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Full Length Research Paper

Deposition of heavy metals (Pb, Sr and Zn) in the county of Obrenovac (Serbia) using mosses as bioindicators

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In this study, the deposition of three heavy metals (Pb, Sr and Zn) in the county of Obrenovac (Serbia) in four moss taxa (Bryum argenteum, Bryum capillare, Brachythecium sp. and Hypnum cupressiforme) is presented. Distribution of average heavy metal content in all mosses in the county of Obrenovac is presented in maps, while long term atmospheric deposition (in mosses Bryum argenteum and B. capillare) and short term atmospheric deposition (in mosses Brachythecium sp. and H. cupressiforme) is discussed and given in tables. Areas of the highest contaminations are highlighted.

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

INTRODUCTION

The idea of using mosses to measure atmospheric heavy metal deposition was developed already in the late 1960's (Rhüling and Tyler, 1968; Tyler, 1970) and well established in the Scandinavian countries in the 1980's.

It is based on the fact that mosses, especially the carpetforming species, obtain most of their nutrients directly from precipitation and dry deposition. Nowadays, this method is widely used in many countries (Schaug et al., 1990; Sérgio et al., 1993; Kuik and Wolterbeek, 1995; Berg and Steinnes, 1997a; Pott and Turpin, 1998; Sucharova and Suchara, 1998; Grodzinska et al., 1999; Tsakovski et al., 1999; Spezzano, 2000; 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).

Moreover, some bryophytes are known to be heavy metal bioindicators in their environments (Samecka- Cymerman et al., 1997; Onianwa, 2001; Nimis et al., 2002; Cuoto et al., 2004; Schröder and Pesch, 2004) and

are often used in environmental monitoring (Rasmussen and Andersen, 1999; Giordano et al., 2004; Cuny et al., 2004; Gstoettner and Fisher, 1997; Zechmeister 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, in as much 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 (Schintu et al., 2005). The metals studied were chosen according to significants of their presence in environments (eg. Lantzy and Mackenzie, 1979).

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 (Thöni et al., 1996; Faus-Kessler et al., 2001; Fernández and Carballeira, 2001; Cuoto et al., 2004).

Mosses are better than other higher plants in scanning heavy metal deposition because:

- i. They are perennial without deciduous periods.
- ii. They have a high cation exchange capacity that allows them to accumulate great amounts of heavy metals

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between apoplast and symplast compartments without damaging vital functions of the cells (Vásquez et al., 1999); one of the main factors influencing cation exchange capacity is the presence of polygalacturonic acids on the external part of cell wall and proteins in the plasma membrane (Aceto et al., 2003).

iii. Mosses do not posses thick and strong protective layers like cuticles.

More about hyperaccumulation of metals in plants and mosses can be found in Prasad and Freitas (2003). *B. argenteum* has already been shown to have special metal accumulation peculiarities (Aceto et al., 2003; Vukojevi et al., 2004, 2005).

It should also be noted that this time-integrated way of measuring patterns of heavy metal deposition from the atmosphere in 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 (Berg and Steinnes, 1997b).

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

This study represents a part of wider heavy metals surveillance in mosses in the county of Obrenovac (W. Serbia) (Sabovljevi et al., 2005, 2007; Vukojevi et al., 2006). The county of Obrenovac was chosen due to its heavy industry and power plants. It is situated west of the Serbian capital Belgrade on the right river side of the Sava river. Its possition is also good heavy metal deposition in relation to traffic influence which is concentrate in some part while in the others road network is not well developed. Also, relative proximity to west Serbian border and other counties surrounding Obrenovac, give us possibility to identify trans-boundary influence to the deposition of atmospheric heavy metal in the county of Obrenovac.

MATERIAL AND METHODS

The acrocarpous mosses *B. argenteum* and *B. capillare* were used to research long-term atmospheric deposition, while the *pleurocarpous Brachythecium* sp. and *H. cupressiforme* were used to scan short term atmospheric deposition in the county of Obrenovac (Serbia). *H. cupressiforme* is one of the standard species used in Europe for heavy metal deposition surveys (Buse et al., 2003), whereas the other three standard species used for this purpose in Europe do not grow in the Obrenovac region. In judging which other species are eligible for heavy metal deposition monitoring, the experience of Thöni (1996), Herpin et al. (1994), Siewers and Hairpin (1998), Zechmeister (1994) was consulted.

As far as possible, moss sampling followed the guidelines set out in the experimental protocol for the 2000/2001 survey (UNECE, $\frac{1}{2}$

2001). The procedure is given in detail in Rühling (1998).

Each sampling site was located at least 300 m from main roads and populated areas and at least 100 m from any other 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 repeat moss samples were collected from each site. Dead material and litter were removed from the samples. Green parts of the mosses were used for 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 (Garmin) were digitalized on maps with the OziExplorer 3.95.3b (© D&L Software), and WinDig 2.5 Shareware (© D.Lovy) softwares. All material was collected during November of 2002. Not more than one site was chosen per square measuring 50 x 50 m. Seventy-five out of 129 localities were chosen for comparison and further analyses based on all investigated species present and yearly biomass. In total 512 samples were analyzed. After collecting, samples were dried as soon as possible in a drying oven to a constant dry weight (dw) at a constant temperature of 35°C, then stored at -20°C.

Following homogenization in a porcelain mortar, the samples were treated with 5 + 1 parts of nitric acid and perchloric acid (HNO3:HClO4 = 5:1) and left for 24 h. 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 the volume of samples was then normated to 50 ml.

Pb, Sr and Zn were detected by atomic absorbance (AAS - Atomic Absorbance Spectrophotometry, Philips Pye Unicam SP9 instrument). The content of lead and zinc were determined with a flame of acetylene/air, while strontium was detected using flame of acetylene/nitrogen-suboxide.

For the explanation of the results and their map presentation, the following statistical parameters were used: average values, standard deviation, minimum and maximum values and percent deviation. Since the county of Obrenovac is flat in spatial analysis topographic parameters were not taken into accounts. Map making and interpolation of precise data were made with Agis v1.71 32bit (© Agis Software, 2001) software.

RESULTS AND DISCUSSION

Since it was impossible to find all the sampled species at any precise locality, the average of all specimens is given on extrapolated map to get an idea of heavy metal deposition in the county of Obrenovac (Figure 1, 2 and 3). However, if one separate the values of deposition obtained from pleurocarpous (Brachythecium sp. and H. cupressiforme) and acrocarpous (B. argenteum and B. capillare) mosses, it can be clearly 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 substrate and get most of deposited heavy metals with the substrate solution (metals are deposited over a period of time that is longer than their pauciennial life span).

The lead loading is the greatest in the urban area

Table. 1. The exact value of studied heavy metals in certain localities in mosses (Ba - *Bryum argenteum,* Bc - *Bryum capillare,* Br - *Brachythecium* sp. and Hc - *Hypnum cupressiforme*).

Sample	Locality and	Pb	Sr	Zn
No.	sample type	mg/g	mg/g	mg/g
1	Vinogradi Hc	0.0000 ± 0	0.0354 ± 0.0111	0.1628 ± 0.0406
2	Moštanica 1 Hc	0.0000 ± 0	0.0575 ± 0.0098	0.3429 ± 0.0711
3	Iskra 1 Bc	0.0624 ± 0.0112	0.0685 ± 0.0178	1.2755 ± 0.0999
4	Iskra 2 Bc	0.0418 ± 0.0099	0.0523 ± 0.0092	0.3147 ± 0.0594
5	Iskra 1 Hc	0.0254 ± 0.0102	0.0431 ± 0.0092	0.2601 ± 0.0655
6	Iskra 2 Bc	0.0206 ± 0.0071	0.0595 ± 0.0079	0.1499 ± 0.0667
7	Rvati 1 Bc	0.0412 ± 0.0098	0.1096 ± 0.0300	0.2760 ± 0.0712
	Deponija B ulaz 1			
9	Bc	0.0316 ± 0.0079	0.0751 ± 0.0101	0.1431 ± 0.0687
10	Zabrežje 1 Bc	0.0341 ± 0.0105	0.0637 ± 0.0119	0.3071 ± 0.0800
11	Uš e 2 Bc	0.1112 ± 0.0147	0.0633 ± 0.0085	0.3855 ± 0.0881
12	Vinogradi Bc	0.0558 ± 0.0141	0.0433 ± 0.0087	0.2912 ± 0.0746
13	Iskra 1 Ba	0.0511±0.0099	0.0726 ± 0.0198	1.1182 ± 0.0988
14	Uš e 2 Hc	0.0483 ± 0.0122	0.0798±0.0177	0.1558 ± 0.0578
15	Uš e 1 Bc	0.0339 ± 0.0141	0.0492 ± 0.0147	0.2726 ± 0.0406
16	Urozv Br	0.0478 ± 0.0121	0.0977 ± 0.0204	0.2214 ± 0.0822
17	Zabrežje 2 Hc	0.0454 ± 0.0111	0.0327 ± 0.0105	0.2085 ± 0.0798
18	Orašac 1 Hc	0.0564 ± 0.0139	0.0303 ± 0.0099	0.2063 ± 0.0801
19	Hotel Ba	0.1744 ± 0.0278	0.0746 ± 0.0147	0.2480 ± 0.0831
20	Moštanica 1 Hc	0.0390 ± 0.0089	0.0319 ± 0.0110	0.1511 ± 0.0523
21	Grabovac 1 Hc	0.0344 ± 0.0111	0.0344 ± 0.0072	0.1393 ± 0.0698
22	Šab.put nadv. Bc	0.1390 ± 0.0228	0.0974 ± 0.0201	0.2590 ± 0.0852
23	Vrani Hc	0.0528 ± 0.0079	0.0399 ± 0.0100	0.1973 ± 0.0701
24	Jasenak 2 Br	0.0435 ± 0.0099	0.0494 ± 0.0108	0.1620 ± 0.0656
25	Dren 1 Br	0.0531 ± 0.0112	0.0314 ± 0.0085	0.2007 ± 0.0802
26	Veliko Polje 1 Hc	0.0229 ± 0.0103	0.0702 ± 0.0181	0.2702 ± 0.0768
27	Grabovac 1 Bc	0.0149 ± 0.0059	0.0248 ± 0.0047	0.1546 ± 0.0418
28	Belo Polje 1 Bc	0.0084 ± 0.0011	0.0626 ± 0.0084	0.1475 ± 0.0402
29	Brovi 1 Bc	0.0302 ± 0.0104	0.0296 ± 0.0044	0.1450 ± 0.0299
30	Ljubini 2 Br	0.0243 ± 0.0049	0.0279 ± 0.0019	7.1756 ± 2.0019
31	Hotel Hc	0.1736 ± 0.0284	0.0873 ± 0.0184	0.1991 ± 0.0778
32	Grabovac 1 Br	0.0322 ± 0.0066	0.0321 ± 0.0098	0.1423 ± 0.0689
33	Ljubini 2 Bc	0.0304 ± 0.0085	0.0318 ± 0.0084	0.1748 ± 0.0966
34	Veliko Polje 4 Hc	0.0236 ± 0.0088	0.0302 ± 0.0077	0.1024 ± 0.0455
35	Zabran 3 Hc	0.0309 ± 0.0105	0.0279 ± 0.0057	0.1056 ± 0.0506
36	Zabran 1 Hc	0.0776 ± 0.0158	0.0406 ± 0.0100	0.1564 ± 0.0677
37	Orašac 3 Hc	0.0000 ± 0	0.0372 ± 0.0112	1.2261 ± 0.0712
38	Orašac 2 Hc	0.0251 ± 0.0094	0.0323 ± 0.0149	0.1417 ± 0.0455
39	Zabran 2 Br	0.0427 ± 0.0089	0.0610 ± 0.0188	0.1664 ± 0.0450
40	Belo Polje 1 Ba	0.0128 ± 0.0041	0.0502 ± 0.0158	0.1772 ± 0.0551
41	Orašac 2 Br	0.0054 ± 0.0021	0.0238 ± 0.0048	0.1411 ± 0.0433
42	Ljubini 1 Br	0.0583 ± 0.0107	0.0452 ± 0.0078	0.5350 ± 0.0444
43	Grabovac nad. Ba	0.0607 ± 0.0145	0.0523 ± 0.0099	0.1609 ± 0.0288

Table 1. Contd

44	Joševa Hc	0.0988 ± 0.0288	0.0450 ± 0.0149	0.9341 ± 0.0408
45	Brovi 2 Br	0.0622 ± 0.0222	0.0608 ± 0.0209	0.5501 ± 0.0519
46	Jasenak 2 Ba	0.0519 ± 0.0171	0.0432 ± 0.0121	0.3539 ± 0.0473
47	Garbovac nadv. Br	2.0597 ± 0.0722	0.0653 ± 0.0132	8.4667 ± 2.0012
48	Baljevac 1 Bc	0.3078 ± 0.0411	0.0312 ± 0.0100	0.1658 ± 0.0400
49	Joševa Bc	0.0387 ± 0.0101	0.0325 ± 0.0107	0.1294 ± 0.0399
50	Joševa Br	0.0379 ± 0.0099	0.0393 ± 0.0111	0.0949 ± 0.0257
51	EPS Bc	0.0275 ± 0.0061	0.0608 ± 0.0152	0.1935 ± 0.0473
52	Konatice II Br	0.1010 ± 0.0299	0.0825 ± 0.0186	0.6416 ± 0.0898
53	Zabran 1 Ba	0.0399 ± 0.0086	0.0410 ± 0.0122	0.1649 ± 0.0488
54	Mislo inl 1 Br	0.0318 ± 0.0087	0.0449 ± 0.0101	0.2073 ± 0.0741
55	Brovi 1 Hc	0.0439 ± 0.0107	0.0253 ± 0.0059	0.1537 ± 0.0600
56	Mislo in 4 Hc	0.0720 ± 0.0149	0.0279 ± 0.0061	0.2078 ± 0.0812
57	Stubline 2 Hc	0.0930 ± 0.0188	0.0755 ± 0.0155	0.3101 ± 0.0888
58	Konatice 1 Bc	0.0404 ± 0.0171	0.0230 ± 0.0099	0.1377 ± 0.0780
59	Zabran 3 Ba	0.0954 ± 0.0159	0.0374 ± 0.0111	0.1172 ± 0.0711
60	Jasenak Hc	0.0339 ± 0.0091	0.0268 ± 0.0077	0.1351 ± 0.0569
61	Konatice 2 Ba	0.0543 ± 0.0098	0.0677 ± 0.0188	0.2887 ± 0.0602
62	Veliko Polje 4 Bc	0.0352 ± 0.0066	0.0295 ± 0.0087	0.1519 ± 0.0664
63	Mislo in 1 Br	0.0302 ± 0.0156	0.0290 ± 0.0076	0.5344 ± 0.0588
64	Veliko Polje 3 Bc	0.1885 ± 0.0301	0.0483 ± 0.0102	8.3966 ± 2.9801
65	Konatice II Bc	0.0383 ± 0.0100	0.0297 ± 0.0100	0.1468 ± 0.0780
66	Mislo in 6 Ba	0.0000 ± 0	0.0013 ± 0.0001	0.0603 ± 0.0118
67	Stubline 1 Hc	0.0769 ± 0.0200	0.0541 ± 0.0099	0.2788 ± 0.0888
68	Šab.put nadv. Ba	0.1010 ± 0.0209	0.0668 ± 0.0177	0.5173 ± 0.0683
69	Dren 1 Hc	0.0484 ± 0.0102	0.0341 ± 0.0122	0.2022 ± 0.0712
70	Zabran 2 Bc	0.0553 ± 0.0119	0.0996 ± 0.0183	0.3909 ± 0.0944
71	Baljevac 2 Hc	0.0356 ± 0.0123	0.0344 ± 0.0104	0.1380 ± 0.0606
72	Mislo in 5 Ba	0.0685 ± 0.0141	0.0399 ± 0.0100	1.3275 ± 0.0999
73	Orašac 1 Br	0.0447 ± 0.0145	0.0299 ± 0.0074	0.1505 ± 0.0569
74	Konatice II Hc	0.0477 ± 0.0154	0.0727 ± 0.0143	0.1882 ± 0.0600
75	Šab.put 1 Br	0.0298 ± 0.0076	0.0566 ± 0.0108	0.2176 ± 0.0711
76	TENT B 3 Bc	0.0894 ± 0.0118	0.0295 ± 0.0048	0.3443 ± 0.0621
77	Šab.put 1 Hc	0.0606 ± 0.0100	0.0326 ± 0.0069	0.1751 ± 0.0722
78	Ratari 2 Br	0.0377 ± 0.0093	0.0485 ± 0.0099	0.2570 ± 0.0741
79	TENT B 1 Hc	0.0542 ± 0.0029	0.0159 ± 0.0048	0.1347 ± 0.0841
80	TENT B 2 Hc	0.0101 ± 0.0005	0.0393 ± 0.0077	0.1377 ± 0.0844
81	Ratari 1 H.C.	0.0340 ± 0.0061	0.0684 ± 0.0122	0.1189 ± 0.0701
82	Uš e Skela Bc	0.0000 ± 0	0.0476 ± 0.0100	0.2354 ± 0.0498
83	Ratari 2 Ba	0.0286 ± 0.0068	0.0497 ± 0.0101	0.4590 ± 0.0599
84	TENT B 4 Ba	0.0522 ± 0.0061	0.0725 ± 0.0139	0.2785 ± 0.798
85	TENT B 2 Br	0.0132 ± 0.0012	0.0345 ± 0.0100	0.1575 ± 0.0498
86	TENT B 1 Br	0.0000 ± 0	0.0181 ± 0.0064	0.1438 ± 0.0586
87	TENT B 4 Bc	0.0143 ± 0.0070	0.0292 ± 0.0084	0.2070 ± 0.0877
88	TENT B 3 Bc	0.0231 ± 0.0047	0.0246 ± 0.0082	0.1627 ± 0.0652

Table 1. Contd

89	Orašac 1 BRA	0.0138 ± 0.0066	0.0657 ± 0.0187	0.1320 ± 0.0636
90	Uš e Skela Br	0.0587 ± 0.0084	0.2906 ± 0.1001	0.2507 ± 0.0780
91	Šab.put 1 Bc	0.0225 ± 0.0077	0.0358 ± 0.0049	0.1754 ± 0.0483
92	TENT B ulaz Br	0.0000 ± 0	0.0235 ± 0.0084	0.1791±0.0488
93	Deponija 1 Br	0.0169 ± 0.0051	0.0451 ± 0.0144	0.1943 ± 0.0496
94	TENTB 2 Bc	0.0000 ± 0	0.0065 ± 0.0009	0.0987 ± 0.0223
95	Konatice 1 Hc	0.0319 ± 0.0099	0.0164 ± 0.0093	0.1140 ± 0.0318
96	Mislo in 6 Br	0.0536 ± 0.0108	0.0201 ± 0.0086	0.1153 ± 0.0452
97	Mislo in 3 Br	0.1523 ± 0.0255	0.0662 ± 0.0133	0.1986 ± 0.0551
98	Mislo in 6 Bc	0.0115 ± 0.0083	0.0255 ± 0.0098	0.1614 ± 0.0566
99	Jasenak 2 Ba	0.0214 ± 0.0081	0.0313 ± 0.0112	0.1953 ± 0.0600
100	Mislo in 4 Bc	0.0097 ± 0.0008	0.0209 ± 0.0100	0.1630 ± 0.0606
101	Zabran 1 Br	0.0000 ± 0	0.0313 ± 0.0105	0.1933 ± 0.0569
102	Rojkovac 1 Bc	0.0680 ± 0.0102	0.0576 ± 0.0141	0.1697 ± 0.0563
103	Rojkovac 1 Br	0.0258 ± 0.0095	0.0491 ± 0.0133	0.3952 ± 0.0896
104	Rvati 1 Br	0.0000 ± 0	0.0147 ± 0.0047	0.3944 ± 0.0892
105	Rojkovac 1 Ba	0.0927 ± 0.0175	0.0645 ± 0.0201	0.3129 ± 0.0841
106	Moštanica 3 Br	0.0055 ± 0.0009	0.0476 ± 0.0114	0.2062 ± 0.0777
107	Razu Br	0.0110 ± 0.0012	0.0105 ± 0.0055	0.2157 ± 0.0786
108	Uš e 3 Br	0.0348 ± 0.0053	0.0592 ± 0.0120	0.2659 ± 0.0746
109	Duboko 3 Hc	0.0458 ± 0.0074	0.0218 ± 0.0098	0.1255 ± 0.0269
110	Zabrežje 1 Br	0.0436 ± 0.0064	0.0508 ± 0.0122	0.2391±0.0800
111	Zabran 3 Br	0.0340 ± 0.0044	0.0254 ± 0.0084	0.1380 ± 0.0606
112	Moštanica 2 Bc	0.0365 ± 0.0071	0.0508 ± 0.0142	0.1430 ± 0.0627
113	Razu Ba	0.0005 ± 0	0.0514 ± 0.0132	0.1847 ± 0.0633
114	Rvati 3 Br	0.0000 ± 0	0.0289 ± 0.0099	0.2329 ± 0.0700
115	TENT A 1 Br	0.0218 ± 0.0069	0.0599 ± 0.0141	0.3512 ± 0.0768
116	Moštanica 3 Bc	0.0343 ± 0.00	0.0506 ± 0.0109	0.4131 ± 0.0998
117	Zabrežje 2 Br	0.0302 ± 0.0088	0.0390 ± 0.0100	0.2272 ± 0.0882
118	Urozv Bc	0.0270 ± 0.0100	0.0564 ± 0.0123	0.2699 ± 0.0866
119	Depoija 1 Hc	0.0000 ± 0	0.0179 ± 0.0123	0.1572 ± 0.0811
120	Zabrežje 2 Ba	0.0377 ± 0.0110	0.0388 ± 0.0149	0.1791 ± 0.0812
121	Moštanica 1 Bc	0.0423 ± 0.0111	0.0550 ± 0.0167	0.1756 ± 0.0855
122	Vinogradi Ba	0.0650 ± 0.0122	0.0401 ± 0.0097	0.1873 ± 0.0880
123	Urozv Hc	0.0394 ± 0.0128	0.0400 ± 0.0099	0.2956 ± 0.0981
124	Razu Hc	0.0401 ± 0.0198	0.0409 ± 0.0107	0.1684 ± 0.0823
125	Duboko 1 Ba	0.0493 ± 0.0113	0.0133 ± 0.0108	0.1193 ± 0.0799
126	Vinogradi Br	0.0310 ± 0.0123	0.0144 ± 0.0073	0.1029 ± 0.0771
127	Duboko Br	0.0713 ± 0.0141	0.0640 ± 0.0149	0.2590 ± 0.0822
128	TENT A 1 Bc	0.0364 ± 0.0048	0.0589 ± 0.0188	0.1168 ± 0.0598
129	Zabrežje 2 Bc	0.0329 ± 0.0074	0.0418 ± 0.0149	0.2849 ± 0.0799
Mean		0.0607	0.0466	0.4378
Median		0.0371	0.0409	0.1939
Standard Deviation		0.1829	0.0298	1.2009
Standard Error		0.0162	0.0026	0.1062

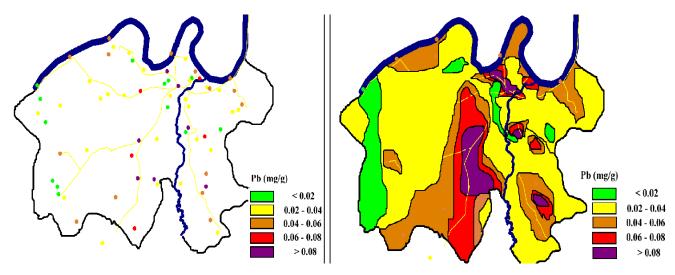


Figure 1. Exact values and position (left) and extrapolated map of county of Obrenovac (right) of lead (Pb) deposition in analysed moss sample.

(North central), along the main roads and industrial sites (Figure 1). The less lead loaded area of the county of Obrenovac is Western most part and some smaller parts out of main communication routes and with lot of green surfaces.

The lead is not essential for living beings but it is toxic both for plants and animals. The toxicity is high due to reaction of lead-ions with free SH groups in the proteins and inhibition of the enzyme activity by replacing the metal-ion centres (e.g Ca ions). Acute intoxications are rare, however chronicle damages of liver, kidneys, nervesystems or blood production and are often. Carcinogenic effect of lead itself is not clear. Plants suffer only by high lead concentrations, by strong chloroses (Kaim and Schwederewski, 2005).

Lead is often in the earth crust (36. most often element of crust; Scheffer and Schachtschabel, 1984). There are more than 200 minerals containing lead, however only few are economically used. It is present in soil due to anthropogenic activities, and in general more in agriculture soils than in soils covered by vegetation and forests. The average in earth crust is 16g/t (Thöni and Setler, 2004). The yearly production is ca. 6 million tons, of which ca. 60% comes from recycling (Merian, 1984, Metallgesellschaft, 1993).

Almost 90% of lead emission world-wide comes from burning fossil oils and derivatives. The other main sources of lead are accumulators (Treub, 1996). Pacyna and Pacyna (2001) report world year emission of 300.000t and naturally emission is ca. 5.800t yearly (Lantzy and Mackenzie, 2001). In Europe recently, the trend is lead emission decreasing (Pacyna and Pacyna, 2001). The border value of lead presence in drink water is 0.01 mg/l (Thöni and Setler, 2004).

Strontium is not among the heavy metal deposition threats considering that 70% of the Obrenovac County

has no high values of strontium accumulated in mosses (Figure 2). The areas situated around Bari heavy industry and Termo power plant are the regions with the highest loads. Moderate loads could be also determined along the main traffic communication routes.

Strontium belongs to alkaline earth metal and posses high chemical reactivity especially with water and oxygene. It replaces easily Ca and other related ions and therefore could be problematic for living beings (Kaim and Schwederewski, 2005). Naturally it occurs in minerals celestine and srontianite (Scheffer and Schachtschabel, 1984). Its isotope is radioactive. It is used in colour TV screen industry and also in radiotherapy in medicine but also in battery production and pyrotechnics.

It is the 22nd most common element in earth crust (ca. 0.014%). World production of strontium ores is about 140.000t/year (Scheffer and Schachtschabel, 1984). Foods containing strontium ranges from very low e.g. in corn (0.4 ppm and oranged (0.5 ppm) to high, e.g. in cabbage (45 ppm), onions (50 ppm) and lattuce (74 ppm). Strontium compounds that are water-insoluble can become water-soluble, as a result of chemical reactions. The water-soluble compounds are a greater threat to human health than the water-insoluble ones. Therefore, water-soluble forms of strontium have the opportunity to pollute drinking water. Fortunately the concentrations in drinking water are usually quite low.

The uptake of high strontium concentrations is generally not known to be a great danger to human health. Some allergic reaction to strontium can occur. For children exceeded strontium uptake may be a health risk, because it can cause problems with bone growth. When strontium uptake is extremely high, it can cause disruption of bone development. But this effect can only occur when strontium uptake is in the thousands of ppm

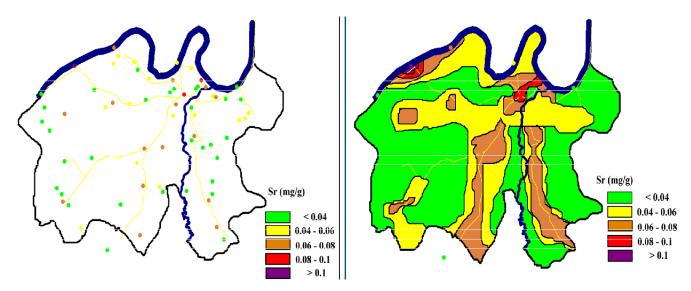


Figure 2. Exact values and position (left) and extrapolated map of county of Obrenovac (right) of strontium (Sr) deposition in analysed moss sample.

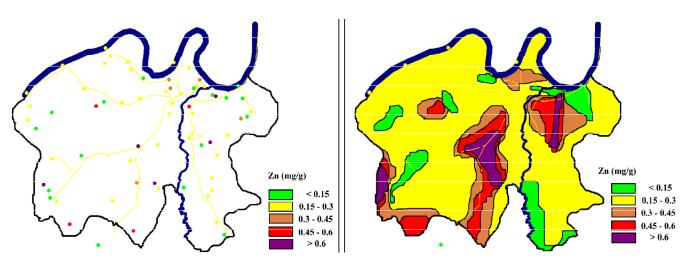


Figure 3. Exact values and position (left) and extrapolated map of county of Obrenovac (right) of zinc (Zn) deposition in analysed moss sample.

range. Strontium levels in food and drinking water are not high enough to be able to cause these effects. Radio-active strontium is much more of a health risk than stable strontium. When the uptake is very high, it may cause anaemia and oxygen shortages and at extremely high concentrations it is even known to cause cancer as a result of damage to the genetic materials in cells. The highest deposition sites for the zinc in the county of Obrenovac are localised in smaller central areas, Southwestern and North-eastern county parts (Figure 3). The deposited zinc origin in Central and North-eastern areas is autochthonous, due to the local emission sources, according to results obtained. In South-western region it

is probably trans-boundary deposited from the sources out of Obrenovac county territory by long- or short-range transport.

In contrast to lead, zinc is essential for live. It is part of many enzymatic centres. It toxicity is expressed in high concentration by yellowing young plant leaves and plant dead while in animals it causes infertility and skin diseases. Also, the deficiency of zinc has huge consequences to living beings (Merian, 1984).

Zinc is the 24th most common element in the earth crust (83 g/t), present in many minerals combined with other metals (Scheffer and Schachtschabel, 1984). It comes in sols in values from 76 ppm in non calk soils up to 125

ppm in calk soils. Mosses can have it accumulated in high concentration (ca. 20 µg/mg) due to its high presence in substrate in-dependently of zinc emission (Zechmeister, 1997).

Anthropogenic emission is up to 840.000 t/year and natural 35.800 t/year (Lantzy and Mackenzie). The tolerated upper value in drink water is 5 mg/l (Thöni and Setler, 2004). It is used in rust protection of iron and steel materials. It has wide use in different industrial processes and some of its compounds are toxic and carcinogenic. The emitters of zinc are coloured metal industry, traffic and coil power plants.

Conclusion

Lead and zinc are deposited in the county of Obrenovac both from the local and outer sources while strontium is not highly accumulated in mosses. The effort should be made to reduce heavy traffic trough the urban zones and to make green zones as barriers around source spots indicated. Besides, the public pressure to use highly innovative and cleaner technologies, special attention in agriculture field in the area of heavy deposition of these trace metals should be established as well environmental improvement both bν control environmental condition qualities and reduction of treats.

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