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ASSESSMENT OF ATMOSPHERIC DEPOSITION OF HEAVY METALS AND OTHER ELEMENTS IN BELGRADE USING THE MOSS BIOMONITORING TECHNIQUE AND NEUTRON ACTIVATION ANALYSIS

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Оценка выпадения тяжелых металлов и других элементов в г. Белграде
с помощью мхов-биомониторов и нейтронного активационного анализа

Образцы мха семейства *Brachythecium sp. (B. rutabulum* и *B. salebrosum)* и *Eurhynchium sp. (E. hians* и *E. striatum)*, собранные осенью 2004 г., использовались для оценки атмосферных выпадений тяжелых металлов и других элементов в г. Белграде. Концентрации 36 элементов (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Dy, Hf, Ta, W, Hg, Th, U) были определены в образцах мха и в собранных вместе с ними образцах поверхностных почв. Высокие значения фактора обогащения As, Zn, Mo, Br, Sb, Se, Hg и Cl, рассчитанные относительно континентального элементного состава земной коры, свидетельствуют об антропогенном воздействии на городскую среду, связанном, главным образом, с интенсивным движением транспорта и продуктами сжигания нефти. Показано, что концентрации элементов, характерных для продуктов сжигания нефти, были существенно ниже в образцах мха, собранных в 2004 г., чем в аналогичных образцах, собранных в Белграде в 2000 г. Уровень концентраций V, Cr, Ni и As во мхе настоящего исследования аналогичен данным, полученным в соседних странах, но он значительно превышает уровень содержания этих элементов в странах с фоновым уровнем загрязнения. Установлено, что оба используемых семейства мхов аккумулируют элементы сходным образом, и, таким образом, все изученные в данной работе виды могут использоваться для биомониторинга городских территорий.

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Aničić M. et al.

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Assessment of Atmospheric Deposition of Heavy Metals and Other Elements in Belgrade
Using the Moss Biomonitoring Technique and Neutron Activation Analysis

This study aimed at assessing atmospheric deposition of heavy metals and other elements using the moss genera *Brachythecium sp.* (*B. rutabulum* and *B. salebrosum*) and *Eurhynchium sp.* (*E. hians* and *E. striatum*) collected in autumn 2004 in the urban area of Belgrade. The concentrations of 36 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Dy, Hf, Ta, W, Hg, Th, U) were determined in moss and local topsoil samples by instrumental neutron activation analysis. The concentration of elements in moss positively correlated to those obtained for topsoil. High enrichment factors for As, Zn, Mo, Br, Sb, Se, Hg, and Cl, calculated to continental crust composition, gave an evidence for anthropogenic impact on urban area, mainly due to intensive vehicular traffic and fossil fuel combustion. The concentrations of elements in moss, characteristic for fossil fuel combustion, obtained in this study, were substantially lower than in the previous investigation (2000) conducted in the area of Belgrade. The level of concentrations for V, Cr, Ni, and As in moss from this study correlated to those measured for neighboring countries, and were several times higher than the base-level data from low polluted areas. The level of accumulated elements in both investigated moss genera were similar and all studied species could be combined for biomonitoring purposes in urban areas.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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INTRODUCTION

The moss monitoring technique, first introduced in Scandinavia, has shown to be very suitable for studying atmospheric deposition of heavy metals and other elements as well [1, 2]. It has been well established that bryophytes are among the most effective types of organisms for biomonitoring due to their numerous biological features, widespread occurrence and tendency to accumulate and retain pollutants [3]. Terrestrial mosses have several advantages as biomonitors when compared to higher plants: 1) they lack developed root system; 2) low variability of morphology through the growing season; 3) they lack cuticula; 4) high surface-to-volume ratio, and 5) high cation exchange capacity (CEC) [4, 5]. It is assumed that moss intakes nutrients directly from the atmosphere. Procedures of sampling and chemical analysis of bryophytes are relatively simple and cheap. They are evergreen and perennial plants, so it is easy to collect them throughout the year and over large territories [6, 7].

Most studies have been carried out in northern Europe and the northeastern USA, and the majority of large-scale projects have successfully used the mosses *Hylocomium splendens, Pleurozium schreberi, Hypnum cupressiforme*, and *Scleropodium purum* (in Spain) as recommended species [6–8]. All mentioned species have similar physiognomy, as they grow in denser mats able to produce a higher rate of bioaccumulation. As previously recommended species are not widespread in arid areas of southern countries of Europe, it was necessary to find corresponding alternate moss species for monitoring studies, especially on a local scale. Also, naturally growing moss is rarely present in urban areas, and sometimes it is very difficult to find and sample sufficient quantity of moss material for analysis, and one of the criteria for a choice of suitable biomonitor is the species abundance [9–11].

The present research is focused on the implementation of two moss genera, *Brachythecium sp.* and *Eurhynchium sp.* for assessing atmospheric deposition of heavy metals and other elements in the urban area of Belgrade. These species have already been used for biomonitoring purposes in some other European countries [12–14] as alternative, when other recommended species were unavailable. Interspecies comparison showed that *Brachythecium sp.* and *Eurhynchium sp.* could be used along with *Hylocomium splendens, Pleurozium schreberi*, and *Hypnum cupressiforme.* The studied species often grow together (in turf), they could

be hardly separated, and it was of interest to get an insight in comparability of their element accumulation levels.

The sources and mechanisms other than atmospheric deposition, such as resuspension of local soil dust, throughfall precipitation and remains of other plants, might significantly contribute to the concentrations observed [15–18]. According to [19], the concentration of some elements in moss may be seriously influenced by crust-related elements such as Cr, V Al, Fe, Sc contaminating the moss from nonatmospheric sources. To avoid such a problem the moss could be washed before analysis. It was supposed that rinsing of moss samples prior to analysis removes plant remains, epiphytic organisms, dust, etc. and also reduces local contamination by removing soil mineral particles [20, 21]. However, it has been pointed out that moss species have high CEC, and washing the moss might significantly distort the results [4, 5, 22]. In order to avoid superficial contamination of samples some authors used a jet of air to remove impurities [23]. Surveys on atmospheric deposition, as a rule, are based on total element analysis of unwashed moss samples [5].

The objectives of this investigation were: 1) to evaluate the accumulation ability of the moss genera: *Brachythecium sp.* and *Eurhynchium sp.* sampled in urban area; 2) to compare the concentration of elements between unwashed and washed (prior to analysis) moss samples; 3) to estimate the levels of heavy metals and other elements in moss and topsoil samples at urban locations, and 4) to carry out a source apportionment of elements in moss and local topsoil samples.

The results presented in this work were a part of integrated project «Air quality studies in urban areas» which also includes the determination of heavy metals concentrations in suspended particulate matter, bulk atmospheric deposition, soil and plant leaves, as well as natural and man-made radionuclides (Be-7, Cs-137, Pb-210) and ground level ozone concentration.

MATERIALS AND METHODS

Studied Sites. The study was carried out in the city of Belgrade, the capital of Serbia and Montenegro, with population of more than 1.8 million. It is located at the confluence of the rivers Sava and Danube (Fig. 1).

The total number of vehicles in the year 2004 was more than 360 000, including 23 000 of heavy-duty vehicles and over 1 000 city buses using diesel. The average age of passenger cars is more than 15 years, which means that leaded gasoline (0.4 $g \cdot l^{-1}$ Pb) is still in use in the country. There are many very old buses and trucks in the streets and they could be a significant major source of pollutants, knowing that diesel vehicle exhaust contains 10–20 times more particulate matter than that of gasoline vehicles [24]. There are 18 big heating plants with a total capacity of 2018 MW, run with natural gas or crude

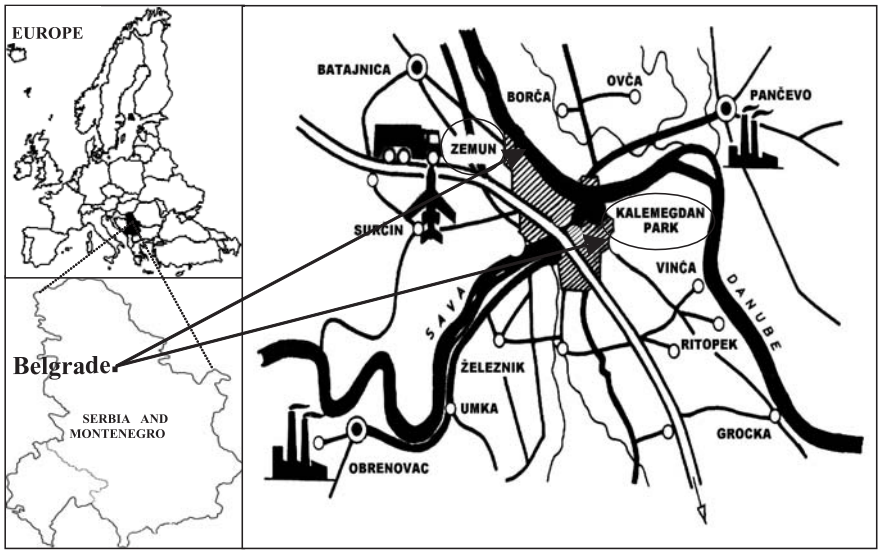

Fig. 1. Map of sampling sites in Belgrade

oil and 59 smaller plants run only with crude oil (approximately 193 MW). Fuel used for domestic heating is mainly coal or crude oil.

The climate of Belgrade [25] is moderately continental, with fairly cold winters and warm summers. Maximum precipitation occurs at the beginning of summer (June) and minimum precipitation occurs in February. The prevailing wind is N–NW, but the characteristic wind «Košava» (SE-ESE) blows with an annual frequency of 26% and an average speed of 4 m s^{-1}. This wind effectively improves the horizontal dispersion and dilution of pollutants in the ground-level atmosphere of the city of Belgrade.

The mosses were sampled in the late autumn of 2004 from two sites in the city of Belgrade: Kalemegdan Park, in the central part of the city ($H = 117$ m, $\varphi = 44^\circ\,49'\,30''$ N, $\lambda = 20^\circ\,27'\,03''$ E) and Zemun, suburban part of Belgrade, on the right bank of Danube river $H = 85\mathrm{m}\varphi = 44^\circ\,51'\,19''$ N, $\lambda = 20^\circ 23'\,27''$ E) (Fig. 1).

Moss Sampling. Two moss genera were sampled at the studied sites: *Brachythecium sp.* (***B. rutabulum***, Hedw., B. S. G. and ***B. salebrosum***, Web. et Mohr, B. S. G.) and *Eurhynchium sp.* (***E. hians***, Hedw., Lindb. and ***E. striatum***, Hedw., Schimp). The species within the same genera are very similar in physiognomy (the differences can be observed only by microscope) and were collected in composite samples without separating. Collection of moss samples was performed according to recommendations of the study: «Heavy metals in

European mosses: 2000/2001 survey» [8]. At the studied sites, 5 subsamples, for both moss genera, were collected within a 30×30 m^2 area, at least 100 m away from main roads and 50 m from smaller roads and houses. Samples were taken at least 5 m from the base of any tree so as not to be directly exposed to throughfall precipitation. Sampling and handling were carried out using polyethylene gloves and bags.

In the laboratory, the samples were carefully cleaned from all dead material and attached litter, then only green and green-brown moss upper parts from the two–three last years were analyzed. After that, a short rinsing procedure of 30 s was applied to a half of the samples to avoid potential disturbance of CEC [22, 26]. The rest of the samples were not subjected to washing, as recommended in «Heavy metals in European mosses: 2000/2001 survey» [8]. All samples were dried for 48 hours at 35 °C to constant weight prior to analysis.

Soil Sampling. Topsoil (3–10 cm) samples were collected by a polyethylene tool and gloves at the same sites as moss samples. After removal of the litter, the uppermost 3 cm of the soil profile was sampled. Because of the heterogeneity of the substrate, 5 subsamples (ca. 300 g) were taken from the sites. Prior to analyses, soil samples were dried in the laboratory, at room temperature (20 ± 2 °C) to constant weight. Each subsample was devided into 6 equal parts and the same amount of soil was taken from each part to obtain a well-homogenized sample. Such samples were sieved using a 2 mm mesh discarding the retained material and further powdered in a mortar to $\approx$ 0.1 mm particles. Afterwards, the samples were dried in an oven for 4 h at 105 °C [27]. About 0.1 g of so prepared soil samples were taken for analyses.

Analysis. Heavy metals and other element concentrations in the moss and soil samples were determined by Instrumental Neutron Activation Analysis (INAA). INAA was performed at the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia. Most element concentrations were determined by INAA with detection limits within the range of 0.01–10 μg/g. The five subsamples of moss were combined into a well-homogenized sample from which three «pellets» were taken for three measurements for each moss species. Approximately 0.3 g of well-homogenized moss and 0.1 g of soil, were packed in aluminum cups for long-term irradiation or heat-sealed in polyethylene foil bags for short-term irradiation at the IBR-2 fast pulsed reactor. The irradiation facility characteristics are presented in Table 1. The short irradiation (2 minutes for soil and 3 minutes for moss samples) in channel 2 (Ch2) was used for short-lived radionuclides (Mg, Al, Cl, K, Ca, Ti, V, Mn, I, Dy). The long irradiation for 100 h in the Cd-screened channel 1 (Ch1) was used to determine elements associated with long-lived radionuclides (Na, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, Cs, Ba, La, Ce, Sm, Tb, Hf, Ta, W, Hg, Th, U). Gamma-ray spectra were measured four times using a high-purity Ge detector after decay periods of 5 and 10 min following the short irradiation and after 3 and 20 d following the

long irradiation, respectively. The low temperature during irradiation of samples (60–70 °C) provides determination of elements present in the samples in volatile form [28].

Table 1. Flux parameters of irradiation positions [28]

Irradiation positions	$\Phi_{\text{th}}\cdot 10^{12}$, n·cm^{-2} · s^{-1}	$\Phi_{\text{th}}\cdot 10^{12}$, n·cm^{-2} · s^{-1}	$\Phi_{\text{th}}\cdot 10^{12}$, n·cm^{-2} · s^{-1}	T, °C
	$E = 0 \div 0.55$ eV	$E = 0.55 \div 10^5$ eV	$E = 10^5 \div 25\ 10^6$eV	
Ch1 (Cd-screened)	0.023	3.3	4.2	70
Ch2	1.23	2.9	4.1	60

Quality Control. To provide quality control (QC), content of elements yielding short- and long-lived isotopes in moss samples was determined using certified reference materials issued by the International Atomic Energy Agency: lichen (IAEA-336), cabbage (IAEA-359) and standard reference material SRM-1575 (Pine Needles) from the US NIST (National Institute of Standards and Technology). A content of elements in soil samples was determined using certified reference material: lake sediment (SL-1) by the IAEA and standard reference material: coal (SRM 1632c) and coal fly ash (SRM 1633b) by US NIST. For the short irradiation, the three reference materials were irradiated together with 10 experimental samples. In the case of long irradiation, the three reference materials were packed and irradiated together with 7–9 samples in each transport container.

RESULTS

According to the majority of large-scale moss monitoring projects [6, 8, 14, 15], surveys of atmospheric deposition are commonly based on the total element analysis of unwashed moss samples. However, a recommendation by some other authors is a washing pretreatment [20]. In order to clear up these approaches, the element concentrations in the washed and unwashed (prior to analysis) moss samples have been determined in this study. A difference in obtained concentration (μg·g^{-1}) of 36 elements in so prepared samples was within the specific experimental error for the used analytical methodology. Hence, in the further data presentations, only the data from unwashed samples have been taken into consideration.

The mean concentrations (μg·g^{-1}) of 36 elements in the unwashed samples of *Brachythecium sp.* and *Eurhynchium sp.* and in topsoil for both studied sites are presented in Table 2. A comparison of element concentrations in moss between the two studied areas showed a difference for some elements. The concentrations

Table 2. Concentrations ($\mu g \cdot g^{-1}$) of elements in the moss species *Brachythecium sp.* and *Eurhynchium sp.* and in topsoil at studied sites (Zemun, Kalemegdan Park)

	Zemun			Kalemegdan Park		
Element	*Brachythecium sp.*	*Eurhynchium sp.*	Topsoil	*Brachythecium sp.*	*Eurhynchium sp.*	Topsoil
Na	545	757	7212	313	307	950
Mg	16950	22760	20680	10173	8290	6374
Al	5000	6685	53270	2147	1940	12733
Cl	642	565	89	817	332	109
K	10705	10637	13637	9760	7264	3280
Ca	12590	14937	72780	18647	12340	346200
Sc	0.90	1.0	12	0.27	0.33	2.9
Ti	329.20	539	4368	137	160	886
V	10.0	14	67	9.9	9.5	18
Cr	7.0	9.2	112	4.6	4.5	126
Mn	90	114	682	56	57	201
Fe	3000	3504	31367	1057	1295	7783
Co	0.80	1.3	14	0.42	0.68	4.3
Ni	8.2	13	60	6.8	9.2	45
Zn	34	37	115	41	40	43
As	0.95	1.6	9.6	1.0	1.14	11
Se	0.06	0.09	0.65	0.12	0.14	0.58
Br	1.8	2.5	9.6	2.9	3.7	3.7
Rb	8.1	11	90	6.7	7.7	22
Sr	29	36	91	50	42	373
Mo	0.52	0.59	14	1.2	0.75	1.8
Sb	0.18	0.22	1.6	0.29	0.35	1.1
I	0.19	0.26	6.7	0.30	0.31	4.0
Cs	0.39	0.59	5.1	0.22	0.22	2.7
Ba	44	64	385	33	28	117
La	3.0	3.7	37	1.1	1.5	8.5
Ce	3.9	7.0	88	1.7	3.1	20
Sm	0.40	0.77	6.8	0.20	0.25	2.4
Tb	0.05	0.09	0.80	0.02	0.03	0.31
Dy	0.81	1.2	8.0	0.42	0.38	2.0
Hf	0.42	0.78	8.2	0.22	0.24	1.3
Ta	0.05	0.10	1.6	0.02	0.03	0.35
W	0.32	0.29	14	0.16	0.19	6.2
Hg	0.48	0.43	14	0.18	0.38	11
Th	0.62	1.1	12	0.27	0.34	2.8
U	0.07	0.14	2.9	0.23	0.10	2.4

of Na, Al, Sc, Ti, Cr, Mn, Fe, Ni, Zn, Rb, Cs, La, Ce, Sm, Tb, Dy, Hf, Ta, W, Hg, and Th in moss from the Zemun site were higher than concentrations of the same elements in moss from the other site, Kalemegdan Park. On the contrary, the concentrations of some other elements: Ca, Br, Sr, Mo, and U were higher at

Kalemegdan Park. In topsoil samples, the differences in obtained concentrations generally followed the same pattern as in moss from the same site. The exception was some elements such as Br and U, which were higher in soil from Zemun, and Cr and Zn, which were higher at Kalemegdan Park.

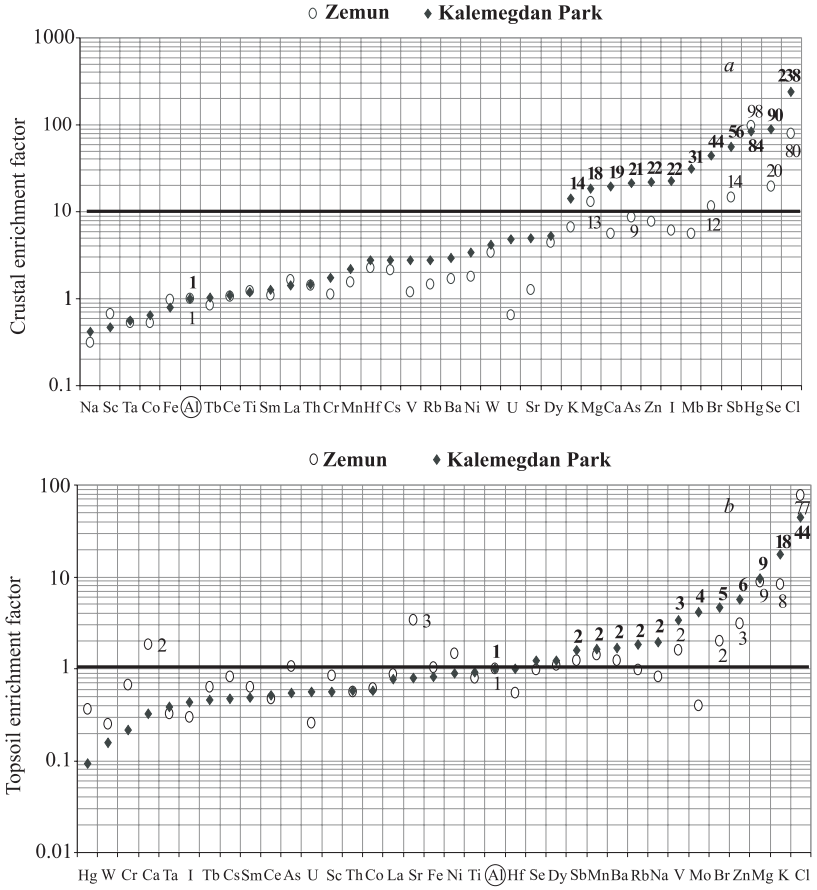

Fig. 2. Enrichment factors (EF) of elements in moss, sampled at Zemun and Kalemegdan Park, calculated to: *a*) EF = $[\mathrm{E/Al}]_{\mathrm{moss}}$ / $[\mathrm{E/Al}]_{\mathrm{Crust}}$, the crustal element composition given by Mason (1966) [30]; *b*) EF = $[\mathrm{E/Al}]_{\mathrm{moss}}$ / $[\mathrm{E/Al}]_{\mathrm{topsoil}}$, the concentration of elements in local topsoil determined in this study

To assess the contribution of anthropogenic in relation to crustal sources, the enrichment factor (EF) has been calculated for each element. The EF of an element (E) in moss relative to crustal reference material (R) is defined as:

$$\mathrm{EF} = [\mathrm{E/R}]_{\mathrm{moss}}/[\mathrm{E/R}]_{\mathrm{Crust}},$$

where $[E/R]_{moss}$ and $[E/R]_{Crust}$ refer to the concentration ratios of element E to reference material R in moss and in crust, respectively. The average element concentrations of the natural crust are usually used instead of the crust composition of the studied area, as detailed data for different areas are not easily available. In this study, the average values of heavy metal and other element concentrations in topsoil at the studied sites were measured in order to evaluate the influence of local soil element pollution to moss content. Hence, the EFs of elements in moss from this study were calculated according to the earth's crustal mean abundances of the elements given by Mason (1966), (Fig. 2, a) and also according to element concentrations in topsoil samples at studied sites (Fig. 2, b). Al was used as a reference element since it is almost entirely derived from crustal sources [29]. If EF approaches unity, crustal material is likely the predominant source for an element; if EF is > 10, the element has a significant fraction contributed by noncrustal sources.

High EFs for K, Mg, Ca, As, I, Zn, Mo, Br, Sb, Se, Hg, and Cl (from 14 to 238) were calculated according to the crustal values. However, the EFs for the same elements, determined according to the local topsoil element content, were significantly lower (from 2 to 77).

Figure 3 presents the median concentration levels ($\mu g \cdot g^{-1}$) of V, Cr, Ni, and As in moss from Belgrade area for the year of 2004 and Bor copper basin (Serbia), Northern Serbia, Bosnia-Herzegovina, Macedonia, Bulgaria, Romania, and Hungary for the year of 2000.

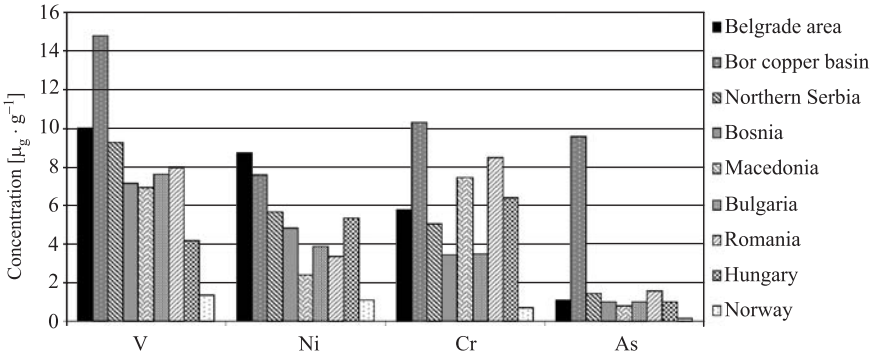

Fig. 3. Median concentrations of V, Cr, Ni, and As in moss from Belgrade area (2004) and some European countries (2000)

The results from Norway (2000), also included in Fig. 3, demonstrate an area with generally low levels of heavy metals in moss [8]. The concentration level in moss samples from Belgrade was especially high for V and Ni, while the values for Cr and As were within the range of concentrations in the neighboring

countries. For the compared elements in relation to Bor copper basin in Serbia [31], only the concentration of Ni was higher for Belgrade urban area.

Figure 4 shows a comparison of concentrations of elements, characteristic for oil combustion processes (V, Mn, I, As, Br, La, Sm, Cr, Ni, Co, Rb, Sb, Cs, Ce, Tb, Hf, Ta, and Th), measured in this study with previously obtained data (2000) from the wider area of Belgrade [31]. The 2004 levels were considerably lower than those in 2000.

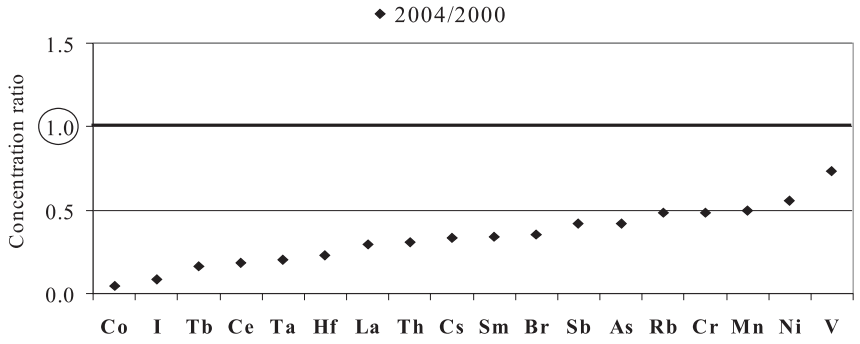

Fig. 4. Concentration ratios for elements in moss from Belgrade area for the years 2004/2000

DISCUSSION

Data Analyses. Very high correlation (Pearson's coefficient $R = 0.99$) was obtained between the concentrations of 36 determined elements in washed and unwashed moss samples of *Brachythecium sp.* and *Eurhynchium sp.* from Zemun and Kalemegdan Park. It is very likely that careful cleaning of moss samples prior to analyses was sufficient. These results support the common approach, i. e. without washing of samples prior to chemical analysis.

Element concentrations in two moss species and in topsoil for both studied sites are presented in Table 2. Generally, higher concentrations for some elements (Cr, Mn, Ni, Rb, Cs, La, Ce, Sm, Tb, Hf, Ta, and Th) in moss samples from Zemun were probably a consequence of air pollution originating from the oil refinery and petrochemical industry complex in the town of Pančevo (situated about 20 kilometers east from Belgrade). In this case, the pollutants can easily be transported by the strong local wind «Košava» and deposited in significant amounts at the studied area, as there are no prominent topographic barriers. Also, the international Danube river traffic might be a source of heavy fuel combustion products (Mn, Fe, V, and Ni). The coal-fired power plant in the city of Obrenovac (20 km SE of Belgrade) also is a significant source of heavy metals and other

elements. The other investigated site, Kalemegdan Park, is surrounded by heavy traffic roads, frequently loaded with trucks. The elements found in moss from this site, such as Ca, V, Cr, Fe, Co, Ni, Zn, Br, Mo, Sb, and Ba, are characteristic for road traffic in general. At each studied site, for a majority of elements, the concentrations in topsoil correlated with those in moss samples. It might be suggested that topsoil could also significantly contribute to moss content of elements. Also, it is in accordance with Steinnes (1992) assertions that the sources of trace element composition of mosses, in addition to atmospheric supply of air pollutants, are: mineral particles (mainly windblown dust) from local soil, and vegetative factor from living or dead plant tissue.

The element concentrations in both investigated moss genera, *Brachythecium sp.* and *Eurhynchium sp.*, were at a similar level (Table 2). For a majority of the 36 determined elements, the difference between the moss contents in the two genera was within the range of experimental error (10–30%). Exceptions were the concentrations of Ce, As, Co, Th, Sm, Tb, Ta (Zemun) and Cl, Co, Mo, U (Kalemegdan Park) where the difference exceeded the experimental error for each element. An explanation for some elements (Th, Tb, Ta, and U) may be found in low levels in moss samples, close to the detection limits. From the previous discussion, it might be suggested that both moss species, found in sufficient quantity for sampling in the urban area of Belgrade, could be combined for biomonitoring purposes. The results obtained for *Brachythecium sp.* were chosen to further estimate a level of heavy metal and other element air pollution in the area of Belgrade in comparison with the corresponding results from other authors.

Source Apportionment. The enrichment factors determined in this study with reference to the composition of Earth's crust given by Mason (1966) (Fig. 2, a) showed that elements Mg, Br, Sb, Se, Cl and Hg at Zemun, and K, Mg, Ca, I, As, Zn, Mo, Br, Sb, Hg, Se, and Cl at Kalemegdan Park were clearly of noncrustal origin (EF $>$ 10). Some of these enriched elements in moss may originate from natural sources, such as resuspension of soil and road dust (K, Ca) and leaching from living or dead plant tissue (Mg, Zn), but can also be derived partly from anthropogenic sources. Elements such as Br, Sb, As, Mo, and Zn are considered as indicators of emission from fossil fuel combustion processes, including vehicle exhausts [32, 33]. The highest EFs were observed for Cl, Hg, and Se which are important tracers for coal combustion [34]. The fuel used in the complex of coal-fired power plants of Nikola Tesla A and Nikola Tesla B, in the city of Obrenovac, 20 km south-west from Belgrade, as well as for local domestic heating in Belgrade, is mainly lignite-brown coal (high in As) or crude oil. These fuels are significant sources of the enriched elements at both studied sites [35]. Kalemegdan Park is surrounded with heavy traffic roads, with trucks very frequently present. Leaded gasoline and diesel fuel (still widely used in Belgrade) contain a large amount of Br and Mo [32]. Tire and brake lining wear

as well as other metallic parts of vehicles might be a significant source of Sb [33]. Concentrations of the enriched elements from this study were in accordance with some previous investigations of air quality of the urban Belgrade in the vicinity of Kalemegdan Park [36–38]. The main sources of the enriched elements in moss from the site Zemun were probably the nearby oil refinery complex (Mg, Br, Sb, Se, Cl, and Hg) in the town of Pančevo and the international Danube river traffic with heavy fuel combustion products.

Fig. 2, *b*, on the other hand, shows the EFs calculated in moss according to the average concentrations of the elements in local topsoil at both studied sites. The calculated EF values for K, Mg, Ca, I, As, Zn, Mo, Br, Sb, Hg, Se, and Cl were significantly lower than the corresponding EF values based on the continental crustal composition according to Mason (1966). This confirmed a significant contamination of local topsoil with these elements from atmospheric deposition. Values of EF calculated on the basis of urban topsoil composition thus are not suitable anthropogenic source apportionment in moss.

Comparison of the Concentration Levels in Moss from Belgrade and Some Other European Countries. The results from this study for the Belgrade urban area (2004) were compared with the previous data (2000) observed in the Bor copper basin (Serbia), some neighboring countries (Bosnia-Herzegovina, Macedonia, Bulgaria, Romania, and Hungary), and Norway representing an area with low levels of air pollution [8]. Especially interesting for evaluation, as carcinogenic and toxic elements [39, 40], the obtained median concentrations for V, Cr, Ni, and As in this study were presented in relation to some other corresponding data (Fig. 3). Such comparison gave an insight into a level of heavy metal and other element air pollution in Belgrade urban area in relation to the highest polluted industrial area in Serbia (Bor copper basin), base-level moss content (data from Norway) and concentration levels in adjacent countries. The value for V in the Belgrade urban area (10.0 $\mu g \cdot g^{-1}$) was higher than in other adjacent countries (4–8 $\mu g \cdot g^{-1}$) and over 7 times higher than the level in Norway (1.4 $\mu g \cdot g^{-1}$). The concentration of Ni was higher in Belgrade urban area (9.3 $\mu g \cdot g^{-1}$) in relation to Bor copper basin (7.6 $\mu g \cdot g^{-1}$), also to adjacent countries (3–6 $\mu g \cdot g^{-1}$) and 9 times higher than in Norway (1.1 $\mu g \cdot g^{-1}$). The level of Cr concentration in Belgrade area (5.8 $\mu g \cdot g^{-1}$) was of the same order as in the countries in the region (3.5–6.4 $\mu g \cdot g^{-1}$) and 8 times higher than in Norway (0.7 $\mu g \cdot g^{-1}$). The value for As in the Belgrade area was 1.1 $\mu g \cdot g^{-1}$ (similar to adjacent countries, close to 1 $\mu g \cdot g^{-1}$) and 11 times higher than in Norway (0.1 $\mu g \cdot g^{-1}$). In general, the results for the above-mentioned elements obtained for the Belgrade urban area correlated to the results from adjacent countries where fossil fuel is still a major energy source resulting in higher heavy metal and other element air pollution.

A comparison of the results for moss concentrations from this study to the previous data from a wider area of Belgrade for 2000 [31] indicated a decreasing

trend of pollution for the elements characteristic of oil combustion processes, such as: V, Mn, I, As, Br, La, Sm, Cr, Ni, Co, Rb, Sb, Cs, Ce, Tb, Hf, Ta, and Th (Fig. 4). The higher moss levels in 2000 might be a consequence of the NATO military action on Serbia and Montenegro in the spring of 1999, when the area of Belgrade was exposed to high pollution due to extensive destruction of oil refineries, warehouses and other industrial complexes.

CONCLUSION

The following conclusions can be drawn from this work:

1) The studied moss genera, *Brachythecium sp.* and *Eurhynchium sp.*, could be combined for biomonitoring purposes in urban areas as there were no differences in element accumulation levels, i.e. the differences for the majority of elements were within specific analytical error of INAA.

2) According to EFs calculated relative to the crustal composition, the main sources of heavy metals and other elements in the Belgrade atmosphere were: traffic emissions, individual heating sources and the coal-fired power plants as well as soil dust resuspension.

3) The concentrations of V, Cr, Ni, and As obtained in this study were up to 10 fold higher than background levels (Norway) and correlate with results from the adjacent countries where coal is still a major energy source.

4) The concentration of elements characteristic for oil combustion in moss from the area of Belgrade showed a decreasing trend for 2004 in relation to the previously obtained data (2000).

The results presented in this paper are a first attempt to evaluate efficiencies of indigenous moss species, for assessment of air pollution in the Belgrade urban area.

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