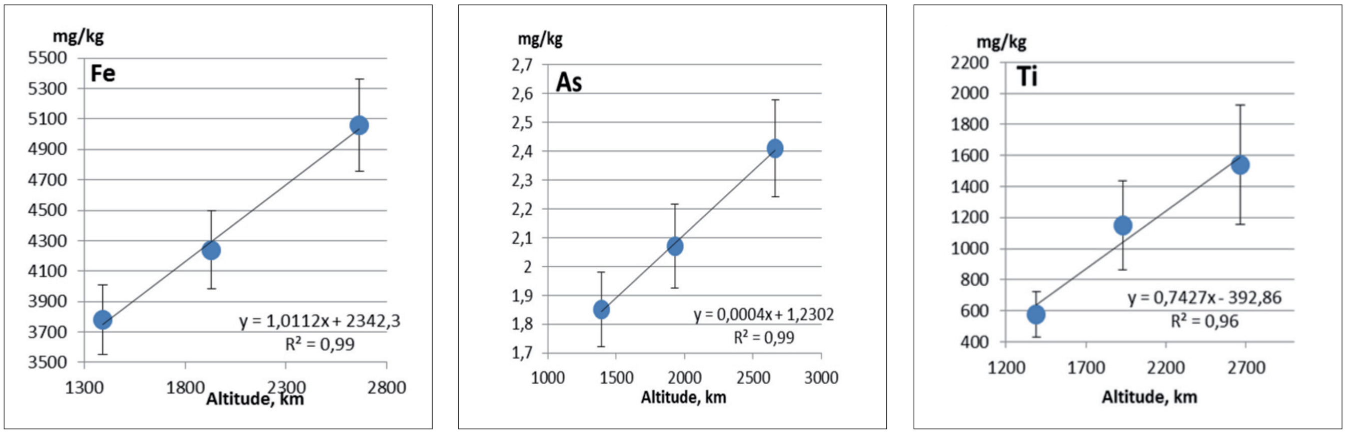

Figure 4. Concentrations of some elements versus the sampling altitude in Greater Caucasus.

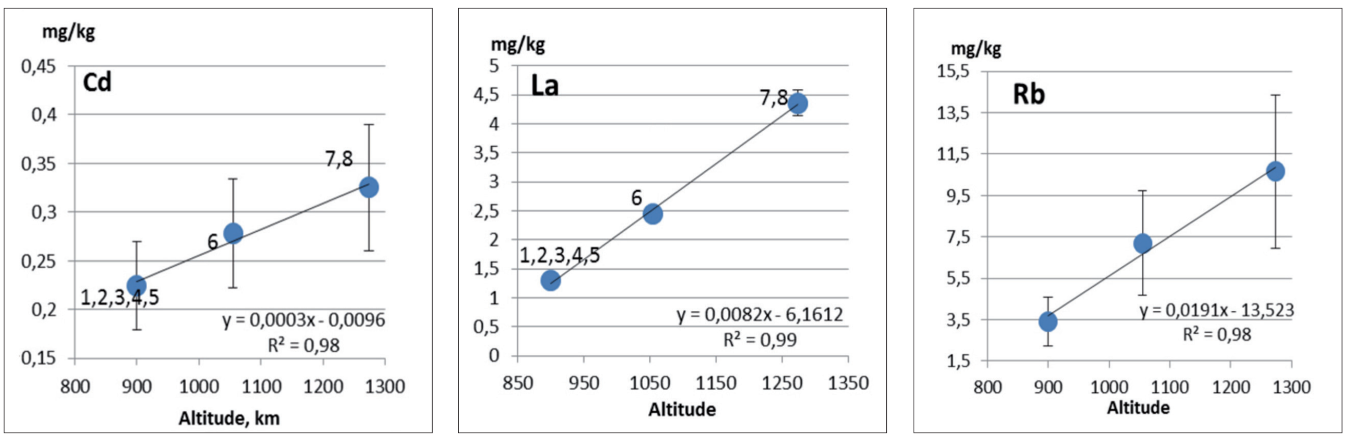

Figure 5. Concentrations of some elements versus the sampling altitude in Lesser Caucasus.

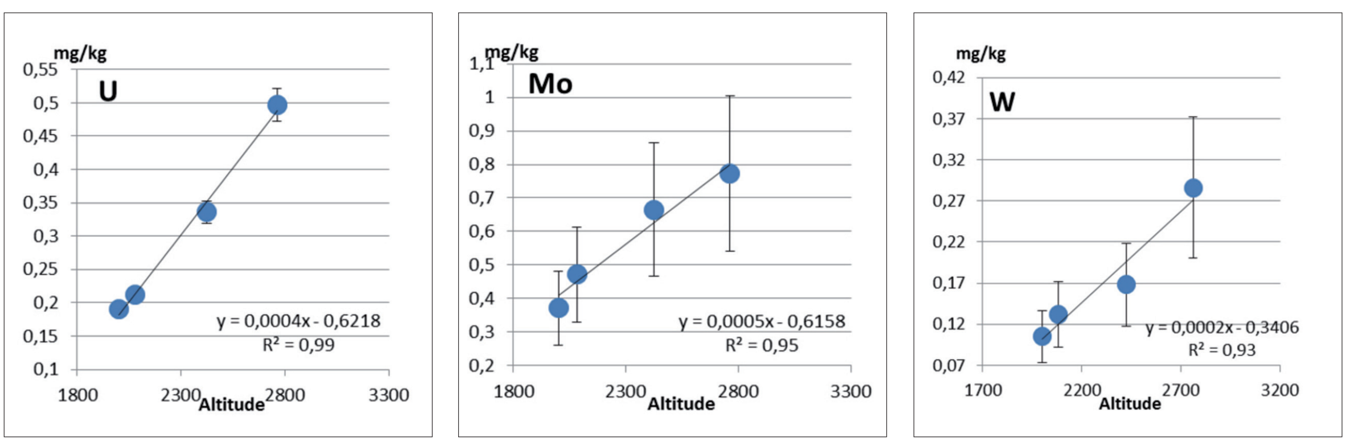

Figure 6. Concentrations of some elements versus the sampling altitude in Akhaltsikhe and Ninotsminda districts.

Conclusions

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 Georgian mountainous regions characterized by mining and metallurgical enterprises. The experience of this study can be successfully used in the other regions of the Caucasus.

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