ELEMENTAL COMPOSITION OF MOSS AND LICHEN SPECIES IN EASTERN SERBIA

by

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Instrumental neutron activation analysis is used to determine a content of 47 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, Sb, I, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Lu, Hf, Ta, W, Au, Hg, Th, and U) in mosses (*Homolothecium sp.*, *Hypnum cupressiforme* Hedw., and *Brachythecium mildeanum* (Schimp.) Schimp.) and lichen (*Cladonia fimbriata* (L.) Fr.) collected in three locations in Eastern Serbia over years 2006-2010. Concentrations of six elements (Zr, Nd, Gd, Tm, Yb, and Lu) in mosses in Serbia are measured for the first time. For other elements, the obtained concentrations fall within the ranges reported for mosses and lichens in Europe, but no declining trend in concentrations of V, Cd, Cr, Zn, Ni, Fe, and Cu, that has been described in the literature, can be inferred from our results. Factor analysis shows that terrigenous and industrial components are the highest contributing factors to the elemental composition and that the most polluted measurement site is in the vicinity of a copper mining and smelting complex.

Key words: biomonitoring, moss, lichen, instrumental neutron activation analysis, elemental composition, factor analysis

INTRODUCTION

Mosses and lichens are considered good bioindicators of atmospheric pollution in the environment. Elemental composition of both species depends highly on material exchange with the atmosphere as they have no rooting system. Therefore, their elemental content is generally a result of precipitation and dry deposition. Since their first use in the Scandinavian countries as a complementary method to classical instrumentation pollution monitoring [1, 2], biomonitoring capacity of both plant species has been well established for heavy metals [3] and radionuclides [4]. Mosses and lichens as biomonitors of radiocaesium have been especially studied after the Chernobyl nuclear plant accident in 1986 [5-8], and more recently as monitors of other airborne radionuclides [9-13]. Mosses and lichens have also been used in studies of contamination by depleted uranium [14]. Transplanted mosses have further been utilised within the so-called moss bag technique, to monitor airborne pollution in industrial and urban areas [15-18].

Uptake of elements is a complex process that depends not only on their nature and characteristics, but also on the physicochemical and biological processes in the plants [19, 20]. Some essential metals for living organisms (*e. g.*, Fe, Cu, Zn, Co, Mo, and Mn) are highly toxic at high concentrations. In contrast, metals such as Hg, Pb, Sn, Ni, Cr, and As, which are not essential for living organisms, are toxic at quite low concentrations [21]. Both mosses and lichens retain metals in quantities higher than their biological requirements [20], but the accumulation capacity of mosses seems to exceed that of lichens [22, 23].

Since the first joint moss survey conducted over 1995-1996 [24], moss biomonitoring has become a part of pollution monitoring programmes in most of the European countries. This method gives evidence of anthropogenic impact in urban areas (such as vehicular traffic and fossil fuel combustion) and can be used to identify sources of environmental pollution by heavy metals (such as ore exploitation and agricultural activities) [25, 26]. In Serbia, mosses as biomonitors have been used in a number of studies. For example, the first systematic study, covering northern parts of the country

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and identifying the spatial distribution of different elements in mosses as well as pollution sources, was conducted in 2000 [27]. This study implied relatively high concentrations of copper, molybdenum, iron, caesium, arsenic, and vanadium in Serbia.

Serbia is one of the participating countries in the International Cooperative Programme (ICP) Vegetation (http://icpvegetation.ceh.ac.uk/index.html). It took part in the European moss surveys conducted in 2000 [28] and 2005 [29], but not in 2010 [30]. While in 2000, only the northern parts of Serbia were investigated [27], in 2005, sampling was performed uniformly and 80 % of the country's area was covered by moss measurements [31]. The sampling locations in both studies included the region of Eastern Serbia and the majority of the collected samples contained *Hypnum cupressiforme* Hedw. [32]. *Hypnum cupressiforme* species is the first choice for moss samples in areas where the preferred species *Pleurozium schreberi* and *Hylocomium splendens* are not readily available [32, 33].

In our study, the moss samples were collected in Eastern Serbia over 2006-2009, and their elemental composition was determined. Three moss species were collected; one was *Hypnum cupressiforme*, as recommended by the ICP Vegetation Programme. Since our sampling locations represented a subset of the locations covered in earlier moss surveys, the obtained results could give an indication of the pollution over the period during which Serbia did not take part in the European moss surveys of the ICP Vegetation Programme. Those surveys are one of the most comprehensive undertakings in environmental monitoring across Europe, and their spatial and temporal coverage enables drawing conclusions such as the spatial concentration gradients and temporal trends. In that sense, a significance of our results could lie in bridging the gap in Serbia's moss survey participation.

Another objective of our study was to assess variations in elemental composition between different sampling sites in Eastern Serbia by means of moss and lichen species. We described a relationship between different elements using factor analysis, which helped us to identify underlying associations as well as signatures of the pollution sources in the region.

MATERIAL AND METHODS

Sampling sites

Samples of moss and lichen species were collected in the region of Eastern Serbia (fig. 1). The sampling area included small towns of Sokobanja and Gamzigrad, and the Djerdap National Park. Sokobanja (mean elevation 400 m a.s.l.), a spa town with the population of about 8000, is located between the Carpathian and Balkan Mountains and is a popular tourist destination in Serbia. Approximately 50 km northeast of Sokobanja, at an altitude of 160-180 m a.s.l., lies another small spa town, Gamzigrad (population around 1000). Further north, stretching for about 100 km along the right bank of the Danube, the Djerdap National Park is located. With the total area of around 640 km^2, the park encompasses a narrow forested region with the width 2-8 km, and the altitude 50-800 m a.s.l. The climate of the region is continental, with cold winters and hot summers.

Figure 1. The region of Southeast Europe (left) with the inset showing the location of Eastern Serbia; sampling sites in Eastern Serbia (right), Sokobanja, Gamzigrad, and Djerdap are given in white circles, and the main pollution sources in the region, Bor, Prahovo, and Majdanpek in black circles; the number of moss and lichen samples collected at each site is also denoted

The main sources of environmental pollution in the region of Eastern Serbia are the Bor copper mining and smelting complex, Majdanpek mining basin, and Prahovo chemical factory (fig. 1). The Copper Mines Bor complex includes one underground and two open pits, two plants for mineral processing, one non-metal mine, as well as a copper smelter and refinery with two lines that have been operational since 1961 and 1971 (http://rtb.rs/en/ accessed November 29, 2016). The copper mine Majdanpek, with an open pit and concentrator, and Prahovo, a facility for production of superphosphates and various granulates, were both a part of the Copper Mines Bor complex since its foundation, until 2012 when Prahovo was privatised (http://www.elixirprahovo.rs/en accessed March 7, 2017). The Bor complex has been identified as the major pollution source in Eastern Serbia [27, 34].

SAMPLING AND SAMPLE PREPARATION

Samples of mosses were randomly collected in two locations, Sokobanja and the Djerdap National Park (the number of samples per site is given in fig. 1), during years 2006, 2008, and 2009, respectively. Three different species were collected: *Homolothecium sp., Hypnum cupressiforme* Hedw., and *Brachythecium mildeanum* (Schimp.) Schimp. For each location, *Homolothecium sp*. and *Brachythecium mildeanum* (Schimp.) Schimp. contributed at least 50 % and 25 %, respectively, to the total number of samples. In other words, the maximum contribution of the *Hypnum cupressiforme* Hedw. samples was 25 % of the total. Samples of the lichen species *Cladonia fimbriata* (L.) Fr. were also randomly collected in two locations, Gamzigrad and the Djerdap National Park (the number of samples per site is given in fig. 1), over years 2006-2009 and in 2010, respectively.

Samples of whole plants, both mosses and lichens, were collected. In Sokobanja, the samples were taken at the town forested park and along the town river bank; in Gamzigrad, along the town river bank and local hills; while in the Djerdap National Park, following the approval of the authorities sampling was performed by the rangers to minimise the environmental disturbance.

At the sampling sites, the plants were sealed in plastic bags and transported to the Institute for Application of Nuclear Energy, Serbia, where they were cleaned of mechanical impurities (*e. g.*, soil, grass, and tree bark) and then air dried at room temperature. The dried samples were packed in paper bags and kept intact in a storage room of the Institute until 2012 when they were repacked in plastic bags, labelled and shipped to the Joint Institute for Nuclear Research, in Dubna, Russia, for instrumental neutron activation analysis (hereinafter, INAA).

Prior to the analysis, the samples were further dried to a constant weight at 30-40 °C for 48 hours. The samples were neither washed nor homogenised, as the previous application of INAA in moss biomonitoring has shown that samples of 0.3 g were sufficiently large to be used without homogenisation [2]. The moss samples were palletised before irradiation using simple press forms. For short irradiation, samples of about 0.3 g were heat-sealed in polyethylene bags. For long irradiation, samples of the same weight were packed in aluminium cups. The lichen samples were packed in the same manner but without a prior palletisation.

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

Instrumental neutron activation analysis is an accurate and reliable method for performing a multielement analysis in a large set of samples and has been used in a number of different environmental studies [25, 35, 36]. In our study, the INAA was performed at the pulsed fast reactor IBR-2 at the Frank Laboratory of Neutron Physics of Joint Institute for Nuclear Research, in Dubna, Russia [35, 37, 38]. A content of 47 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, Sb, I, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Lu, Hf, Ta, W, Au, Hg, Th, and U) was determined using short- and long-time activation. The obtained gamma spectra were registered and analysed as described in [39, 40].

To provide quality control, a content of elements yielding short- and long-lived isotopes in the moss and lichen samples was determined using certified reference materials issued by the International Atomic Energy Agency: lichen (IAEA-336), tomato leaves (SRM-1573a), and coal fly ash (SRM-1633b). For short irradiation, the three reference materials were irradiated together with ten experimental samples. For long irradiation, the reference materials were packed and irradiated together with seven to nine samples in each transport container.

FACTOR ANALYSIS

The measured elemental composition was further investigated using factor analysis, a multivariate method that allows an identification of common characteristics of a number of variables. Factor analysis explores mutual correlations of the variables, and then groups the variables according to the strength of their correlation. The underlying common influence for each group is called “a factor” which, under the assumption of factor analysis, cannot be measured directly.

Results of factor analysis are given as factor loadings that quantify the contribution of each variable to a factor. Factors with high factor loadings are better accounted for by the variables. "Explained variance" is another result given in factor analysis. It stands for a percent of the total variance of the variables that is explained by a given factor, and it is used to assess an influence of that factor on the total set of the variables.

RESULTS AND DISCUSSION

Mosses

A content of 47 elements was determined in the samples of mosses at two locations, Sokobanja and the Djerdap National Park. Concentrations of six elements (Zr, Nd, Gd, Tm, Yb, and Lu) are reported for mosses in Serbia for the first time. Table 1 gives the means, standard deviations and ranges of the measured concentrations in all moss samples per each location.

In an attempt to investigate temporal and spatial variations in moss elemental composition, we compared our results to the literature data, namely to the European moss surveys and local studies in Serbia. Elements of special interest, as reported in [30], their mean and median concentrations are given in tab. 2. We compared: a) the mean concentrations measured in mosses in Serbia over years 2006-2009 to the concentrations given in [30] for the 2010 European moss survey; and b) the median concentrations in Serbia to the median concentrations in 2010 reported for Serbia's neighbouring countries: Albania, Bulgaria, Croatia, Macedonia, and Romania [30].

Most of the obtained concentrations were within the range of the mean values reported for Serbia's neighbouring countries (tab. 2). This agrees with the general spatial pattern of heavy metals in mosses – an increase from Northwest to Southeast Europe [41], whereby in Albania a high content of heavy metals is detected. Thus, in mosses collected during years 2010-2011, the median values of As, Cr, Ni, Al, and Fe were higher in Albania than in the rest of Europe [42], which was influenced, to some extent, by the regional industrial activities [43]. There were two exceptions, however - arsenic and mercury in our study (tab. 2) showed concentrations comparable to the highest concentrations of the given ranges for Europe [30].

Arsenic is moderately toxic to plants but more toxic and carcinogenic to mammals [24]. The major source of anthropogenic arsenic emission was coal combustion in the early 1990, but later, "non-ferrous metals industry" and "other manufacturing industries and construction" were identified as the primary sources [32]. The highest measured concentrations of As reported in [30] were larger than 1.6 $mgkg^{-1}$, and they were detected in the countries east of Serbia, including its nearest neighbours, Bulgaria and Romania. The As abundance in mosses in the Balkan countries is a consequence of the soil mineral composition [34]. The median of the As concentrations found in our study was higher by a factor of two than the median concentrations reported for years 2000 and 2005 (tab. 3), which can, to a certain extent, be explained by the fact that the soils in the investigated region of Eastern Serbia contain remarkably high concentrations of As [44]. However, its anthropogenic sources, such as the burning of coal, which can contain concentrated As [45], are also expected to contribute to the observed concentrations.

Mercury, on the other hand, is very toxic to most organisms [24]. Its main sources of anthropogenic emission in 2005 were "public electricity and heat production", and "manufacturing industries and construction" [32]. However, due to its greater (than the other elements) hemispheric long-range transport, mosses in Europe showed a relatively homogeneous spatial distribution of mercury that did not follow the general pattern of an increase from Northwest to Southeast Europe [46]. The mean mercury concentration in our study was comparable to the highest concentrations measured in moss samples from Albania [30], but the median was lower than the median in year 2000 (tab. 3).

As a result of their lower emissions and depositions across Europe, a general decrease in concentrations of elements of special interest in mosses in Europe since 1990 has been found [41, 47]. For example, the largest decrease in the median concentration in mosses since 1990 were reported for lead (77 %), vanadium (55 %), and cadmium (51 %), followed by a decline of less than 50 % in chromium, zinc, nickel, iron and copper [41]. However, sporadic regions with no change or even an increase in concentrations were also noted [41]. A decrease in the concentration of elements of special interest could not be supported firmly by our results (tab. 3). An exception may be cadmium whose concentration in moss is: (a) largely influenced by a long-range transport of air pollution [41], and, (b) a good indicator of cadmium atmospheric deposition [48].

We further calculated the elemental concentration ratios for mosses sampled in Sokobanja and the Djerdap National Park. The ratios were between 0.4 and 2.3, indicating that there were no major differences between the sampling locations.

We also compared moss elemental composition to the results of the moss studies conducted in Serbia, but in significantly different environments. Results for mosses collected in Belgrade, the capital of Serbia, in 2004 were reported in [25]. In [49], moss samples were collected near the Nikola Tesla power plant (approximately 25 km west of Belgrade) in 2009. An earlier study, whereby moss sampling was performed in 2002, also covered the area around this power plant

Table 1. Elemental composition (in mgkg^{-1}): (mean standard deviation) and range (min-max) of the moss species per each location; symbols of the elements not previously reported for mosses in Serbia are given in bold

	Sokobanja			Djerdap National Park	
Element	Mean st. dev.		Range	Mean st. dev.	Range
Na	400	250	94.9-873	650 370	151-1240
Mg	570	390	152-1460	430 100	252-534
Al	4200	2200	1060-10100	4100 1400	1840 -5900
Cl	520	760	83.2-2750	260 220	42.6-756
K	7300	2000	4750-11900	6800 2200	3830 -11200
Ca	25000	16000	11900-61600	13800 4100	7640 -19000
Sc	0.9	0.6	0.185-2.53	0.9 0.4	0.272-1.52
Ti	290	210	57.8-788	260 100	100-408
V	7.2	3.6	2.06-15.2	7.0 2.5	2.55-10
Cr	8.1	5.6	1.82-22	9.2 3.7	2.52-13.8
Mn	98	50	42.6-216	117 45	42.7-184
Fe	2900	2000	588-7700	3100 1300	890-4930
Ni	5.0	2.5	1.42-10.8	4.7 1.6	2.3-6.46
Co	1.09	0.76	0.255-3	1.26 0.58	0.382-2.2
Cu	13	5	5.88-23.5	12 3	7.96-16.3
Zn	30	8	14-46.4	40 17	17.7-67.5
As	2.9	1.5	0.434-5.35	2.8 1.4	0.513-4.82
Se	0.22	0.05	0.103-0.299	0.31 0.12	0.152-0.498
Br	4.2	2.1	2.2-10.9	3.6 1.2	1.45-5.05
Rb	10	5	4.35-25.7	9 4	3.65-15
Sr	30	15	12.2-68.8	42 18	12.1-68.4
Zr	27	32	3.87-150	20 10	6.37-37.4
Mo	0.36	0.17	0.139-0.633	0.5 0.2	0.167-0.927
Ag	0.055	0.013	0.0198-0.0826	0.056 0.046	0.025-0.0751
Cd	0.21	0.22	0.0358-0.821	0.19 0.14	0.0601-0.438
Sb	0.23	0.08	0.121-0.348	0.41 0.19	0.113-0.627
I	1.5	0.4	0.841-2.64	1.4 0.5	0.701-2.06
Ba	41	21	11.9-83.2	72 31	32.4-124
Cs	0.7	0.5	0.0992-1.66	0.6 0.6	0.149-1.98
La	3	3	0.638-11.3	3 2	0.946-5.78
Ce	6	5	0.917-21.6	5 3	1.37-8.89
Nd	4	2	1.07-8.61	4 3	0.841-9.99
Sm	0.6	0.4	0.1-1.86	0.5 0.3	0.063-0.882
Eu	0.13	0.06	0.0256-0.298	0.13 0.04	0.0556-0.185
Gd	0.5	0.6	0.044-2.22	0.5 0.4	0.0445-1.3
Tb	0.07	0.06	0.014-0.228	0.06 0.03	0.0186-0.107
Dy	0.4	0.3	0.149-1.03	0.3 0.1	0.209-0.475
Tm	0.4	0.6	0.0251-2.54	0.7 1.1	0.0534-3.37
Yb	0.22	0.17	0.0632-0.71	0.26 0.12	0.0794-0.471
Lu	0.22	0.26	0.00246-1.14	0.16 0.20	0.00109-0.514
Hf	0.6	0.7	0.116-3	0.5 0.3	0.12-0.956
Ta	0.07	0.06	0.0145-0.205	0.07 0.03	0.0219-0.124
W	0.4	0.1	0.178-0.71	0.3 0.1	0.227-0.513
Au	0.019	0.015	0.00461-0.0705	0.017 0.013	0.00384-0.0396
Hg	0.18	0.17	0.0169-0.551	0.24 0.21	0.0352-0.54
Th	0.98	0.79	0.166-3.38	0.81 0.39	0.241-1.32
U	0.36	0.29	0.0319-1.25	0.31 0.13	0.0797-0.456

[50-53]. The comparison showed that our chosen sampling sites were much less polluted than the urban and industrial sites covered in those studies.

For example, we found a pronounced difference in the Mg concentrations between the urban site, Belgrade, on one hand, and Sokobanja and the Djerdap

Table 2. The mean and median concentrations of the elements of special interest measured in mosses in Serbia over 2006-2009, and notes on a comparison to the results of [30]

Element	Mean [mgkg^{-1}]	Median [mgkg^{-1}]	Comparison with [30]	
			Mean	Median compared to the neighbours
Arsenic	2.9	2.8	The highest values	Higher
Cadmium	0.21	0.11	Within the range	Lower
Chromium	8.4	7.1	Within the range	Higher
Copper	12.4	12	Within the range	Higher
Iron	2920	2250	Within the range	Higher
Mercury	0.20	0.12	The highest values	Higher, except in Albania
Nickel	4.9	4.7	Within the range	Higher, except in Albania
Vanadium	7.2	7.0	Within the range	Higher
Zinc	34	33	Within the range	Within the range
Aluminum	4160	3980	Within the range	Higher
Antimony	0.28	0.27	Within the range	Higher

Table 3. The median values (in mgkg^{-1}) of elements measured in Serbia within the European surveys in 2000 [28] and 2005 [29], and the median in our moss samples collected over 2006-2009

Element	2000	2005	2006-2009
Aluminum	Not measured	3946	3980
Vanadium	9.26	5.76	7.0
Chromium	5.07	6.44	7.1
Iron	2360	2267	2250
Nickel	5.65	4.43	4.7
Copper	16.9	11.1	12
Zinc	32.6	29.0	33
Arsenic	1.44	1.41	2.8
Cadmium	Not measured	0.26	0.11
Antimony	Not measured	0.24	0.27
Mercury	0.386	Not measured	0.12

National Park, on the other hand. The Mg concentrations were approximately 20 times higher in the Belgrade samples. The concentration of Mg in mosses shows a seasonal pattern [54], and the observed differences could partly result from the inherent seasonal variations. Further, as discussed in [25], Mg in mosses could be of anthropogenic origin or a result of leaching from higher plants. It should be noted that those differences in the Mg concentrations were not evident in a comparison to the Nikola Tesla power plant location [49]. Instead, in that location, Ni, Co, Cd, and Hg showed higher concentrations than in our sampling sites.

The nickel concentration in the soil varies with geological and anthropogenic input, and its anthropogenic sources include coal fly ash, waste from metal manufacturing, atmospheric deposition, urban refuse, and sewage sludge [55]. Nickel is one of the elements that plants largely take up from the soil [3]. Concentrations of this element in mosses around the Nikola Tesla power plant were higher than in our samples (by a factor of 4), although in [49] it was noted that only Cd measured in the vicinity of the power plant did not fall in the range of concentrations reported for Serbia [32]. Indeed, higher concentrations of nickel have been associated with coal-burning power plants [56], but also oil refineries [34].

For some of the investigated elements, the range of the obtained concentration spanned one or more orders of magnitude (tab. 1). For example, the Ti concentrations measured in Sokobanja gave the standard deviation which was ~70 % of the mean. A similar result was found in [27], where the minimum and maximum Ti concentrations in the moss samples of Northern Serbia were shown to differ thirtyfold. The main source of Ti in the moss samples is dry deposition of soil particles ([57] and our factor analysis, see below), and the wide range of measured Ti concentrations in our samples is likely a result of the soil composition and other factors that influence its bioavailability and accumulation [58].

The concentrations of six elements in mosses in Serbia that are reported here for the first time showed higher concentration maxima than the ones reported for samples of *Hylocomium splendens* collected in Norway during 1995 [57]. That study showed that the concentrations of Nd, Gd, Tm, Yb, and Lu in moss were primarily influenced by the dry deposition of the soil particles. The similarities in the mean concentrations of these elements in mosses in Serbia with the results of [59] for samples of *Hypnum cupressiforme* collected in Albania during 2010 and 2011, would, therefore, indicate a similar soil composition in those two countries.

LICHEN

Table 4 gives a content of 47 elements determined in the samples of lichen. Similarly to the obtained concentrations in mosses, the elemental composition of the lichen samples exhibited some relatively large ranges of values. This finding could partially be explained by the fact that the main source of heavy metals in the thalli of the lichens of the genus *Cladonia* is the substrate composition in the immediate vicinity [60].

Table 4. Elemental composition (in mgkg^{-1}): (mean standard deviation) and range (min-max) of the lichen species per each location

	Djerdap National Park		Gamzigrad	
Element	Mean st. dev.	Range	Mean st. dev.	Range
Na	350 70	240-442	600 280	205-1310
Mg	340 130	230-598	530 350	297-1420
Al	1370 570	750-2130	4500 1100	2630-6500
Cl	720 350	233-1110	110 20	69.5-127
K	3800 500	3030-4430	7200 1400	5870-10800
Ca	13300 18000	1200-46100	17000 6000	6420-28400
Sc	0.29 0.11	0.206-0.442	1.2 0.2	0.73-1.52
Ti	120 40	73.3-187	340 110	184-535
V	2.9 1.2	1.65-4.73	8.8 1.9	5.05-10.7
Cr	3.1 0.9	1.91-4.78	8.0 2.0	4.37-11.6
Mn	125 122	19-368	92 22	39.9-128
Fe	930 350	582-1610	3400 800	1820-4490
Ni	1.7 0.5	1.17-2.37	5.0 1.2	3.05-7.05
Co	0.46 0.15	0.328-0.744	1.40 0.37	0.756-2
Cu	4 2	1.66-7.12	30 8	22-48.5
Zn	22 0	12.2-36.6	47 7	32-56.2
As	1.4 0.4	0.871-1.86	6.6 2.0	3.62-10.6
Se	0.38 0.06	0.31-0.485	0.57 0.11	0.433-0.82
Br	3.8 0.9	2.96-5.81	2.8 0.8	1.7-3.88
Rb	2.3 1.4	0.515-3.81	7 2	4.12-9.8
Sr	17 10	6.91-33.5	41 13	13.7-53.5
Zr	8 3	3.57-13.4	19 ± 8	9.63-37.3
Mo	0.25 0.07	0.175-0.394	1.0 0.3	0.413-1.6
Ag	0.07 0.03	0.0378-0.145	0.08 0.03	0.0424-0.145
Cd	0.10 0.02	0.0599-0.131	0.34 0.23	0.154-0.862
Sb	0.27 0.09	0.148-0.404	0.54 0.24	0.346-1.01
I	2.1 0.3	1.81-2.81	1.5 0.5	0.675-2.46
Ba	76 73	7.91-197	69 26	34.3-129
Cs	0.22 0.11	0.0814-0.405	0.5 0.2	0.314-0.878
La	1.0 0.4	0.535-1.61	2.9 0.8	1.3-3.97
Ce	1.8 0.7	0.895-2.64	5 1	2.43-7.31
Nd	5 2	3.32-9.6	5 3	1.31-11
Sm	0.16 0.07	0.0813-0.3	0.5 0.1	0.237-0.698
Eu	0.04 0.01	0.018-0.0505	0.11 0.04	0.0254-0.169
Gd	0.03 0.02	0.0124-0.0726	0.4 0.5	0.0431-1.32
Tb	0.028 0.13	0.0139-0.0456	0.07 0.03	0.03-0.122
Dy	0.16 0.06	0.0789-0.236	0.4 0.1	0.273-0.721
Tm	0.033 0.016	0.014-0.0613	0.24 0.24	0.0396-0.595
Yb	0.06 0.02	0.0254-0.0932	0.25 0.06	0.136-0.335
Lu	0.05 0.05	0.00596-0.136	0.14 0.21	0.00146-0.682
Hf	0.12 0.05	0.0534-0.21	0.4 0.1	0.207-0.618
Ta	0.022 0.008	0.0117-0.0333	0.06 0.02	0.0309-0.0911
W	0.22 0.11	0.119-0.453	0.28 0.05	0.224-0.377
Au	0.04 0.04	0.00855-0.135	0.025 0.015	0.00338-0.0508
Hg	0.3 0.1	0.107-0.459	0.3 0.2	0.0161-0.684
Th	0.20 0.07	0.122-0.311	0.90 0.35	0.369-1.5
U	0.083 0.027	0.0489-0.108	0.41 0.11	0.243-0.557

A comparison of the concentration ratios for lichen sampled in Gamzigrad and the Djerdap National Park showed values mostly greater than one, although still less than ten. These higher metal concentrations in lichen in Gamzigrad are most likely an evidence of the environmental pollution in the nearby Bor copper

mining and smelting complex (fig. 1), the major pollution source in Eastern Serbia [27, 34]. The ratios also showed a paired increase in gadolinium and thulium concentrations in Gamzigrad, possibly arising from the fact that thulium is often found with minerals that contain gadolinium.

We further compared our results to the results of [61], wherein samples of two lichen species (neither was *Cladonia fimbriata*) were collected during 2009 in two sites close of the city of Nis, an urban and industrial centre of Southeastern Serbia. Our results showed elevated concentrations of Fe, Mn, Cu, Ti, and Cr in lichen from both the Djerdap National Park and Gamzigrad. The differences were most pronounced for titanium, the content thereof was of an order of magnitude higher in our samples. As already mentioned, Ti in the moss samples originates primarily from the dry deposition of soil particles ([57] and our factor analysis, see below), so these differences likely mirror the soil composition at the sampling sites.

FACTOR ANALYSIS

Factor analysis was performed to identify: (a) the underlying factors to which the measured concentrations can be associated, and (b) the most polluted measurement site. Five identified factors explain around 37 %, while the strongest contributing factor explains as much as 21 % of the total variance in the measured elemental concentrations (tab. 5).

Factor 1 showed very high loading factors for 25 elements which are found in most types of soil [27, 34]. Therefore, factor 1 can be classed as a terrigenous component, although its influence can be combined with anthropogenic activities, such as ferrous-nickel metal industry [34, 62].

Factor 2 contributed around 6 % to the total variance of the measurements and had a high loading factor for five chalcophile elements (Cu, Zn, As, Se, and Sb) and Mo. All these elements except Zn were also grouped in a factor analysis conducted by [34] and were classed as an industrial component. To corroborate this finding, we also analysed factor scores, and the factor 2 scores showed the highest values for the samples taken from Gamzigrad. Specifically, three out of eleven samples exhibited scores higher than 2, seven samples scores higher than one, and only one sample gave factor 2 score less than 1. This implies that Gamzigrad, although a town of no industrial activities, is under an influence of the Bor copper mining and smelting complex, which is located roughly 30 km north of Gamzigrad, and is the major pollution source in Eastern Serbia [27, 34]. Hence, our results show that even at a distance of 30 km, the signature of the pollution source is evident and detectable in lichens.

Each of the remaining three factors from factor analysis contributed around 3 % to the total variance of the measurements and encompassed 16 investigated elements.

Table 5. Factor analysis results – factor loadings as a function of the measured elements; for each element, the highest factor loading is given in bold

Element	F1	F2	F3	F4	F5
Na	**0.61**	0.43	–0.10	0.34	–0.10
Mg	**0.66**	0.11	0.07	0.43	0.12
Al	**0.84**	0.35	0.16	0.03	–0.04
Cl	–0.29	–0.19	**0.77**	0.01	0.24
K	0.36	0.33	**0.64**	–0.29	–0.12
Ca	0.10	0.00	**0.77**	0.27	–0.06
Sc	**0.85**	0.44	0.05	0.05	–0.01
Ti	**0.84**	0.29	–0.03	0.15	0.15
V	**0.83**	0.44	0.14	0.07	0.09
Cr	**0.95**	0.18	0.01	0.09	0.07
Mn	0.39	–0.07	–0.07	**0.66**	–0.09
Fe	**0.93**	0.31	0.01	0.06	0.09
Ni	**0.89**	0.29	0.19	0.02	0.08
Co	**0.89**	0.36	0.03	0.14	0.05
Cu	0.20	**0.83**	0.03	–0.14	–0.09
Zn	0.43	**0.72**	0.06	–0.11	–0.06
As	0.29	**0.83**	0.25	0.07	0.15
Se	–0.25	**0.76**	–0.20	0.32	0.22
Br	–0.05	–0.18	**0.70**	–0.04	–0.04
Rb	**0.87**	0.06	0.27	–0.11	–0.10
Sr	0.58	0.51	–0.04	0.12	–0.12
Zr	**0.84**	–0.13	–0.09	0.16	0.34
Mo	0.23	**0.85**	–0.13	0.15	–0.04
Ag	0.08	0.35	–0.02	**0.75**	0.00
Cd	0.16	0.41	0.32	–0.05	**0.70**
Sb	0.12	**0.72**	–0.30	0.30	0.04
I	0.01	–0.03	0.26	**0.72**	0.18
Ba	0.18	0.19	–0.13	**0.71**	0.08
Cs	0.50	0.12	**0.74**	0.03	0.13
La	**0.97**	0.05	0.04	0.07	0.15
Ce	**0.96**	0.07	–0.03	0.08	0.15
Nd	0.06	0.06	0.01	0.11	**0.46**
Sm	**0.94**	0.02	0.05	0.07	0.17
Eu	**0.86**	0.18	0.16	–0.05	–0.13
Gd	**0.73**	0.00	0.03	–0.03	0.53
Tb	**0.94**	0.10	0.03	0.19	0.16
Dy	**0.88**	0.20	0.04	0.03	0.03
Tm	0.49	–0.06	–0.14	0.02	**0.61**
Yb	**0.91**	0.24	0.01	0.00	0.05
Lu	0.54	–0.12	0.10	0.05	0.70
Hf	**0.88**	–0.09	–0.09	0.09	0.29
Ta	**0.98**	0.09	0.03	0.08	0.05
W	**0.80**	–0.11	–0.03	–0.02	–0.04
Au	–0.14	–0.05	0.08	**0.62**	–0.30
Hg	0.09	0.14	0.05	0.35	**–0.74**
Th	**0.94**	0.10	0.02	0.01	0.16
U	**0.89**	0.24	–0.09	0.01	0.21
Explained variance [%]	21.05	5.92	3.30	3.45	3.21

It might be worth noting that the factor analysis implied a strong mutual relationship for some of the elements reported here for the first time. For example, the concentrations of Gd and Tm seem to be strongly

influenced by factors 1 and 5 (tab. 5). As already mentioned, thulium is often found with minerals that contain gadolinium, so the relationship of the elements in the moss composition is most likely a reflection of the soil characteristics. A future study of the elemental composition in biomonitors should also include an analysis of the soil sample composition hence a significance of different influencing parameters, including pollution sources, could be resolved [25, 59, 63].

CONCLUSIONS

Instrumental neutron activation analysis used in this study allowed determination of concentrations of 47 elements in mosses (*Homolothecium sp., Hypnum cupressiforme* Hedw., *Brachythecium mildeanum* (Schimp.) Schimp.) and lichen (*Cladonia fimbriata* (L.) Fr.) collected in three locations in Eastern Serbia over 2006-2010. The study provided an insight into the moss composition over a period that bridged the gap in Serbia's participation in the European moss surveys of the ICP Vegetation Programme: Serbia took part in the 2000 and 2005 but not in the 2010 moss survey. Further, the high sensitivity of INAA enabled determination of concentrations of six elements (Zr, Nd, Gd, Tm, Yb, and Lu) that have not been measured in mosses in Serbia before.

The measured concentrations in the moss samples were within the ranges previously reported for Serbia and its neighbouring countries. Arsenic and mercury in our study, with the mean of 2.9 $mgkg^{-1}$ and 0.20 $mgkg^{-1}$, respectively, showed very high concentrations that are comparable to the highest values given for Europe. A general decrease in concentrations of elements of special interest which has been reported in mosses across Europe could not be supported by our results.

The obtained concentration ratios in mosses revealed no significant differences between the sampling sites. In lichen, however, higher concentrations of a number of elements were measured at the Gamzigrad site, located near the Bor complex, which is the major source of pollution in the investigated region. Apart from the elevated copper concentrations, that site also registered increased concentrations of gadolinium and thulium.

Factor analysis was performed to determine the major factors that contribute to the measured concentrations as well as to single out the most polluted measurement site. The results of factor analysis additionally supported the findings for pollution in Gamzigrad, and showed that lichens bear a recognizable signature of the pollution source located 30 km away. Moreover, factor analysis showed that the highest two contributing factors to the variance of the investigated elements were of terrigenous and industrial character. In a future study aiming to distinguish these major contributing factors, concurrent analyses of soil and biomonitor elemental composition should be performed.

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AUTHORS' CONTRIBUTIONS

A. A. Čučulović and R. D. Čučulović collected the moss and lichen samples. M. V. Frontasyeva and her co-workers at the Frank Laboratory of Neutron Physics of the Joint Institute for Nuclear Research conducted the INAA measurements and performed factor analysis. J. V. Ajtić, D. Z. Sarvan and B. M. Mitrović interpreted the results and discussed them in reference to the literature data. All the authors contributed to the manuscript preparation and approved its final version.

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ЕЛЕМЕНТАРНИ САСТАВ МАХОВИНА И ЛИШАЈЕВА У ИСТОЧНОЈ СРБИЈИ

Садржај 47 елемената (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, Sb, I, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Tm, Yb, Lu, Hf, Ta, W, Au, Hg, Th, U) у узорцима маховина (*Homolothecium sp., Hypnum cupressiforme* Hedw. i *Brachythecium mildeanum* (Schimp) Schimp.) и лишајева (*Cladonia fimbriata* (L.) Fr.) одређен је помоћу инструменталне наутронске активационе анализе. Узорци су током 2006-2010 прикупљени на три локације у источној Србији. Концентрације шест елемената (Zr, Nd, Gd, Tm, Yb, Lu) у маховинама у Србији мерене су по први пут. Концентрације осталих елемената налазе се у опсезима који су у литератури објављени за маховине и лишајеве у Европи. Наши резултати не указују на опадајући тренд у концентрацијама V, Cd, Cr, Zn, Ni, Fe и Cu, који је дат у појединим европским студијама. Факторска анализа показује да су теригена и индустријска компонента фактори са највишим утицајем на елементарни састав маховина и лишајева, као и да је најзагађенија локација у близини Рударско-топионичарског басена Бор.

Кључне речи: биомониторинг, маховине, лишајеви, инструментална неутронска активациона анализа, елементарни састав, факторска анализа