Arch. Biol. Sci., Belgrade, 58 (2), 95-104, 2006.

DETERMINATION OF HEAVY METAL DEPOSITION IN THE COUNTY OF OBRENOVAC (SERBIA) USING MOSSES AS BIOINDICATORS II: CADMIUM (Cd), COBALT (Cd), AND CHROMIUM (Cr)

V. VUKOJEVIĆ¹, M. SABOVLJEVIĆ^{1,4}, ANETA SABOVLJEVIĆ¹, NEVENA MIHAJLOVIĆ², GORDANA DRAŽIĆ², and Ž. VUČINIĆ³

¹Institute of Botany, Faculty of Biology, University of Belgrade, 11000 Belgrade, Serbia and Montenegro ²INEP, 11080 Zemun, Serbia and Montenegro

³Center of Multidisciplinary Studies, University of Belgrade, 11000 Belgrade, Serbia and Montenegro ⁴Nees Institue of Plant Biodiversity, Rheinische Friedrich Wilhelms University of Bonn, 53115 Bonn, Germany

Abstract - In the present study, the deposition of three heavy metals (Cd, Co and Cr) in the county of Obrenovac (Serbia) is determined using four moss taxa (*Bryum argenteum*, *Bryum capillare*, *Brachythecium* sp. and *Hypnum cupressiforme*) as bioindicators. Distribution of average heavy metal content in all mosses in the county of Obrenovac is presented in maps, while long term atmospheric deposition (in the mosses *Bryum argenteum* and *B. capillare*) and short term atmospheric deposition (in the mosses *Brachythecium* sp. and *Hypnum cupressiforme*) are discussed and in tables. Areas of the highest contaminations are highlighted.

Key words: Heavy metal deposition, mosses, bioindicators, Serbia

UDC 582.32(497.11):57.047

INTRODUCTION

Surveillance of heavy metals in mosses was originally established in the Scandinavian countries in the 1980s. However, the idea of using mosses to measure atmospheric heavy metal deposition was developed already in the late 1960s (R h ü l i n g and T y l e r, 1968; T y l e r, 1970). It is based on the fact that mosses, especially the carpet-forming species, obtain most of their nutrients directly from precipitation and dry deposition. Nowadays, this method is widely used in many countries (S c h a u g et al., 1990; S é r g i o et al., 1993; K u i k and W o l terbeek, 1995; Berg and Steinnes, 1997a; Pott and Turpin, 1998; Sucharova and Suchara, 1998; Grodzinska et al., 1999; Tsakovski et al., 1999; Fernández et al., 2000, 2002; Gerdol et al., 2000; Loppi and Bonini, 2000; Figueira et al., 2002; Schilling and Lehman, 2002; Salemaa et al., 2004; Peñuelas and Filella, 2002; Cucu-Man et al., 2002). Mosses have also been used to analyze contaminants spreading around thermal power plants (Tonguç, 1998; Carballeira and Fernández, 2002) or oil-fired power plants (Genoni *et al.*, 2000).

Moreower, some bryophytes are known to be heavy metal bioindicators of heavy metals in their environments (S a m e c k a – C y m e r m a n *et al.*, 1997; O n i a n – w a, 2001; N i m i s *et al.*, 2002; C u o t o *et al.*, 2003; S c h r ö d e r and P e s c h, 2004) and are often used in environmental monitoring (R a s m u s s e n and A n – d e r s e n, 1999; G i o r d a n o *et al.*, 2004; C u n y *et al.*, 2004; G s t o e t t n e r and F i s h e r, 1997; Z e c h – m e i s t e r *et al.*, 2005).

In the present investigations, we decided to use two acrocarpous moss species (*Bryum argenteum* Hedw. and *Bryum capillare* Hedw.) that can give us an idea of long term atmospheric deposition, inasmuch as they are attached to the substrate and also accumulate metals deposed during the last few decades in the surface layers of substrate. In addition, some other *Bryum* species are considered from the standpoint of trace metal deposition (S c h i n t u *et al.*, 2005).

Two pleurocarpous taxa (*Brachythecium* sp. and *Hypnum cupressiforme* Hedw.) were used to scan short term atmospheric deposition of heavy metals, considering that these taxa are not strongly attached to the substrate and accumulate mostly from precipitation (T h ö n i *et al.*, 1996; F a u s – K e s s l e r *et al.*, 2001; F e r n á n d e z and C a r b a l l e i r a , 2001; C u o t o *et al.*, 2004).

Mosses are better than other higher plants in scanning heavy metal deposition because: they are perennial without deciduous periods; they have high cation exchange capacity that allows them to accumulate great amounts of heavy metals between the apoplast and symplast compartments without damaging vital functions of the cells (V á s q u e z et al., 1999). One of the main factors influencing cation exchange capacity is the presence of polygalacturonic acids on the external part of the cell wall and proteins in the plasma membrane (A c e t o et al., 2003). Mosses do not possess thick and strong protective layers like cuticles. More about hyperaccumulation in plants and moss metal accumulation peculiarities can be found in Prasad and Freitas (2003). Bryum argenteum has already been shown to have special metal accumulation peculiarities (A c e t o et al., 2003; V u k ojević et al., 2005).

Also, this time-integrated way of measuring patterns of heavy metal deposition from the atmosphere to terrestrial ecosystems, besides being spatially oriented, is easier and cheaper than conventional precipitation analyses, as it avoids the need for deploying large numbers of precipitation collectors. The higher trace element concentration in mosses compared to rain water makes analysis more straightforward and less prone to contamination (B e r g and S t e i n n e s, 1997b).

Use of mosses to investigate heavy metal deposition shows transboundary heavy metal pollution and can indicate the paths by which atmospheric pollutants enter from other territories or reveal their sources within the investigated area.

Although 15 heavy metals were analyzed in all, only deposition and distribution of cadmium, cobalt and, chromium are treated in the present study, due to limitation of space. The presence and distribution of aluminum, arsenic and boron in the county of Obrenovac as screened by mosses were considered in an already published paper (S a b o v l j e v i ć *et al.*, 2005). The content of cadmium in the Earth's crust is estimated to be 0.13 g/t. Pure cadmium minerals are very rare. In nature it usually occurs in minerals together with zinc. Cadmium is obtained as a collateral product in zinc production, and this accounts for more than 95% of all its production (S t o e p p l e r, 1991). Yearly production is ca. 20000 t (M e t a l l g e s e l l s c h a f t, 1993). Cadmium is widely used in ship and vehicle manufacturing to protect steel plating from corrosion, as well as in production of nickel-cadmium batteries. It is used as a neutron absorber in photocells and in nuclear technologies. Owing to its high toxicity in the environment, the use of cadmium has decreased slightly in the last decades (T r e u b, 1996).

Plants (cultivated or wild) accumulate cadmium in high quantities. The roots and leaves suffer most from accumulation of cadmium, which causes abnormal development, necrosis, and death (B e r g m a n n, 1988). Small quantities of cadmium are extremely toxic for humans and animals. Cadmium replaces zinc in zinc containing enzymes, which causes Itai-Itai disease with lethal consequences. The chronic presence of cadmium binds calcium out of bones, causing osteoporosis. In addition, it causes high blood pressure and has cancerogenic, mutagenic, and teratogenic effects (M e r i a n, 1984).

Emission should not exceed 0.1 mg/m^3 , and maximmum permissible values are 1.5 ng/m^3 in terrestrial ecosystems, 0.1 mg/l in water, and 0.005 mg/l in drinking water (T h ö n i and S e i t l e r, 2004).

Cobalt is present in the Earth's crust in quantities 18 g/t and together with scandium is the rarest element in its upper layers. This heavy metal is a collateral product in production of nickel, cupper and lead (G r e e n w o o d and E a r n s h a w, 1988). The yearly production is ca. 24300 t (M e t a l l g e s e l l s c h a f t, 1993). Cobalt is widely used in the alloy tungsten carbide, and some 10 % of produced cobalt is employed in the making of permanent magnets. The rest of produced cobalt is used in the ceramics and paint industries (T r e u b, 1996). Cobalt is present in traces in the air. In supstrata and water emission is highly present and can form sediments. Anthropogenic emission is ca. 4400 t and natural ca. 7000 t (L a n t z y and M a c k e n z i e , 1979). Although cobalt is essential for humans, animals, and plants, especially as a component of vitamin B12, in higher quantities it is toxic. In humans and animals cobalt dust and salt cause cancer, while in plants only very high concentrations cause abnormalities (M e r i a n, 1984; B e r g m a n n, 1988). The emission limit is 1 mg/m^3 and 0.5 mg/l in water.

Chromium is one of the most widely present elements in the Earth's crust. It is extensively used for chromization, in engineering, and in the manufacture of vehicles, airplanes, chemicals, etc. The yearly production is ca. 13 million tons (M e t a l l g e s e l l s c h a f t, 1993). Emission of chromium in both air and water occurs at the highest rate in the metallurgy industry. A certain part of chromium emission (Cr(VI)) comes from the cement and concrete industry.

The toxic effect of chromium to plants is known only from *ex vivo* experiments (S c h e f f e r and S c h a c h t s c h a b e l, 1984). For animals and humans, chromium is an essential element. It is known for its role in insulin effects (glucose tolerance factor), which occur due to the role of chromium in glucose exchange. The effects of Cr(III) and metallic Cr are not precisely known, but Cr(VI) complexes cause acute and chronic toxicity. Chromate and dichromate from cement can be severely toxic. Chromium dust and/or acidic deposition can cause lung cancer (M e r i a n , 1984). Emission tolerated by law is 5 mg/m³. The limit of chromium in soil is 50 mg/kg. In water it is 2 mg of all Cr/I [(0.1 mg Cr(VI)/l)], while in drinking water it is 0.02 mg Cr(VI)/l.

MATERIAL AND METHODS

The acrocarpous mosses *Bryum argenteum* and *Bryum capillare* were used to research long-term atmospheric deposition, while the pleurocarpous *Brachythecium* sp. and *Hypnum cupressiforme* were used to scan short term atmospheric deposition in the county of Obrenovac (Serbia). *Hypnum cupressiforme* is one of the standard species used in Europe to survey heavy metal deposition survey (B u s e *et al.*, 2003), while the other three are standard in Europe, but do not grow in this region. In estimating which other species are eligible for use in monitoring heavy metal deposition, we relied on the experience of T h ö n i (1996), H e r p i n *et al.* (1994), S i e w e r s and H a i r p i n (1998), Z e c h m e i s t e r (1994), and R o s s (1990).

As for as possible, moss sampling was conducted according to guidelines set out in the experimental protocol for a survey performed in 2000/2001 (UNECE, 2001). Details of the procedure are given in R ü h l i n g *et al.* (1998). Each sampling site was located at least 300 m from main roads and populated areas and at least 100 m from any road or single house. In forests or plantations, samples were collected in small open spaces to preclude any effect of canopy drip. Sampling and sample handling were carried out using plastic gloves and bags. About three moss samples were collected from each site. Dead material and litter were removed from the samples. Green parts of mosses were used for the analyses.

The county of Obrenovac was chosen for this investigation because of its industry and location.

Each sampling site was GPS located with a precision of ± 10 m, and GPS data (Germin) were digitalized on the maps using the following softwares: OziExplorer 3.95.3b, © D&L Software Pty. Ltd.; and WinDig 2.5 Shareware, © D.Lovy.

All material was collected during November of 2002.

Not more than one site was chosen in a 50x50 m square. Seventy-five localities were chosen out of 129 for comparison and further analyses. The selection was based on the presence of all investigated species and yearly biomass.

More than 500 samples were analyzed.

After collecting, samples were dried as soon as possible in a drying oven to constant dry weight (dw) at a constant temperature of 35° C, then stored at -20° C.

Following homogenization in porcelain, the samples were treated with 5+1 parts of nitric acid and perchloric acid (HNO₃:HClO₄ = 5:1) and left for 24 hours.

After that, a Kjeldatherm digesting unit was used for digestion at 150-200°C for about one hour. Digested samples were filtered on qualitative filter paper to dispose of silicate remains, and volume of the samples was then normated to 50 ml.

Cadmium, cobalt, and chromium were detected by AAS on a Pye Unicam SP9 atomic absorbance spectrophotometer from Philips using the flame of acetylene/nitrogen-suboxide.

For explanation of the results and their map presentation, the following statistical parameters were used: av-



Fig. 1. Maps of the county of Obrenovac showing sampling sites (a) and extrapolated maps of average deposition of selected elements in mosses (b). 1. cadmium deposition 2. cobalt deposition 3. chromium deposition.

	Locality and species			Cd	Co	Cr
Sample No.	sampled	Longitude	Latitude	(mg/g)	(mg/g)	(mg/g)
1	Vinogradi H.c.	20.163702	44.391758	0.0103	0.0217	0.0000
2	Moštanica 1 H.c.	20.183672	44.384249	0.0131	0.1377	0.0000
3	Iskra 1 B.c.	20.155235	44.392722	0.0068	0.0048	0.0790
4	Iskra 2 B.a.	20.152826	44.393284	0.0061	0.0346	0.0315
5	Iskra 1 H.c.	20.155235	44.392722	0.0079	0.0000	0.0000
6	Iskra 2 B.c.	20.152826	44.393284	0.0038	0.0295	0.0403
7	Rvati 1 B.c.	20.118796	44.396930	0.0192	0.0589	0.0448
9	Deponija B entr. 1 B.c.	20.023331	44.383735	0.0061	0.0514	0.0490
10	Zabrežje 1 B.c.	20.121273	44.411245	0.0082	0.0206	0.0377
11	Ušće 2 B.c.	20.066441	44.419235	0.0055	0.0427	0.0779
12	Vinogradi B.c.	20.163702	44.391758	0.0027	0.0000	0.0421
13	Iskra 1 B.a.	20.155235	44.392722	0.0054	0.0405	0.0675
14	Ušće 2 H.c.	20.066441	44.419235	0.0041	0.0555	0.0411
15	Ušće 1 B.c.	20.070343	44.414738	0.0095	0.0622	0.0000
16	Urozv Bra	20.079770	44.389043	0.0070	0.0590	0.0538
17	Zabrežje 2 H.c.	20.133796	44.408293	0.0095	0.0386	0.0293
18	Orašac 1 H.c.	20.021819	44.336717	0.0046	0.0385	0.0176
19	Hotel B.a.	20.127451	44.394049	0.0025	0.0504	0.0542
20	Moštanica 1 H.c.	20.183672	44.384249	0.0061	0.0192	0.0000
21	Grabovac 1 H.c,	20.046934	44.359997	0.0039	0.0217	0.0132
22	Šab.put nadv. B.c.	20.094085	44.391367	0.0120	0.0756	0.0971
23	Vranić H.c.	20.152122	44.347529	0.0029	0.0326	0.0223
24	Jasenak 2 Bra.	20.156246	44.360071	0.0036	0.0658	0.0520
25	Dren 1 Bra.	20.023224	44.358238	0.0040	0.0451	0.0343
26	Veliko Polje 1 H.c.	20.108648	44.365954	0.0102	0.0430	0.0000
27	Grabovac 1 B.c.	20.046934	44.359997	0.0028	0.0234	0.0000
28	Belo Polje 1 B.c.	20.118064	44.382783	0.0039	0.0606	0.0704
29	Brović 1 B.c.	20.072201	44.335108	0.0034	0.0379	0.0231
30	Ljubinić 2 Bra.	20.026762	44.334832	0.0278	0.0335	0.0183
31	Hotel H.c.	20.127451	44.394049	0.0049	0.0560	0.0551
32	Grabovac 1 Bra.	20.046934	44.359997	0.0032	0.0365	0.0333
33	Ljubinić 2 B.c.	20.026762	44.334832	0.0034	0.0484	0.0364
34	Veliko Polje 4 H.c.	20.109057	44.341908	0.0028	0.0371	0.0536
35	Zabran 3 H.c.	20.137615	44.396905	0.0035	0.0256	0.0000
36	Zabran 1 H.c.	20.139396	44.398268	0.0055	0.0283	0.0329
37	Orašac 3 H.c.	20.016612	44.343855	0.0382	0.0877	0.0000
38	Orašac 2 H.c.	20.020860	44.340639	0.0027	0.0320	0.0195
39	Zabran 2 B.a.	20.142377	44.401672	0.0035	0.0220	0.0201
40	Belo Polje 1 B.a.	20.118064	44.382783	0.0046	0.0481	0.0614
41	Orašac 2 Bra.	20.020860	44.340639	0.0025	0.0248	0.0323
42	Ljubinić 1 Bra.	20.037630	44.322132	0.0029	0.0422	0.0330
43	Grabovac B.a.	20.092788	44.365167	0.0024	0.0393	0.0410
44	Joševa H.c.	20.060545	44.310742	0.0071	0.0631	0.0518
45	Brović 2 Bra.	20.088929	44.318537	0.0043	0.0365	0.0392
46	Jasenak 2 B.a.	20.156246	44.360071	0.0043	0.0352	0.0355
47	Garbovac Bra.	20.092788	44.365167	0.0080	0.0759	0.1032
48	Baljevac 1 B.c.	20.152044	44.340743	0.0052	0.0573	0.0669
49	Joševa B.c.	20.060545	44.310742	0.0037	0.0472	0.0351
50	Joševa Bra.	20.060545	44.310742	0.0050	0.0387	0.0287
51	EPS B.c.	20.120401	44.388845	0.0058	0.0288	0.0211
52	Konatice II Bra.	20.148928	44.337410	0.0093	0.0561	0.0532

Table. 1. Deposition of Cd, Co and Cr in the county of Obrenovac screened by mosses. Abbreviations: H.c. – *Hypnum cupressiforme*, Bra. – *Brachythecium* sp., B.c. – *Bryum capillare*, B.a. – *Bryum argenteum*

V. VUKOJEVIĆ et al.

Table. 1. Continued.

	Locality and species			Cd	Co	Cr
Sample No.	sampled	Longitude	Latitude	(mg/g)	(mg/g)	(mg/g)
53	Zabran 1 B.a.	20.139396	44.398268	0.0055	0.0167	0.0305
54	Mislođinl 1 Bra.	20.136579	44.383096	0.0069	0.0513	0.0469
55	Brović 1 H.c.	20.072201	44.335108	0.0072	0.0242	0.0442
56	Mislođin 4 H.c.	20.134067	44.369616	0.0042	0.0219	0.0320
57	Stubline 2 H.c.	20.091649	44.345095	0.0113	0.1006	0.1256
58	Konatice 1 B.c.	20.162150	44.316265	0.0044	0.0221	0.0314
59	Zabran 3 B.a.	20.137615	44.396905	0.0079	0.0155	0.0282
60	Jasenak H.c.	20.143804	44.365736	0.0057	0.0336	0.0569
61	Konatice 2 B.a.	20.155831	44.322960	0.0081	0.5012	0.0936
62	Veliko Polje 4 B.c.	20.109057	44.341908	0.0044	0.0480	0.0875
63	Mislođin 1 Bra.	20.133857	44.387041	0.0057	0.0424	0.0722
64	Veliko Polje 3 B.c.	20.106117	44.344670	0.0199	0.0681	0.0777
65	Konatice II B.c.	20.148928	44.337410	0.0051	0.0573	0.0747
66	Mislođin 6 B.a.	20.164676	44.371027	0.0003	0.0028	0.0102
67	Stubline 1 H.c.	20.086353	44.357185	0.0068	0.0482	0.0480
68	Šabac road B.a.	20.094085	44.391367	0.0064	0.0631	0.0000
69	Dren 1 H.c.	20.023224	44.358238	0.0054	0.0544	0.0331
70	Zabran 2 B.c.	20.142377	44.401672	0.0036	0.0533	0.0556
71	Baljevac 2 H.c.	20.129432	44.342383	0.0046	0.0451	0.0769
72	Mislođin 5 B.a.	20.150813	44.367274	0.0048	0.0422	0.0385
73	Orašac 1 Bra.	20.021819	44.336717	0.0043	0.0383	0.0405
74	Konatice II H.c	20.148928	44.337410	0.0063	0.0282	0.0285
75	Šabac raod 1 Bra.	20.049094	44.396566	0.0069	0.0487	0.0534
76	TENT <b 3="" b.c.<="" td=""><td>20.003761</td><td>44.379624</td><td>0.0192</td><td>0.1081</td><td>0.0658</td>	20.003761	44.379624	0.0192	0.1081	0.0658
77	Šabac road 1 H.c.	20.094085	44.391367	0.0069	0.0251	0.0000
78	Ratari 2 Bra.	20.058939	44.387315	0.0038	0.0464	0.0053
79	TENT <b 1="" h.c.<="" td=""><td>19.593841</td><td>44.380930</td><td>0.0091</td><td>0.0328</td><td>0.0399</td>	19.593841	44.380930	0.0091	0.0328	0.0399
80	TENT <b 2="" h.c.<="" td=""><td>20.010398</td><td>44.374841</td><td>0.0023</td><td>0.0190</td><td>0.0208</td>	20.010398	44.374841	0.0023	0.0190	0.0208
81	Ratari 1 H.c.	20.065292	44.389672	0.0054	0.0438	0.0355
82	Ušće (Skela) B.c.	20.031781	44.409564	0.0025	0.0839	0.0383
83	Ratari 2 B.a.	20.058939	44.387315	0.0043	0.0471	0.0605
84	TENT <b 4="" b.a.<="" td=""><td>20.005827</td><td>44.387162</td><td>0.0059</td><td>0.0583</td><td>0.0347</td>	20.005827	44.387162	0.0059	0.0583	0.0347
85	TENT <b 2="" bra.<="" td=""><td>20.010398</td><td>44.374841</td><td>0.0029</td><td>0.0311</td><td>0.0441</td>	20.010398	44.374841	0.0029	0.0311	0.0441
86	TENT <b 1="" bra.<="" td=""><td>19.593841</td><td>44.380930</td><td>0.0083</td><td>0.0399</td><td>0.0546</td>	19.593841	44.380930	0.0083	0.0399	0.0546
87	TENT <b 4="" b.c.<="" td=""><td>20.005827</td><td>44.387162</td><td>0.0115</td><td>0.0268</td><td>0.0392</td>	20.005827	44.387162	0.0115	0.0268	0.0392
88	TENT <b 3="" b.c.<="" td=""><td>20.003761</td><td>44.379624</td><td>0.0060</td><td>0.0414</td><td>0.0756</td>	20.003761	44.379624	0.0060	0.0414	0.0756
89	Orašac 1 Bra.	20.021819	44.336717	0.0116	0.0687	0.0198
90	Ušće Bra.	20.031781	44.409564	0.0099	0.0998	0.1138
91	Šabac road 1 B.c.	20.049094	44.396566	0.0083	0.0405	0.0673
92	TENT <b bra.<="" entr.="" td=""><td>20.002958</td><td>44.394451</td><td>0.0165</td><td>0.0555</td><td>0.1183</td>	20.002958	44.394451	0.0165	0.0555	0.1183
93	Depoija 1 Bra.	20.087035	44.407417	0.0093	0.0442	0.0000
94	TENT <b 2="" b.c.<="" td=""><td>20.010398</td><td>44.374841</td><td>0.0042</td><td>0.0119</td><td>0.1013</td>	20.010398	44.374841	0.0042	0.0119	0.1013
95	Konatice 1 H.c.	20.162150	44.316265	0.0045	0.0273	0.0529
96	Mislođin 6 Bra.	20.164676	44.371027	0.0037	0.0277	0.0337
97	Mislođin 3 Bra.	20.136294	44.371922	0.0054	0.0416	0.0380
98	Mislođin 6 B.c.	20.164676	44.371027	0.0046	0.0475	0.0552
99	Jasenak 2 B.a.	20.156246	44.360071	0.0071	0.0421	0.0641
100	Mislođin 4 B.c.	20.134067	44.369616	0.0061	0.0486	0.0513
101	Zabran 1 Bra.	20.139396	44.398268	0.0088	0.0307	0.0337
102	Rojkovac 1 B.c.	20.117592	44.401807	0.0055	0.0409	0.0533
103	Rojkovac 1 Bra.	20.117592	44.401807	0.0104	0.0473	0.0617

	Locality and species			Cd	Co	Cr
Sample No.	sampled	Longitude	Latitude	(mg/g)	(mg/g)	(mg/g)
104	Rvati 1 Bra	20.118796	44.396930	0.0139	0.0721	0.0493
105	Rojkovac 1 B.a.	20.117592	44.401807	0.0089	0.0748	0.0768
106	Moštanica 3 Bra.	20.175487	44.380355	0.0069	0.0578	0.0923
107	Razu Bra.	20.065879	44.410726	0.0077	0.0432	0.0263
108	Ušće 3 Bra.	20.084220	44.411524	0.0044	0.0361	0.0512
109	Duboko 3 H.c.	20.176888	44.391497	0.0051	0.0240	0.0351
110	Zabrežje 1 Bra.	20.121273	44.411245	0.0097	0.0449	0.0298
111	Zabran 3 Bra.	20.137615	44.396905	0.0037	0.0490	0.0630
112	Moštanica 2 B.c.	20.180515	44.381400	0.0040	0.0478	0.0567
113	Razu B.a.	20.065879	44.410726	0.0084	0.0407	0.0495
114	Rvati 3 Bra.	20.115276	44.395254	0.0045	0.0445	0.0581
115	TENT <a 1="" bra.<="" td=""><td>20.096950</td><td>44.402553</td><td>0.0063</td><td>0.0527</td><td>0.0722</td>	20.096950	44.402553	0.0063	0.0527	0.0722
116	Moštanica 3 B.c.	20.175487	44.380355	0.0085	0.0449	0.0820
117	Zabrežje 2 Bra.	20.133796	44.408293	0.0074	0.0500	0.0609
118	Urozv B.c.	20.079770	44.389043	0.0071	0.0335	0.0408
119	Depoija 1 H.c.	20.087035	44.407417	0.0028	0.0580	0.0635
120	Zabrežje 2 B.a.	20.133796	44.408293	0.0052	0.0436	0.0530
121	Moštanica 1 B.c.	20.183672	44.384249	0.0043	0.0448	0.0622
122	Vinogradi B.a.	20.163702	44.391758	0.0056	0.0367	0.0315
123	Urozv H.c.	20.079770	44.389043	0.0061	0.0375	0.0428
124	Razu H.c.	20.065879	44.410726	0.0040	0.0407	0.0433
125	Duboko 1 B.a.	20.173260	44.398253	0.0021	0.0349	0.0383
126	Vinogradi Bra.	20.163702	44.391758	0.0046	0.0257	0.0469
127	Duboko Bra	20.146281	44.397974	0.0081	0.0381	0.0557
128	TENT <a 1="" b.c.<="" td=""><td>20.096950</td><td>44.402553</td><td>0.0028</td><td>0.0191</td><td>0.0305</td>	20.096950	44.402553	0.0028	0.0191	0.0305
129	Zabrežje 2 B.c.	20.133796	44.408293	0.0043	0.0454	0.0601
Median				0.0067	0.0470	0.0452

Table. 1. Continued.

erage values, standard deviation, minimum, maximum, and percent deviation. Map making and interpolation of exact data were done with Agis software (v1.71 32bite, © Agis Software, 2001).

RESULTS AND DISCUSSION

Since it was impossible to find all the sampled species at any precise locality, the average of all specimens is given in the map interpolation to get an idea of heavy metal deposition in the county of Obrenovac (Fig. 1). However, if we separate the values of deposition obtained from pleurocarpous (*Brachythecium* sp. and *Hypnum cupressiforme*) and acrocarpous (*Bryum argenteum* and *Bryum capillare*) mosses, it can be clarly seen that the first two give us an idea of short-term deposition and the last two of long-term deposition (Table 1). This can be easily explained in terms of the life forms of these mosses and their uptake of heavy metals. Pleurocarps are not closely attached to the substrate and thus receive the bulk of deposited heavy metals directly from the atmosphere (during their pauciennial life period) while acrocarps are strictly attached to substrata and get most of deposited heavy metals by substrate solution (metals deposed from the time that is longer than their paucienial life span).

Scanning of trace metal (Cd, Co, Cr) content in the county of Obrenovac (W. Serbia) clearly shows that the northwestern, western, and central parts are the most loaded with these three metals, as a result of heavy industry and intense traffic (Fig. 1). Also cadmium is deposited in somewhat higher amounts in the town of Obrenovac, cobalt in the southeastern part of the county, and chromium in its eastern and southeastern parts.

Thus, moss analysis is shown to be a valuable method for monitoring atmospheric deposition of trace elements.

V. VUKOJEVIĆ et al.

REFERENCES

- Aceto, M., Abollino, A., Conca, R., Malandrino, M., Mentasti and E. Sarzanini, C. (2003). The use of mosses as environmental metal pollution indicators. Chemosphere 50, 333-342.
- Berg, T. and Steinnes, E. (1997a). Recent trends in atmospheric deposition of trace elements in Norway as evident from the 1995 survey. The Science of the Total Environment 208, 197-206.
- Berg, T. and Steinnes, E. (1997b). Use of mosses (Hylocomium splendens and Pleurozium schreberi) as biomonitors of heavy metal deposition: form relative to absolute values. Environmental Pollution 98, 61-71.
- Bergmann, W. (ed.) (1988). Ernährunsstörungen bei Kulturpflanzen. Gustav Fischer Verlag, Stuttgart, New York, 1-762.
- Buse, A., Norris, D., Harmens, H., Büker, P., Ashenden, T. and Mills, G. (2003). Heavy metals in European mosses. Centre for Ecology and Hydrology, Bangor.
- Carballeira, A. and Fernández, J. A. (2002). Bioconcentration of the metals in the moss Scleropodoim purum in the area surrounding a power plant. A geotopographical predictive model for mercury. Chemosphere 47, 1041-1048.
- Cuoto, J. A., Fernández, J. A., Aboal., J. R. and Carballeira, A. (2004). Active biomonitoring of element uptake with terrestrial mosses: a comparison of bulk and dry deposition. Science of the Total Environment 324, 211–222.
- Cucu-Man, S., Mocanu, R. and Steinnes, E. (2002). Atmospheric heavy metal survey by means of mosses: regional study (Iaşi, Romania). Environmental Engineering and Management Journal 1(4), 533-540.
- Cuny, D., Denayer, F. O., de Foucault, B., Schumacker, R., Colein, P. and van Haluwyn, C. (2004). Patterns of metal soil contamination and changes in terrestrial cryptogamic communities. Environmental Pollution 129, 289–297.
- Faus-Kessler, T., Dietl., C., Tritschler, J. and Peichl, L. (2001). Correlation patterns of metals in the epiphytic moss Hypnum cupressiforme in Bavaria. Atmospheric Environment 35, 427-439.
- Fernández, J.A., Ederra, A., Núñez, E., Martínez-Abaigar, J., Infante, M., Heras, P., Elías, M.J., Mazimpaka, V. and Carballeira, A. (2002). Biomonitoring of metal deposition in northern Spain by moss analysis. The Science of the Total Environment 300, 115-127.
- Fernández, J. A. and Carballeira, A. (2001). A comparison of indigenous mosses and topsoils for use in monitoring atmospheric heavy metal deposition in Galicia (northwest Spain). Environmental Pollution 114 (3), 431-441.
- Fernández, J. A., Rey, A. and Carballeira, A. (2000) An extended study of heavy metal deposition in Galicia (NW Spain) based on moss analysis. The Science of the Total Environment 254, 31-44.
- Fugeira, R., Sérgio, C. and Sousa, A. J. (2002). Distribution of trace metals in moss biomonitors and assessment of contamination sources in Portugal. *Environmental Pollution* 118, 153–163.
- Genoni, P., Parco, V. and Santagostino, A. (2000). Metal biomonitoring with mosses in the surroundings of an oil-fired power plant in Italy. Chemosphere 41, 729-733.

- Gerdol, R., Bargazza, L., Marchesini, R., Alber, R., Bonetti, L., Lorenzoni, G., Achilli, M., Buffoni, A., De Marco, N., Franchi, M., Pison, S., Giaquinta, S., Palmieri, F. and Spezzano, P. (2000) Monitoring of heavy metal deposition in Northern Italy by moss analysis. Environmental Pollution 108, 201-208.
- Giordano, S., Sorbo, S., Adamo, P., Basile, A., Spagnuolo, V. and Castaldo-Cobianchi, R. (2004). Biodiversity and trace element content of epiphytic bryophytes in urban and extraurban sites of southern Italy. *Plant Ecology* **170**, 1–14.
- Greenwood, N. N. and Earnshaw, A. (1988). Chemie der Elemente. VCH Verlagsgeselschaft, Weinheim. 1-1707.
- Grodzinska, K., Szarek-Lukaszewska, G and Godzik, B. (1999). Survey of heavy metal deposition in Poland using mosses as indicators. Science of the Total Environment **253**, 41-51.
- Gstoettner, E. M. and Fisher, N. S. (1997). Accumulation of cadmium, chromium and zinc by the moss Sphagnum papillosum Lindle. Water, Air and Soil Pollution **93**, 321-330.
- Herpin, U., Markert, B., Siewers, U. and Lieth, H. (1994). Monitoring der Schwermetallbelastung in der Bundesrepublik Deutschland mit Hilf von Moosanalysen. Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit. Ökologie, Forschungbericht 180 02 087, 1-161.
- Kuik, P. and Wolterbeek, H. T. (1995). Factor analysis of atmospheric trace element deposition data in the Netherlands obtained by moss monitoring. Water, Air and Soil Pollution 84, 323-346.
- Lantzy, R.J. and Mackenzie, F. T. (1979). Atmospheric trace metals: global cycles and assessment of man's impact. Geochemica et Cosmochimica Acta 43, 511-525.
- Loppi, S. and Bonini, I. (2000). Lichens and mosses as biomonitors of trace elements in areas with thermal springs and fumarole activity (Mt. Amiata, central Italy). Chemosphere 41, 1333 -1336.
- Merian, E. (ed.) (1984). Metalle in der Umwelt, Verteilung, Analytik und biologiche Relevanz. Verlag Chemie, Weinheim. 1-722. Metallgesellschaft, (1993). Metallstatistik 1982-1992. Metallgesellschaft AG, Frankfurt am Main.
- Nimis, P.-L., Funagalli, F., Bizzotto, A., Codogno, M. and Skert, N. (2002). Bryophytes as indicators of trace metals pollution in the River Brenta (NE Italy). Science of the Total Environment 286, 233-242.
- Onianwa, P. C. (2001). Monitoring atmospheric metal pollution: a review of the use of mosses as indicators. *Environmental Monitoring and Assessment* 71, 13–50.
- Peñuelas, J. and Filella, I. (2002). Metal pollution in Spanish terrestrial ecosystems during the twentieth century. Chemosphere 46, 501–505.
- Pott, U. and Turpin, D. H. (1998). Assessment of atmospheric heavy metals by moss monitoring with *Isothecium stoloniferum* Brid. in the Fraser Valley, B. C. Canada. Water, Air and Soil Pollution 101, 25-44.
- Prasad, M. N. V. and Freitas, H. M. (2003). Metal hyperaccumulation in plants - Biodiversity prospecting for phytoremediation technology. *Electronic Journal of Biotechnology* 6 (3), 285-321.
- Rasmussen, G and Andersen, S. (1999). Episodic release of Arsenic, Copper and Chromium from a wood preservation site monitored

by transplanted aquatic moss. *Water, Air, and Soil Pollution* **109**, 41-52.

- Rhüling, A. (1998). Atmospheric heavy metal deposition in Europe 1995-1996. NORD 1998: 15. Nordic Council of Ministers, Copenhagen.
- Rhüling, A. and Tyler, G. (1968). An ecological approach to the lead problem. Botaniska Notiser 122, 248-342.
- Ross, H. B. (1990). On the use of mosses (Hylocomium splendens and Pleurozium schreberi) for estimating atmospheric trace metal deposition. Water, Air, Soil Pollution 2, 445-455.
- Sabovljević, M., Vukojević, V., Mihajlović, N., Dražić, G. and Vučinić, Z. (2005). Determination of heavy metal deposition in the county of Obrenovac (Serbia) using mosses as bioindicators. I: Aluminum (Al), Arsenic (As), and Boron (B). Archives of Biological Sciences 57 (3), 205-212.
- Salemaa, M., Derome, J., Helmisaari, H.-S., Nieminen, T. and Vanha-Majamaa, I. (2004). Element accumulation in boreal bryophytes, lichens and vascular plants exposed to heavy metal and sulphur deposition in Finland. Science of the Total Environment 324, 141-160.
- Samecka-Cymerman, A., Marczonek, A. and Kampers, A. J. (1997). Bioindication of heavy metals in soil by liverworts. Archives of Environmental Contamination and Toxicology 33, 162-171.
- Scheffer P. and Schachtschabel, P. (1984). Lehrbuch der Bodenkunde, 11. Auflage Ferdinand Enke Verlag, Stuttgart. 1-416.
- Schaug, J., Rambaek, J., Steinnes, E. and Henry, R. C. (1990). Multivariate analysis of trace element data from moss samples used to monitor atmospheric deposition. *Athmospheric Environment* 24A, 2625-2631.
- Schilling, J. S. and Lehman, M. E. (2002). Bioindication of atmospheric heavy metal deposition in the Southeastern US using the moss *Thuidium delicatulum. Atmospheric Environment* 36, 1611–1618.
- Schintu, M., Cogoni, A., Durante, L., Cantaluppi, C. and Contu, A. (2005). Moss (Bryum radiculosum) as a bioindicator of trace metal deposition around an industrialised area in Sardinia (Italy). Chemosphere 60, 610–618.
- Schröder, W. and Pesch, R. (2004). Spatial analysis and indicator building for metal accumulation in mosses. Environmental Monitoring and Assessment 98, 131–155.
- Sérgio, C., Sim-Sim, M. and Figueira, R. (1993). Quantificação da deposição de metais pesados em Portugal através da análise de briófitos. Direcção General da Qualidade do Ambiente, Lisboa.
- Siewers, U and Hairpin, U. (1998). Schwermetalleinträge in Deutschland – Moosmonitoring 1995/96. Geologisches Jahrbuch, Sonderhefte, Reihe D, Heft SD 2, Stuttgart, Schweizerbarat, 1-

199.

- Stoeppler, M. (1991). Cadmium. In: Merian, E. (ed): Metals and their compounds in the environment – occurrence, analysis and biological relevance. VCH Verlagsgesellschaft mbH, Weinhein, New York, Basel, Cambridge, 803-851.
- Sucharova, J. and Suchara, I. (1998). Atmospheric deposition levels of chosen elements in the Czech Republic determined in the framework of the International Bryomonitoring Program 1995. Science of Total Environment 223, 37-52.
- Thöni, L. (1996). Vergleich der Elementkonzentrazionen in drei Biomonitormoosen untereinander und mit Depositionfrachten im Bulksammler nach Bergerhoff. BUWAL (ed.), Bern, 1-89.
- Thöni, L. and Seitler, E. (2004). Deposition von Luftschadstoffen in der Schweiz, Moosanalysen 1990-2000. BUWAL, Bern, 1-139.
- Thöni, L., Schnyder, N. and Krieg, F. (1996). Comparison of metal concentrations in three species of mosses and metal freights in bulk precipitations. Fresenius Journal of Analytic Chemistry 354, 703-708.
- Tonguç, Ö. (1998). Determination of Heavy Metal Levels in Some Moss Species Around Thermic Power Stations. *Turkish Journal* of Botany 22: 171-180.
- Treub, L.F. (ed.) (1996). Die chemischen Elemente. S. Hirzel Verlag, Stuttgart, Leipzig. 1-416.
- Tsakovski, S., Simeonov, V., Sawidis, T., Zachariadis, G. and Stratis, J. (1999). Chemometric classification of biomonitoring analytical data for heavy metals. Part II. Mosses as bioindicators. *Toxic. Environmental Chemistry* 69, 287-294.
- Tyler, G. (1970). Moss analyses a method for surveying heavy metal deposition. In: Englund, H.H. and Berry, W. T. (eds.): Proceedings of the Second International Clean Air Congress. Academic Press, New York.
- UNECE (2001). ICP Vegetation experimental protocol for the 2001 seasion. ICP Vegetation Coordination Centre, CEH Bangor, UK.
- Vásquez, M.D., López, J. and Carballeira, A. (1999). Uptake of Heavy Metals to the Extracellular and Intracellular Compartments in Three Species of Aquatic Bryophyte. Ecotoxicology and Environmental Safety 44, 12-24.
- Vukojević, V., Sabovljević, M. and Jovanović, S. (2005) Mosses accumulate heavy metals from the substrata of coal ash. Archives of Biological Sciences 57(2), 101-106.
- Zechmeister, H. (1994). Biomonitoring der Schwermetalldeposition mittels Moosen in Österreich. Monografien des Umweltbundesamtes, Wien, B. 94. 1-147.
- Zechmeister, H., Hohenwallner, D., Riss, A. and Hanus-Illnar, A. (2005). Estimation of element deposition derived from road traffic sources by using mosses. *Environmental Pollution* 138, 238-249.

ДЕТЕРМИНАЦИЈА ДЕПОЗИЦИЈЕ ТЕШКИХ МЕТАЛА У ОПШТИНИ ОБРЕНОВАЦ (СРБИЈА) КОРИШЋЕЊЕМ АНАЛИЗЕ МАХОВИНА КАО БИОИНДИКАТОРА II: КАДМИЈУМ (Cd), КОБАЛТ (Co) И ХРОМ (Cr)

В. ВУКОЈЕВИЋ¹, М САБОВЉЕВИЋ^{1,4}, АНЕТА САБОВЉЕВИЋ¹, НЕВЕНА МИХАЈЛОВИЋ², ГОРДАНА ДРАЖИЋ², и Ж. ВУЧИНИЋ²

¹Институт за ботанику, Биолошки факултет, Универзитет у Београду, 11000 Београд, Србија и Црна Гора ²ИНЕП, 11080 Земун, Србија и Црна Гора

³Центар за мултидисциплинарне студије, 11000 Београд, Србија и Црна Гора ⁴Нес институт за биљни биодиверзитет, Рајнски универзитет Фридриха Вилхелма, 53115 Бон, Немачка

У овој студији дефинисана је депозиција три тешка метала (Cd, Co и Cr) у општини Обреновац (Србија) на бази анализе четири таксона маховина (*Bryum ar*- genteum, Bryum capillare, Brachythecium sp. и Hypnum cupressiforme) као биоиндикатора. Утврђене су области са највишим степеном контаминације.