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# Monitoring of trace element atmospheric deposition using dry and wet moss bags: Accumulation capacity versus exposure time

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## ABSTRACT

To clarify the peculiarities of trace element accumulation in moss bags technique (active biomonitoring), samples of the moss *Sphagnum girgensohnii* Rusow were exposed in bags with and without irrigation for 15 days up to 5 months consequently in the semi-urban area of Belgrade (Serbia) starting from July 2007. The accumulation capacity for 49 elements determined by ICP-MS in wet and dry moss bags was compared. The concentration of some elements, *i.e.* Al, V, Cr, Fe, Zn, As, Se, Sr, Pb, and Sm increased continuously with exposure time in both dry and wet moss bags, whereas concentration of Na, Cl, K, Mn, Rb, Cs, and Ta decreased. Irrigation of moss resulted in a higher accumulation capacity for most of the elements, especially for Cr, Zn, As, Se, Br, and Sr. Principal component analysis was performed on the datasets of element concentrations in wet and dry moss bags for source identification. Results of the factor analysis were similar but not identical in the two cases due to possible differences in element accumulation mechanisms.

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# 1. Introduction

Biomonitoring is a rapid and economical method that has commonly been used for assessing environmental quality and potentially detrimental effects of pollutants to the biosphere [1,2]. Various effective bioindicators have been used so far for assessment of the state of natural ecosystems. These include mosses and lichens, which are commonly regarded as the best bioindicators of air quality as they can accumulate elements to a far greater level than is necessary for their physiological needs. Moreover, mosses can accumulate and concentrate toxic substances that may be present even in low concentrations in the local environment.

Uptake and retention of elements by moss is aided by: (i) numerous small leaves and intricate surfaces (large area/volume ratio); (ii) high permeability of tissue to water and elements; (iii) high water retention capacity; (iv) high cation exchange capacity, due to binding sites on the cell wall [3,4]. Generally, accumulation of trace elements depends on their supply in air, their solubility in water, water availability and humid condition [5,6].

The use of native mosses as biomonitors is a convenient way of determining levels of trace elements atmospheric deposition [7–10]. However, where samples of epiphytic mosses have been difficult to find at locations of interest, such as in urban and industrial areas, transplanted moss has been employed as an option. The "moss bags" technique [11,12] is one of the active biomonitoring methods, where a suitable moss species is sampled from an area with negligible influence from air pollution, properly cleaned from foreign materials, packed into nylon mesh bags, and then exposed at specific locations for defined periods of time to trap deposited elements. *Sphagnum* moss species are most suited for the moss bag method due to their very high element retention properties [13]. Mäkinen [14] found that bags filled with peat and cotton wool will have retention capacities of only 43% and 35% respectively in the comparison to the capacity of a typical *S. moss* bag.

Particulate matter is a predominate form of trace elements emissions in urban areas and uptake capacity of mosses mainly depends on passive physico-chemical entrapment and adsorption of elements on cell walls. Total element contents of mosses may be considered as the result of a balance between an input from wet and dry deposition, and output determined by: (i) washing of particulate materials by rain; (ii) leaching of some ions due to precipitation (especially acid rain); (iii) cation displacement, depending on their relative affinities for binding sites and concentrations; (iv) cellular damage due to environmental stress [3].

The exposure period is especially critical in moss biomonitoring surveys [4]. If exposure time is too long, saturation of exchange sites

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on the moss membrane may occur, and preferential displacement or exchange of elements as well. Also, heavy metals and other elements may "occupy" the exchange sites on moss membrane cells, so that they are effectively immobilized [15]. Little and Martin [12] and Ratcliffe [16] found an exposure period of 4 weeks to be optimal. Goodman et al. [17] found that the retention of metals by mossbags was directly proportional to the exposure time and was linear for up to 10 weeks for Co, Ni, Cu, Zn, Cd, and Pb. Displacement and saturation effects can be avoided by using the minimum exposure periods necessary for detecting trends. The other factor is the bag design, which should keep the humidity of the sample at a stable level to avoid drying [2].

The aim of this study was to assess study cumulative properties of moss *Sphagnum girgensohnii* bags (dry and irrigated – wet) with time as the relations between element accumulation and exposure time at different climatic conditions are not well understood.

# 2. Experimental

## 2.1. Study area

The study was carried out on the roof terrace of the Institute of Physics, ( $\varphi = 44^{\circ}51'$ N,  $\lambda = 20^{\circ}23'$ E,  $H_s = 92$  m) situated on the right bank of the Danube in Zemun (suburb of Belgrade). Belgrade has a moderate continental climate. The year-round average temperature is 11.7 °C, the hottest month is July, with an average temperature of 22.1 °C; annual precipitaion is about 700 mm.

The main source of ambient particulates is old vehicles. Leaded gasoline is still widely used. There are several large heating plants, run with natural gas or crude oil and many smaller plants run only with crude oil. Fuel used for domestic heating is mainly coal or crude oil, as well as natural gas introduced during the last few years. A detailed description of the Belgrade study area was given in Aničić et al. [18].

### 2.2. Experimental design

The moss, *S. girgensohnii* Rusow, was collected in May 2007 from a pristine wetland area located near Dubna, Russian Federation ( $\varphi = 56^{\circ}44'$ N,  $\lambda = 37^{\circ}09'$ E,  $H_s = 120$  m). This background area was chosen on the basis of results obtained by Culicov et al. [19].

In the laboratory, the moss was cleaned from soil particles and other foreign matter and air-dried. About 3 g of air-dried moss was packed loosely in  $10 \times 10 \text{ cm}^2$  bags of nylon net with 1-mm mesh size. The untreated samples were stored in the laboratory at room temperature until exposure.

Using specially constructed holders (1.5 m high) (Fig. 1) placed on a roof terrace, 5–10 m above the street level, the moss bags were exposed to the atmospheric deposition for different exposure periods (0.5–5 months) between June and November 2007. Thus, the moss bags were exposed for ten consecutive 15-day periods. Different treatments, with and without irrigation, were applied to the exposed moss in parallel [20]. The bags were wetted by placing them on the top of a cellulose (100%) sponge with the bottom immersed in distilled water. The whole setup was placed in a polyethylene box (130 mm × 110 mm × 80 mm). Bidistilled deionized water was added to the boxes at intervals of several days depending on the meteorological conditions (precipitation and temperature).

To check for possible contamination, the elemental composition of the unexposed sponge was determined after acid digestion, and the concentrations of all elements reported were below the detection limits. The polyethylene boxes were cleaned before use by soaking in 0.1% nitric acid for 48 h and washed with bidistilled



Fig. 1. Experimental setup: (A) dry, and (B) wet moss bags.

water. Sampling and preparation of moss bags were carried out wearing polyethylene gloves.

## 2.3. Chemical analyses

Initial concentration levels were determined in the unexposed moss material to be considered for the experiments. The moss from exposed bags was removed from the nylon net and air-dried at room temperature. The samples were manually homogenized and dried to constant weight at 40°C. After drying, portions of approximately 0.5 g of moss (dry weight) were digested for 2 h in an ULTRACLAVE microwave digester with 8 ml of concentrated nitric acid (Merck ultra pure) using a standard temperature program. After cooling to room temperature the digested samples were diluted with double-distilled and deionized water to a total volume of 60 ml. The concentrations of 49 elements (Be, Na, Mg, Al, Si, P, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Zn, Ga, As, Se, Rb, Sr, Y, Nb, Mo, Cd, Te, Cs, Ba, La, Ce, Pr, Sm, Eu, Tb, Dy, Er, Tm, Yb, Lu, Hf, Ta, W, Hg, Tl, Pb, Bi, Th, and U) were determined by inductively-coupled plasma mass spectrometry (ICP-MS). The homogeneity tests were performed on five sub-samples of 0.5 g taken from eight randomly chosen moss bags. The homogeneity was evaluated based on the variation in the concentration of the measured elements which were determined by ICP-MS. The results of the test showed no significant difference within the moss bag sub-samples. The relative standard deviation of these results varied from 3% to 6%. Accordingly, one sample (0.5 g) from each bag was analyzed throughout the experiment.

Quality control was performed using two international moss reference samples [21] and tea leaves GBW-07605 (Institute of Geophysical and Geochemical Exploration, Langfang, China). Those reference materials were analyzed in triplicate along with the survey of moss bags samples. The results for the reference materials were within 90–115% (analyzed/certified values, %) of certified values for the measured elements. Blank samples were also analyzed to assess possible contamination during sample preparation.

# Table 1

Average concentrations (µg g<sup>-1</sup> d.w.) of the 49 elements assayed in the initial moss, dry and wet moss bags (mb) of *Sphagnum girgensohnii* exposed from June 2007 for 1–5 months.

Element		Initial moss		Months of exposure									
		N=5	SD	1 N=30	SD	2 N=28	SD	3 N=30	SD	4 N=3	SD	5 N=3	SD
Ве	Dry mb	0.011	0.002	0.017	0.004	0.025	0.005	0.032	0.004	0.036	0.003	0.059	0.013
	Wet mb	0.011	0.002	0.022	0.006	0.028	0.003	0.034	0.005	0.040	0.004	0.049	0.006
Na	Dry mb	112	8.4	92	17.8	98 124	17.2	81	20.3	65 0C	1.1	49 72	3.5
Mg	Wet mb Dry mb	112 1905	8.4 315	158 1734	55.2 207	134 1944	51.3 228	132 2009	55.8 210	96 2120	9.5 103	73 1769	5.6 68
IVIg	Wet mb	1905	315	2156	242	2219	220	2005	210	1997	218	1752	56
Al	Dry mb	167	18	368	64	540	106	716	100	836	5	1321	234
	Wet mb	167	18	465	110	588	75	761	77	955	33	1153	21
Si	Dry mb	340	93	693	234	981	169	1276	175	1489	45	2088	193
	Wet mb	340	93	827	192	1061	137	1381	175	1785	165	2022	98
Р	Dry mb	1793	92	947	208	854	130	714	73	712	20	719	31
Cl	Wet mb Dry mb	1793 541	92 53	1171 139	311 140	1155 102	203 34	1109 63	192 31	1109 86	213 34	1200 42	85 11
CI	Wet mb	541	53	442	260	322	165	342	171	259	87	236	64
К	Dry mb	9574	443	4312	1761	2930	1141	1386	658	713	29	669	33
	Wet mb	9574	443	5133	1768	3463	1613	2722	1255	2203	716	1996	281
Ca	Dry mb	3638	430	4467	661	5395	768	6297	662	7027	648	8264	1366
	Wet mb	3638	430	5842	808	6718	582	7748	839	7650	768	8040	520
Sc	Dry mb	0.02	0.002	0.06	0.01	0.09	0.02	0.13	0.02	0.15	0.00	0.26	0.05
Ti	Wet mb Dry mb	0.02 4.25	0.002 0.26	0.07 7.52	0.02 1.52	0.10 10.95	0.02 2.32	0.14 14.72	0.02 2.28	0.18 16.44	0.01 0.54	0.21 27.66	0.01 4.99
11	Wet mb	4.25	0.20	7.32	1.60	8.93	1.35	14.72	1.69	16.84	1.19	20.01	4.99
v	Dry mb	0.52	0.01	1.13	0.43	1.78	0.78	2.42	0.69	2.72	0.21	5.91	0.87
•	Wet mb	0.52	0.01	1.16	0.32	1.58	0.28	2.08	0.32	2.56	0.25	3.44	0.07
Cr	Dry mb	0.26	0.02	0.83	0.39	1.53	0.73	2.16	0.73	2.33	0.13	5.32	1.44
	Wet mb	0.26	0.02	1.08	0.28	1.78	0.51	2.61	0.46	3.35	0.33	4.36	0.10
Mn	Dry mb	341.4	32.0	379.3	72.9	423.9	63.5	416.1	49.7	451.0	52.7	363.1	39.4
	Wet mb	341.4	32.0	413.0	60.3	391.3	50.2	360.1	57.4	290.7	21.9	259.2	44.5
Fe	Dry mb	150	20	349	69	500	118	665	113	763	13	1229	264
Со	Wet mb	150 0.17	20 0.03	441 0.34	110 0.06	535 0.44	63 0.11	693 0.53	84 0.08	812 0.55	20 0.03	1067 0.76	43 0.16
0	Dry mb Wet mb	0.17	0.03	0.34	0.08	0.44	0.08	0.55	0.08	0.55	0.03	0.76	0.18
Zn	Dry mb	23.7	0.6	29.4	3.3	36.0	5.5	44.7	6.3	47.8	0.05	62.5	7.2
211	Wet mb	23.7	0.6	35.3	4.6	41.6	5.3	49.8	6.3	63.2	14.2	69.4	7.3
Ga	Dry mb	0.041	0.003	0.089	0.021	0.135	0.032	0.188	0.031	0.224	0.006	0.371	0.071
	Wet mb	0.041	0.003	0.107	0.025	0.143	0.020	0.193	0.027	0.245	0.019	0.302	0.017
As	Dry mb	0.10	0.004	0.19	0.07	0.25	0.10	0.31	0.09	0.40	0.04	0.79	0.10
<u> </u>	Wet mb	0.10	0.004	0.33	0.12	0.53	0.25	0.78	0.40	0.95	0.14	1.79	0.14
Se	Dry mb	0.099	0.008	0.113	0.007	0.137	0.016	0.145	0.012	0.167	0.012	0.219	0.022
Rb	Wet mb Dry mb	0.099 50.5	0.008 3.7	0.134 25.3	0.023 8.4	0.151 18.1	0.019 6.8	0.186 8.5	0.028 4.5	0.215 3.6	0.014 0.2	0.277 2.8	0.007 0.2
RD	Wet mb	50.5	3.7	29.3	9.2	20.2	9.2	15.7	6.4	12.1	3.9	12.0	1.5
Sr	Dry mb	6.9	1.0	10.3	1.7	12.4	2.3	14.6	1.8	15.1	1.4	18.0	3.5
	Wet mb	6.9	1.0	15.2	2.8	18.3	2.0	21.1	2.1	19.6	1.3	20.0	3.3
Y	Dry mb	0.053	0.007	0.128	0.021	0.184	0.038	0.242	0.034	0.277	0.010	0.465	0.113
	Wet mb	0.053	0.007	0.151	0.034	0.191	0.030	0.261	0.038	0.349	0.017	0.424	0.009
Nb	Dry mb	0.017	0.002	0.026	0.004	0.034	0.006	0.041	0.005	0.038	0.001	0.053	0.006
Ма	Wet mb	0.017	0.002	0.018	0.008	0.015	0.008	0.015	0.013	0.029	0.006	0.038	0.005
Мо	Dry mb Wet mb	0.126 0.126	0.008 0.008	0.117 0.135	0.015 0.026	0.149 0.171	0.024 0.109	0.175 0.186	0.020 0.023	0.210 0.225	0.021 0.031	0.342 0.259	0.011 0.010
Cd	Dry mb	0.120	0.008	0.135	0.020	0.307	0.042	0.342	0.023	0.225	0.031	0.235	0.010
cu	Wet mb	0.179	0.019	0.296	0.028	0.329	0.104	0.312	0.029	0.334	0.079	0.320	0.015
Те	Dry mb	0.0010	0.0004	0.0016	0.0003	0.0020	0.0003	0.0024	0.0004	0.0024	0.0002	0.0040	0.0003
	Wet mb	0.0010	0.0004	0.0025	0.0014	0.0028	0.0006	0.0034	0.0007	0.0030	0.0004	0.0041	0.0008
Cs	Dry mb	0.205	0.009	0.137	0.027	0.128	0.018	0.119	0.013	0.119	0.004	0.160	0.028
	Wet mb	0.205	0.009	0.151	0.032	0.131	0.025	0.139	0.019	0.150	0.014	0.169	0.007
Ва	Dry mb	19.5	3.9	30.6	6.2	35.9	7.7	39.9	6.7	44.1	7.2	48.0	14.3
15	Wet mb	19.5	3.9	34.6	5.7	36.4	4.8	37.1	5.0	33.1	4.7	34.9	8.6
La	Dry mb Wet mb	0.099 0.099	0.011 0.011	0.251 0.301	0.044 0.068	0.362 0.381	0.075 0.064	0.483 0.537	0.070 0.166	0.564 0.695	0.015 0.043	0.997 0.817	0.309
Ce	Dry mb	0.099	0.011	0.301	0.068	0.381	0.064 0.143	0.537	0.166	0.695	0.043	0.817	0.022 0.592
	Wet mb	0.177	0.010	0.566	0.080	0.087	0.143	1.040	0.331	1.343	0.047	1.525	0.050
Pr	Dry mb	0.019	0.001	0.048	0.009	0.073	0.015	0.099	0.014	0.116	0.005	0.206	0.061
	Wet mb	0.019	0.001	0.060	0.014	0.078	0.014	0.113	0.037	0.147	0.012	0.175	0.008
Sm	Dry mb	0.013	0.001	0.033	0.006	0.051	0.012	0.069	0.011	0.083	0.003	0.144	0.033
	Wet mb	0.013	0.001	0.042	0.010	0.054	0.008	0.079	0.022	0.107	0.012	0.127	0.006
Eu	Dry mb	0.005	0.001	0.01	0.002	0.02	0.003	0.02	0.004	0.02	0.002	0.04	0.009
771-	Wet mb	0.005	0.001	0.01	0.003	0.02	0.002	0.02	0.005	0.03	0.002	0.04	0.003
Tb	Dry mb	0.0018	0.0002	0.0045	0.0008	0.0068	0.0013	0.0091	0.0013	0.0106	0.0004	0.0183	0.0045
	Wet mb	0.0018	0.0002	0.0056	0.0014 0.0024	0.0072	0.0012	0.0103	0.0022	0.0139	0.0013	0.0165	0.0007 0.0121
Dy	Dry mb	0.0057	0.0004	0.0138		0.0203	0.0041	0.0271	0.0039	0.0317	0.0002	0.0536	

#### Table 1 (Continued)

Element		Initial moss		Months of exposure									
				1		2		3		4		5	
		N=5	SD	N=30	SD	N=28	SD	N=30	SD	N=3	SD	N=3	SD
Er	Dry mb	0.005	0.0005	0.012	0.002	0.018	0.004	0.024	0.004	0.027	0.000	0.046	0.011
	Wet mb	0.005	0.0005	0.015	0.003	0.019	0.003	0.026	0.003	0.034	0.002	0.041	0.001
Tm	Dry mb	0.0007	0.0001	0.0016	0.0003	0.0023	0.0005	0.0030	0.0004	0.0035	0.0000	0.0060	0.0013
	Wet mb	0.0007	0.0001	0.0018	0.0004	0.0024	0.0004	0.0032	0.0004	0.0044	0.0003	0.0052	0.0003
Yb	Dry mb	0.0045	0.0006	0.0096	0.0017	0.0141	0.0030	0.0191	0.0027	0.0215	0.0004	0.0371	0.0074
	Wet mb	0.0045	0.0006	0.0113	0.0024	0.0147	0.0023	0.0201	0.0024	0.0268	0.0012	0.0318	0.0017
Lu	Dry mb	0.0006	0.00004	0.0013	0.0002	0.0020	0.0004	0.0027	0.0004	0.0031	0.0000	0.0052	0.0011
	Wet mb	0.0006	0.00004	0.0016	0.0003	0.0021	0.0003	0.0029	0.0003	0.0037	0.0002	0.0045	0.0003
Hf	Dry mb	0.0030	0.0004	0.0054	0.0008	0.0077	0.0017	0.0101	0.0015	0.0108	0.0005	0.0171	0.0032
	Wet mb	0.0030	0.0004	0.0051	0.0019	0.0041	0.0025	0.0047	0.0036	0.0106	0.0048	0.0132	0.0043
Та	Dry mb	0.0009	0.00001	0.0009	0.0001	0.0009	0.0001	0.0008	0.0001	0.0005	0.0001	0.0007	0.0001
	Wet mb	0.0009	0.00001	0.0004	0.0003	0.0002	0.0002	0.0003	0.0001	0.0007	0.0006	0.0005	0.0001
W	Dry mb	0.027	0.002	0.042	0.010	0.061	0.016	0.071	0.014	0.083	0.010	0.118	0.010
	Wet mb	0.027	0.002	0.038	0.010	0.044	0.024	0.039	0.025	0.083	0.010	0.078	0.011
Hg	Dry mb	0.027	0.001	0.036	0.005	0.044	0.006	0.045	0.004	0.045	0.002	0.051	0.006
0	Wet mb	0.027	0.001	0.030	0.004	0.030	0.006	0.030	0.005	0.027	0.003	0.033	0.004
Tl	Dry mb	0.014	0.002	0.029	0.005	0.031	0.007	0.031	0.005	0.026	0.003	0.025	0.002
	Wet mb	0.014	0.002	0.030	0.007	0.029	0.008	0.027	0.006	0.026	0.008	0.034	0.005
Pb	Dry mb	1.69	0.17	4.62	0.98	5.65	1.36	7.22	1.27	8.59	0.56	11.71	2.86
	Wet mb	1.69	0.17	5.34	0.99	6.27	1.01	7.56	1.31	8.95	0.82	10.90	0.70
Bi	Dry mb	0.008	0.0001	0.015	0.007	0.022	0.008	0.029	0.007	0.031	0.002	0.055	0.009
	Wet mb	0.008	0.0001	0.016	0.004	0.019	0.003	0.025	0.006	0.031	0.003	0.036	0.003
Th	Dry mb	0.016	0.0004	0.041	0.008	0.063	0.015	0.087	0.013	0.104	0.008	0.188	0.040
	Wet mb	0.016	0.0004	0.050	0.015	0.070	0.019	0.099	0.016	0.147	0.019	0.165	0.011
U	Dry mb	0.007	0.001	0.015	0.003	0.023	0.007	0.031	0.006	0.036	0.001	0.062	0.013
-	Wet mb	0.007	0.001	0.019	0.004	0.024	0.003	0.033	0.003	0.043	0.003	0.050	0.003

N - number of separate samples (moss bags); SD - standard deviation.

## 2.4. Statistical data analyses

Statistical analyses were carried out by using SAS statistical package (SPSS 8).

Student's *t*-test was used to check for the significant differences of element concentrations measured in dry and wet moss bags, and between different periods of exposure.

Principal component analysis (PCA), was used to identify the possible emission sources of different elements. PCA with Varimax normalized rotation was applied, which can maximize the factor loadings across variables for each factor. Factor loadings >0.71 are typically regarded as excellent and <0.32 as very poor [22]. In this study, all principal factors extracted from the variables with eigenvalues>1.0 were retained, as suggested by the \*Kaiser criterion [23].

# 3. Results and discussion

## 3.1. Elements concentration in the moss bags versus exposure time

The average concentrations  $(\mu g g^{-1})$  of the 49 elements assayed in dry and wet moss bags of *S. girgensohnii* before exposure (initial values), and after exposure for 1, 2, 3, 4 and 5 months are shown in Table 1.

Generally, the obtained concentration levels were in agreement with those observed in a previous study [18] using other techniques for the moss analysis.

Sodium, P, Cl, K, Rb, Cs, and Ta concentrations in exposed moss were below the initial concentrations. Loss of some of these elements from the moss tissue was also observed in several other studies employing moss bags [18,19,24–26]. Leakage of K and other physiologically active elements such as Na, Cl and P may reflect cell damage [24,26] or the displacement of some ions by other incoming ions with greater affinities for the cation exchange sites on moss cell walls [26]. In the case of Mg and Mn there was no significant difference in concentration before and after the moss exposure, as also previously observed [18]. For all other elements the concentrations increased over the exposure periods in both dry and wet moss bags. Linear increase of concentrations during exposure was observed for most elements showing significant difference in accumulation between 1, 2 and 3 months of exposure (p < 0.001). The same trend was observed for 4 and 5 months. Exceptions were the elements: Tl and Hg (wet moss bags) significantly enriched only in 1-month period of exposure. More erratic time trends appeared for Te and W (dry and wet), and Hf and Nb (wet only), cf. Table 1.

Comparison of element accumulation by dry and wet moss bags indicated higher cumulative properties of wet moss for many of the studied elements: Sr, Se, As, Zn, Ca, Mg, Te (p < 0.001), and Al, Cr, Sm, Si, Be, Ce, Co, Mo, Dy, La (p < 0.05). However, Hf, Nb, Ti (p < 0.001), and W (p < 0.05) were more accumulated in dry moss bags.

For some elements, such as Cd, Ba, Bi, Eu, and Ga, accumulation levels were of the same order in wet and dry moss bags.

Also, loss of the elements P, K, Na, Rb, Cs, and Cl from moss tissue during exposure was lower (p < 0.001) lower in wet moss.

Growth and nutrient uptake may be strongly suppressed by intermittent desiccation [15]. Permanently irrigated moss bags buffer the effect of external metrological conditions and can keep a physiological activity during a longer exposure [27]. The wet moss bags (living) may at least partly incorporate the elements in their tissues by active accumulation, being less susceptible to modification by precipitation and thus better reflecting the atmospheric pollution conditions [28]. Still, after a rain event low physiological activity of dry (unwatered) moss is recovered rapidly to a normal level [15,27]. Many elements are added partly with precipitation in dissolved form, and the continued exposure to precipitation may cause some of the initially particle-bound matter to dissolve and become available to active and passive processes on the moss surface affecting dissolved species.

The S. moss species rapidly accumulate cations originating from rainwater and dry deposition, releasing hydrogen ions into the surrounding water in exchange. The cell wall acts like an ion exchanger [28]. These mosses have large number of protonated anionic functional groups (ion exchange sites) in the form of uronic acid (>50%

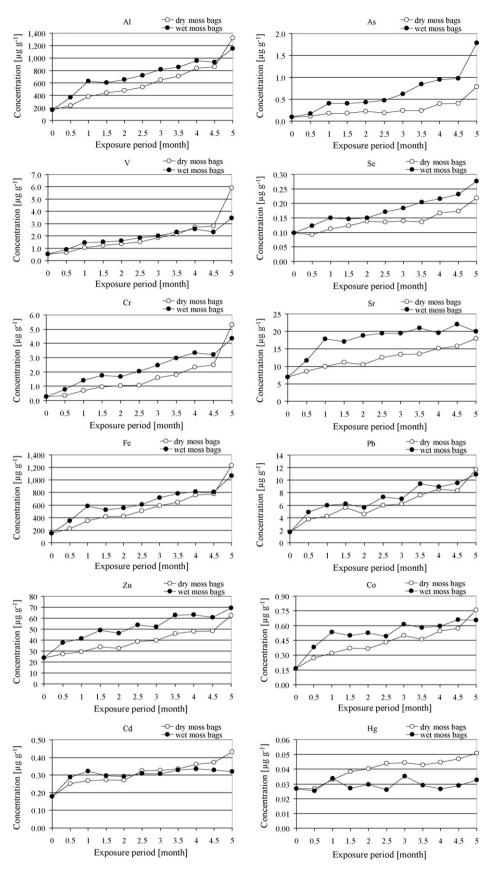


Fig. 2. Concentration (µg g<sup>-1</sup>) of the accumulated elements: Al, V, Cr, Fe, Co, Zn, As, Se, Sr, Cd, Hg, and Pb in moss bags from June to October 2007 in steps of 15 days.

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Table 2
Factor loadings after Varimax rotation for elements determined in dry moss bags.

# Table 3 Factor loadings after Varimax rotation for the elements studied in wet moss bags.

Elements	Factor 1	Factor 2	Factor 3	Factor 4
Ве	0.93	0.18	0.16	0.08
Na	-0.42	-0.65	0.09	-0.06
Mg	0.21	0.24	0.83	-0.27
A1	0.95	0.22	0.20	0.03
Si	0.87	0.30	0.23	-0.11
)	-0.37	<b>-0.85</b>	-0.13	0.07
21	-0.16	- <b>0.80</b>	0.01	-0.14
K	- <b>0.58</b>	<b>-0.74</b>	-0.28	0.04
Ca	0.77	0.15	0.57	0.11
c	0.95	0.24	0.18	-0.02
ï	0.94	0.28	0.14	-0.01
/	0.92	0.25	0.04	0.01
Cr	0.93	0.23	0.06	0.05
Mn	0.06	0.10	0.91	0.11
e	0.94	0.20	0.22	0.10
Co	0.80	0.13	0.37	0.39
ľn	0.86	0.29	0.32	-0.09
Ga	0.95	0.26	0.14	-0.05
As	0.91	0.16	-0.02	0.05
Se	0.87	0.12	0.25	0.00
Rb	-0.62	-0.70	-0.26	0.13
Sr	0.72	0.13	0.54	0.34
·	0.95	0.18	0.21	0.08
۱b	0.79	0.38	0.24	0.11
/10	0.94	0.06	0.09	-0.05
d	0.71	0.19	0.48	0.28
2	0.70	0.22	0.18	-0.19
S	0.09	-0.85	-0.30	0.14
a	0.55	-0.01	0.56	0.51
a	0.96	0.16	0.18	0.03
e	0.96	0.16	0.19	0.04
r	0.96	0.17	0.19	0.02
m	0.96	0.19	0.18	0.02
u	0.94	0.22	0.17	0.02
b	0.94	0.18	0.19	0.04
)y	0.95	0.19	0.20	0.03
rу Г	0.95	0.13	0.19	0.05
'n	0.95	0.21	0.18	0.00
Ъ	0.96	0.23	0.10	0.02
u	0.95	0.23	0.18	0.02
If	0.92	0.26	0.19	-0.04
à	-0.43	-0.07	-0.23	-0.04 <b>0.52</b>
d V	0.80	0.15	0.12	0.03
v Ig	0.60	0.15	0.45	0.03
1g 1	0.06	-0.03	0.45	0.28
b	0.06	0.21	0.23	0.82
b i	0.88	0.30	0.25	
h				0.01
	0.96	0.21	0.13	-0.07
J	0.94	0.25	0.15	0.05
/ariance (%)	0.65	0.11	0.09	0.04

PCA loadings >0.5 are marked in bold.

cation exchange capacity—CEC), whilst phenolic compounds are responsible for about 25% of CEC) [15,29]. The *Sphagnum* species are capable of absorbing great amounts of water and keeping it within its water-carrying large cells [28]. Permanent irrigation of moss enables binding of heavy metal ions for ion exchange sites to a higher extent than in dry moss. Also, water-soluble elements from deposited particles became more available for uptake by moss.

Fig. 2 presents the concentrations of accumulated elements (Al, V, Cr, Fe, Co, Zn, As, Se, Sr, Cd, Hg, and Pb) by dry and wet moss bags with time in steps of 15-days, as well as their initial values. These elements are typical tracers for urban air pollution (motor vehicles, oil burning, coal combustion, waste incineration, etc.). An increasing trend of accumulation with time is evident for all of these elements for both types of moss bags. The elements were accumulated linearly over periods of 4 months. During the fifth month, the concentrations increased rapidly in both types of moss bags, reflecting the start of heating season (coal combustion tracers: Cd, Fe, Hg, Pb, Se, V, Zn) in Belgrade and additional emission

Elements	Factor 1	Factor 2	Factor 3	Factor 4
Ве	0.84	0.08	0.07	0.32
Na	-0.15	- <b>0.88</b>	0.07	-0.07
Mg	-0.06	-0.02	-0.09	0.18
Al	0.97	0.00	0.05	0.15
Si	0.96	0.07	0.05	-0.05
Р	0.17	-0.63	-0.08	0.17
Cl	-0.03	-0.84	-0.09	0.10
К	-0.40	- <b>0.87</b>	0.13	-0.03
Ca	0.72	0.08	-0.09	0.37
Sc	0.98	0.02	0.05	0.05
Ti	0.92	0.06	0.32	0.00
V	0.90	0.24	0.04	0.01
Cr	0.88	0.23	0.00	0.01
Mn	-0.60	-0.11	0.10	0.46
Fe	0.91	0.06	0.05	0.28
Co	0.66	-0.22	0.01	0.60
Zn	0.81	0.10	0.20	0.07
Ga	0.94	0.16	0.06	0.01
As	0.66	0.36	-0.02	0.08
Se	0.83	0.25	-0.02	0.08
Rb	-0.43	- <b>0.85</b>	0.14	0.03
Sr	0.45	0.09	-0.27	0.35
Y	0.98	-0.04	0.07	0.35
Nb	0.16	-0.15	0.93	0.10
Mo	0.45	0.01	-0.04	0.01
Cd	0.45	0.33	0.13	
				0.54
Te	0.35	-0.27	-0.12	0.22
Cs	0.22	-0.76	0.22	-0.06
Ba	0.09	-0.18	-0.15	0.86
La	0.95	-0.06	0.01	0.00
Ce	0.95	-0.07	0.00	0.01
Pr	0.95	-0.07	0.00	0.00
Sm	0.97	-0.01	0.02	0.00
Eu	0.97	0.04	0.02	0.02
Tb	0.98	-0.05	0.06	0.04
Dy	0.99	-0.02	0.06	0.05
Er	0.99	0.02	0.06	0.06
Tm	0.98	0.03	0.07	0.05
Yb	0.98	0.06	0.07	0.05
Lu	0.98	0.04	0.07	0.04
Hf	0.24	-0.03	0.91	-0.06
Та	-0.11	0.10	0.78	-0.03
W	0.24	-0.25	0.73	0.05
Hg	0.12	-0.15	0.19	0.36
Tl	0.01	-0.52	-0.02	0.43
Pb	0.76	0.25	-0.06	0.33
Bi	0.67	0.39	0.10	0.05
Th	0.95	0.07	0.11	-0.06
U	0.97	0.13	0.06	0.06
Variance (%)	0.54	0.11	0.07	0.05

PCA loadings >0.5 are marked in bold.

sources in the winter [30]. In the last exposure period (October), higher enrichment was evident for most of the above elements in dry moss bags than in wet. It may be related to passive phenomena of surface adsorption of fly ash as a dominant residue generated by coal combustion. Coarse and sparingly soluble particles were more efficiently trapped by dry moss bags.

# 3.2. Principal component analysis (PCA)

According to principal component analysis of the data set four factors were extracted for dry and seven for wet moss bags in total. The first four factors for both moss bags are presented on Tables 2 and 3 (factors 5, 6 and 7 accounted for less than 10% of the total variance).

Table 2 presents four extracted factors for the dry moss bags set of data explaining 89% of the total variance. The first factor, explaining most of the variance (65%) had high loadings for most of the elements, representing urban impact which is a mixture of several antropogenic emissions including vehicle traffic, fossil fuel combustion, re-suspended road dust as well as aeolian transport of finely divided material originally derived from soil. The second factor, with 11% of the total variance, showed high factors loading for P, Cs, Cl, K, Rb, and Na, and pointed to the physiologically active elements there were leached from the moss tissue during exposure. Factors 3 and 4 accounting for 9% and 4% of the variance included Mn, Mg, Ca, Ba and Sr; and Tl, Ta and Ba respectively as the most significant elements.

Principal component analysis was also applied for the wet moss bag data (Table 3) and the first three factors explained 77% of the total variance. The first factor, accounting for 54%, of the variance had high loadings for similar set of elements as in the dry moss bags. The second factor described 11% of the variance and was attributed to the major nutritive elements in moss Na, K, Rb, Cl, Cs, P and Tl. The third factor (7%) contained a significant part of Nb, Hf, Ta, and W and factor 4 (5%) contained Ba, Co, and Cd.

Multivariate analysis (PCA) showed the similar pattern of the elements grouping in the factors for dry and wet moss samples. A majority of the elements were grouped in factor 1 indicating the impact of more than one pollution sources characteristic for urban areas without detailed source apportionment. Since in the studied semi-urban area there were no specific strong pollution sources, grouping of the elements by PCA rather presents different accumulation trend of the elements in moss. Factor 1 was strongly correlated with the elements showing positively linear accumulation trend with exposure, while factor 2 contained the elements with decreasing accumulation trend. Elements contained in factors 3 and 4 showed discontinual curve of accumulation with exposure periods. Some of the differentiation of elements in wet moss bags is probably due to different solubility of some elements on dry and wet moss surface, and consequently differences in accumulation of the elements.

# 4. Conclusions

*S. girgensohnii* moss bags, both dry and wet, showed a linear trend of accumulation during 1–5 months of exposure for a majority of the elements studied: Al, Si, Ca, Ti, V, Cr, Fe, Co, Zn, Ga, As, Se, Sr, Cd, Te, Ba, Hg, Pb, and several rare-earth elements. Higher accumulation in wet moss bags was evident for the following elements: Sr, Se, As, Zn, Ca, Mg, Te; Al, Cr, Sm, Si, Be, Ce, Co, Mo, Dy, La, Hf, Nb, Ti, and W.

Very similar trends of element accumulation for dry and wet moss bags indicates that both methods of exposure may be used as appropriate tools for biomonitoring of trace elements in air. However, in cases of relatively low air pollution load wet moss bags could be a better choice by showing higher accumulation capacity, presumably due to prolonged vitality of the moss. In this case exposure periods of up to 5 months may be preferable in order to improve the sensitivity of the method.

Principal component analysis extracted four (for dry moss bags) and seven (for wet moss bags) factors. The first factor, explaining >50% of the variance, can be attributed to mixed urban pollution sources and contained all elements showing a continuously increasing accumulation trend with exposure time.

The results of this work generally confirmed that the use of . *girgensohnii* moss bags is a simple, sensitive and inexpensive way of obtaining extensive information on deposition levels of atmospheric trace elements.

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