BIOMONITORING MANGANA U REGIONU BORA (ISTOČNA SRBIJA) NA BAZI SADRŽAJA U UZORCIMA LIŠĆA, KORENJA I ZEMLJIŠTA DIVLJE KUPINE

MANGANESE BIOMONITORING IN THE REGION OF BOR (EASTERN SERBIA) ON THE BASIS OF THE CONTENT IN THE SAMPLES OF LEAVES, ROOTS AND SOILS OF WILD BLACKBERRY

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U ovoj biomonitoring studiji, nivo prisutnosti mangana (Mn) u Borskom regionu određivan je na bazi njegovog sadržaja u lišću, korenju i zemljištu divlje kupine koja je bila nađena kao prirodno rastuća na svim ispitivanim lokacijama iz urbano/industrijske i ruralne zone (ukupno 8 lokacija). Borski region je bio odabran zbog visokog nivoa zagađenja teškim metalima, kao posledice dugotrajnih intenzivnih rudarsko-metalurških aktivnosti u procesu proizvodnje bakra. Potencijalno zagađenje manganom procenjivano je na bazi izračunatih faktora obogaćenja (engl. Enrichment Factors, EFs), za svaku ispitivanu lokaciju i svaki ispitivani matriks: zemljište, koren (opran) i lišće (neoprano). Takođe, detektovane koncentracije zemljišnog Mn bile su upoređene sa relevantnim vrednostima datim u zakonskoj regulativi. Zemljišni i korenski EFs pokazali su potpuno odsustvo kontaminacije na skoro svim lokacijama, dok su lisni EFs otkrili umerenu do značajnu kontaminaciju na nekoliko lokacija. Na bazi rezultata hemijske analize i obračunatih EFs može se zaključiti da prisustvo Mn u životnoj sredini Bora i okoline nije bilo na nekom značajnom nivou, kao i da je Mn u površinskom zemljištu predominantno geogenog porekla. Istovremeno, lisni EFs su ukazali da su različite rudarsko-metalurške aktivnosti u regionu Bora, u izvesnom stepenu takođe doprinele detektovanim koncentracijama Mn, pre svega preko atmosferske depozicije. Kombinacija zemljišnih i biljnih podataka primenjena u ovom radu, obezbedila je jedan dubinski i tačan uvid u nivo prisutnosti Mn u regionu Bora, što generalno preporučuje ovaj pristup kao jedno od najadekvatnijih rešenja za biomonitoring studije.

Ključne reči: *divlja kupina; faktor obogaćenja; Mn; zemljište*

In this biomonitoring study, the level of manganese (Mn) presence in the region of Bor was evaluated on the basis of its content in leaves, roots, and soil of wild blackberry, which was found as naturally growing at all investigated locations from the urban/industrial and the rural zone (8 locations in total). Bor's region was selected due to the high level of heavy metal pollution, as a consequence of the long-term intensive mining-metallurgical activities in the process of copper production. Possible pollution by manganese was estimated on the basis of the calculated Enrichment Factors (EFs) for each investigated location and each investigated matrix: soil, root (washed), and leaves (unwashed). Also, the detected soil Mn concentrations were compared with relevant values given in legislative regulation. Soil and root EFs showed a total absence of contamination at almost all locations, while leaf EFs revealed moderate to significant contamination at several locations. On the basis of the results of chemical analysis and calculated EFs, it can be concluded that the presence of Mn in the environment of Bor and its surroundings was not at some considerable level, as well as that Mn in surface soil is predominantly of geogenic origin. At the same time, leaf EFs pointed that various mining-metallurgical activities in the region of Bor also contributed to the detected Mn concentrations in some extent, mostly via atmospheric deposition. The combination of soil and plant data applied in this work provided a deep and accurate insight into the level of Mn presence in the region of Bor, which generally recommends this approach as one of the most adequate solutions for biomonitoring studies.

Key words: *enrichment factor; Mn; soil; wild blackberry*

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1 Introduction

The region of Bor is well known as one of the most polluted areas at the complete Balkan Peninsula. More precisely, during the last century, the complete environment of Bor's region was exposed to serious contamination by heavy metals and sulfur-dioxide, emitted from industrial facilities of mining-metallurgical complex dealing with copper ore mining and processing [1, 2, 3].

Numerous biomonitoring studies performed during latest decades by various research teams from Bor, confirmed the presence of high concentrations of heavy metals in all environmental parts – air, water, and soil, especially regarding copper (Cu), arsenic (As), zinc (Zn), lead (Pb), and cadmium (Cd) [1, 4-8]. However, a smaller number of studies were dedicated to the presence of manganese (Mn), as one of the potentially toxic metals; namely, it is known that extreme concentrations of this (essential) metal may cause serious consequences in the environment, and most importantly – in humans. People inhaling dust containing Mn may have negative effects in central nervous system, especially in the extra-pyramidal motor system. The symptoms are very similar to those of Parkinson's disease. Studies suggesting neurotoxicity of orally ingested Mn were also presented to wide scientific community [9].

In this paper, our team evaluated the level of Mn presence in the environment of Bor and its surroundings, in autumn 2012, practically using the data on Mn content in leaves, roots and soils of wild blackberry that was found as naturally growing at all kinds of the investigated locations – urban-industrial (U/I) and rural (R) as well.

2 Materials and methods

Eight sampling sites were chosen for the samples collection as follows: 1) Flotacijsko jalovište (FJ), flotation tailings pond (out of use) in U/I zone; 2) Bolničko naselje (BN), near hospital (U/I zone); 3) Slatinsko naselje (SN), in the close vicinity of FJ (U/I zone); 4) Naselje Sunce (NS), suburb in U/I zone; 5) Oštrelj (O), settlement in R zone; 6) Slatina (S), settlement in R zone; 7) Dubašnica (D), settlement in R zone; and 8) Gornjane (G), settlement in R zone but practically, the control (C) site (situated in a protective position regarding heavy metal pollution). Distances of all sampling sites from the old copper smelter in mining-metallurgical complex in the town of Bor (as the former main source of pollution) are given in Table 1, together with directions of dominant winds.

Table 1 Basic data for the investigated locations in the region of Bor

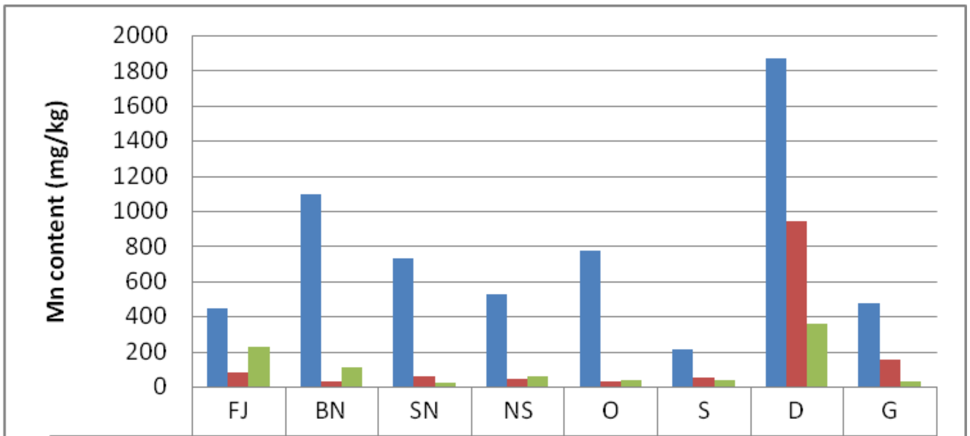
Sampling site	Zone	Distance from the old copper smelter (km)	Dominant wind direction
Flotacijsko Jalovište (FJ)	UI	0.7	WNW and NW
Bolničko naselje (BN)	UI	2.2	E and ESE
Slatinsko naselje (SN)	UI	2.3	WNW and NW
Naselje Sunce (NS)	UI	2.5	E and ENE
Oštrelj (O)	R	4	W and WNW
Slatina (S)	R	7	NW and WNW
Dubašnica (D)	R	17	E and ESE
Gornjane (G)	C	19	S

The preparation of samples and their chemical analysis were described in the study of Nujkić et al. (2016) [8], which reported the content of other heavy metals such as Cu, Pb, Zn, As, Cd, and Ni in the collected wild blackberry parts. Practically, the samples of leaves, roots and the corresponding soils were taken at each investigated site from 3-5 wild blackberry plants. Roots were analyzed as washed, whereas leaves were analyzed as unwashed parts; both kinds of plant parts were later air-dried and milled in a laboratory mill. Dried soil samples were homogenized using 2-mm stainless steel sieve. Prepared samples were mineralized in accordance with the USEPA (United States Environmental Protection Agency) method 3052 [10]. The obtained solutions were analyzed on iCAP 6000 inductively coupled plasma optical emission spectrometer (Thermo Scientific, Cambridge, United Kingdom). The selected emission line for Mn was: 257.610 nm. All measurements were done in triplicate; the obtained results are given in Fig. 1, in mg/kg dry weight (DW).

To assess the level of influence of mining-metallurgical activities on Mn presence in the Bor region (in autumn 2012), the enrichment factor (EF) was calculated for all kinds of samples. EF for each site was simple calculated as: EF = Cpolluted / Ccontrol, where Cpolluted and Ccontrol refer to the concentrations of metal in the wild blackberry organ (or soil) from the polluted site and the control site G, respectively [7, 11, 12]. EF values of 2, indicate the existence of anthropogenic pollution at the level which is not alarming; however, with the increasing of EFs, the contribution of this kind of pollution increases as follows: moderate pollution, EF = 2 – 5; significant pollution, EF = 5 – 20; very high pollution, EF = 20 – 40; and extremely high pollution, EF > 40 [6, 12, 13].

3 Results and discussion

The results of chemical analysis provided accurate data on Mn concentrations in all analyzed samples; they are given in Fig. 1.



	FJ	BN	SN	NS	O	S	D	G
Mnsoil	443.65	1098.5	730	526.5	775.5	211.77	1865	478
Mnroot	81.9	30.26	55.85	40.805	31.625	51.8	942.5	153.6
Mnleaves	224.8	108.15	21.735	58.5	33.75	35.66	357.95	28.755

Fig. 1 Mn content (mg/kg) in wild blackberry leaves, roots, and soils

In the case of soil samples, Mn concentrations ranged from 211.775 mg/kg at the rural site S, to 1865.00 mg/kg at the rural site D. It was obvious that many soil samples from R sites had very similar Mn concentrations with those from U/I zone, which was a first sign that distance from the old copper smelter (placed in the centre of the mining-metallurgical complex) cannot represent some significant influential factor, and practically, that anthropogenic activities in the mentioned complex cannot be considered as some significant sources of Mn in the region of Bor. However, it was also obvious that most of the detected Mn concentrations were to some extent higher than World average soil concentrations (418 mg/kg according to Alloway (2013) [14], and 488 mg/kg, according to Kabata-Pendias (2011) [15]). At the same time, all detected Mn concentrations were below USEPA (United States Environmental Protection Agency) regional screening levels (RSLs) defined for residential and industrial soils, except in the case of the strongest THQ (target hazard quotient) criteria for resident soil; namely, this RSL (at THQ = 0.1) amounts 180 mg/kg. Other USEPA RSLs for Mn amount as follows: 1) 1800 mg/kg for resident soil and 26000 mg/kg for industrial soil at THQ = 1 and target cancer risk (TR) of $1x10^{-6}$; and 2) 2600 mg/kg for industrial soil at THQ = 0.1 and TR of $1x10^{-6}$ [16]. These findings suggested that the investigated soils in the Bor region, cannot be considered as seriously polluted by Mn, which was finally confirmed by calculated soil EFs (Table 2); namely, all calculated values were much lower than 2, except in the cases of the soil samples from the sites D and BN. Some similar situation was observed also in the case of wild blackberry roots, where all EFs were much lower than 2, except in the case of root from the site D, where EF was greatly higher than 2 (EF = 6.14) suggesting a significant pollution at this place (Table 2). Also, the highest Mn concentration was recorded in the case of rural site D (942.50 mg/kg). However, the contents of Mn in root samples were not at the level of the related soil concentrations, which suggested that roots of wild blackberry cannot reflect quite accurately the existing situation in the soil. This is not unexpected because it is well known that plant assimilate metals from soils predominately according to their individual needs, or according to the tactics for avoiding extremely high metal concentrations but often also depending on the important soil parameters such as soil pH, organic matter or cation exchange capacity [14, 15].

Table 2 Calculated EFs

Sampling site	EFsoil	EFroot	EFleaves
FJ	0.93	0.53	7.82
BN	2.30	0.20	3.76
SN	1.53	0.36	0.76
NS	1.10	0.27	2.03
O	1.62	0.21	1.17
S	0.44	0.34	1.24
D	3.90	6.14	12.45

It is interesting to note that at most U/I locations, Mn concentration in the root sample was much lower than Mn content in the related (unwashed) leaf sample. The greatest leaf concentration was recorded at the site D: 357.95 mg/kg, whereas the lowest was found at the site SN (from U/I zone): 21.73 mg/kg. It is also interesting that the calculation of leaf EFs revealed a dissimilar situation regarding the soil and root EFs. Namely, leaf EFs pointed that moderate to significant pollution existed at the sites such as FJ, BN, and D; site NS was at the edge of moderate pollution; this further suggested that unwashed wild blackberry leaves have a very good capability to reflect the level of pollution originating predominately from the atmosphere and mostly of seasonal character. This also corroborated that leaf Mn originated not only from the soil but also from the atmospheric deposition (most probable, resulting from various mining-metallurgical activities in the region of Bor).

4 Conclusion

The results of this work suggested that the presence of Mn in the environment of Bor's region was not at some considerable level, which is in the opposite of the situation with other investigated heavy metals, Cd, Pb, Cu, Zn, and As. More precisely, the data processing showed almost total absence of contamination in the case of the analyzed soils and roots (practically, a great majority of the investigated locations had EF values much lower than 2), while in the case of leaves, some locations showed to be moderately to significantly contaminated (practically, sites FJ, BN, and D had EF values greater than 2). These findings suggest that leaves of wild blackberry have excellent biomonitoring potential to reflect the level of Mn presence in the environment, especially with regard to the seasonal pollution originating from the atmosphere, whereas roots' potentials are not so significant (consequently, roots are not so applicable in soil biomonitoring). On the basis of the complete soil analysis, including the comparisons of the detected Mn concentrations with USEPA RSLs and world soil average concentrations, it can be concluded that the presence of Mn in surface soils in the Bor region is predominantly of geogenic origin, while leaf analysis showed that various mining-metallurgical activities cannot be totally excluded as possible anthropogenic sources of Mn in the complete environment of the same region. It can be concluded that the combination of soil and plant data applied in this work provided a deep and accurate insight into the level of Mn presence in the region of interest, which recommends this approach as one of the most adequate for biomonitoring studies.

Acknowledgments

The Ministry of Education, Science and Technological Development of Serbia financially supported this research (Projects No. III46010, OI172031, OI172047 and OI172060).

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