University of Belgrade
Technical Faculty Bor

PROCEEDINGS

XXIII International Conference
Ecological Truth

Editors
Radoje V. Pantovic
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EcoIst '15

Hotel "PUTNIK", Kopaonik, SERBIA
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PUBLISHER:
UNIVERSITY OF BELGRADE - TECHNICAL FACULTY IN BOR, BOR, JUNE 2015

FOR THE PUBLISHER:
DEAN: Prof. dr Milan ANTONIJEVIC

EDITOR IN CHIEF:
Prof. dr Radoje PANTOVIC

TECHNICAL EDITOR
Zeljko PAJKIC, MSc.

PRINTED BY:
“TERCIJA” Bor

CIP - Каталогизација у публикацији -
Народна библиотека Србије, Београд

502/504(082)
613(082)

INTERNATIONAL Conference Ecological Truth (23rd ; 2015 ; Kopaonik)
Proceedings / XXIII International Conference "Ecological Truth", Eco-Ist '15, 17-20 June 2015, Kopaonik, Serbia ; ŠorganizersĆ University of Belgrade, Technical Faculty, Bor ... Šet al.Ć ; edited by Radoje V. Pantovic and Zoran S. Markovic. - Bor : Technical Faculty, 2015 (Bor : Tercija). - XIX, 797 str. : ilustr. ; 25 cm

Tiraž 250. - Bibliografija uz svaki rad. - Registar.

ISBN 978-86-6305-032-7

1. Technical Faculty (Bor)
a) Животна средина - Заштита - Зборници b) Здравље - Заштита - Зборници

COBISS.SR-ID 215721740

ORGANIZER:

UNIVERSITY OF BELGRADE – TECHNICAL FACULTY BOR

Co-ORGANIZERS:

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Society of Young Researchers - Bor

GENERAL SPONSOR:

The Ministry of Education, Science and Technological Development of the Republic of Serbia

XXIII International Conference
"ECOLOGICAL TRUTH" ECO-IST'15
17 – 20 June 2015, Hotel "PUTNIK", Kopaonik, SERBIA

THE CONTENT OF MANGANESE IN SOILS AND PLANTS OF BOR MINE OVERBURDEN SITE (SERBIA, SE EUROPE)

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ABSTRACT

Manganese is ubiquitous element in nature, being abundant constituent of soils and having essential role as micronutrient in plants. However, some interactions of manganese in diverse natural processes are not yet fully understood. This paper analyses the results of manganese content screening for frequent wild plants of Bor mine waste overburden, defines main relations with characteristics of overburden mine soils and presents the extent of its transfer in wild plants of this area.

Key words: manganese, overburden soil, wild plants.

INTRODUCTION

Manganese is a common metal in the Earth's crust and its presence in soils mainly results from Mn in the parent material. Manganese mobility in soil is sensitive to conditions such as acidity, oxido-reduction processes, organic matter content, biological activity and moisture [1]. The solubility of soil manganese is mainly controlled by redox potential and soil pH, where low pH or low redox potential favor the reduction of insoluble manganese oxides which increase the solubility of Mn^{2+} [2]. Manganese oxides have high adsorption activity for heavy metals. This is especially important for mine soil environments prone to acidification and leaching, where these oxides exhibits strong control on the mobility and bioavailability of many bio-essential and toxic heavy metals [3].

Manganese is also essential microelement for plants, taking role in photosynthesis process, lipid biosynthesis, protecting cells against reactive oxygen species and being cofactor of certain enzymatic activities in plants [4]. The critical deficiency levels of Mn in plants are similar, varying between 15 to 25 kg [5], regardless of plant species or cultivar or prevailing environmental conditions. However, the excess of this micronutrient is toxic for plants. The critical toxicity for Mn concentration varies widely among plant species and environmental conditions [1]. Even within a same species, the critical toxicity concentration can vary among its cultivars [6]. Besides disparity among Mn levels that induce toxicity, the symptoms of this toxicity in plant species may also be diverse [7]. Chlorosis and brown necrotic spots on leaves are frequently observed indicators of the Mn toxicity in plants [8]. Plant uptake of Mn is merely a function of the Mn oxidation state in the soil. The most soluble species in soil, Mn^{2+}, is also the most efficiently accumulated in plants [1]. It is therefore considered that Mn content of plants is a direct function of the soluble Mn pool in soils [5]. A mobilization of Mn^{2+} is produced by the rhizosphere acidification due to the release of H^+ or low molecular weight organic acids from plant roots [9]. Availability of manganese increases in acidic soils or anaerobic conditions [23]. Therefore, manganese is considered to be among the most important toxic metals in acid soils [10].

MATERIALS AND METHODS

The study area is placed on the margins of the town of Bor (44°04'25" N, 22°05'26"E, SE Serbia, Europe). Copper ore exploitation process in this area has resulted in formation of overburden piles covering an area of approximately 150 ha. They consist of non-selectively deposited volcanic rocks, mainly andesite and its volcaniclastic equivalents. This area is selectively covered with wild herbaceous species.

A total of 52 composite soil samples were taken from the upper 20 cm layer of the sampling plots. The soil samples were air-dried and then sieved through a 2 mm sieve. A soil–water solution (1:2.5) was used for determining the active soil acidity, while the 1M KCl solution was used for measuring the potential acidity of mine overburden soil. Soil electrical conductivity (EC) was measured with conductivity cell in 1:2.5 soil-water solution, while oxido-reduction potential (Eh) was measured meter with a platinum electrode, previously polished and tested by ZoBell's solution [11]. The saturated calomel electrode (0.244 V at 25 °C) was used as a reference electrode. Organic carbon was measured by the method of Tjurin [12] and total nitrogen contents were determined by the method of Kjeldahl [13]. The contents of plant-available forms of phosphorus and potassium were analyzed with the Al-method [14]. Soil textural classes (sand, silt and clay) were examined by dispersion with sodium-pyrophosphate following sedimentation with international pipette-B method. Pseudo-total Mn was extracted by aqua regia digestion (International standard ISO 11466: 1995). Pseudo-total contents give an assessment of the maximum potentially soluble or mobile contents of Mn, not bounded in silicates. Available fraction of Mn was extracted in 0.05 M EDTA. Manganese concentrations were determined by ICP-OES (SpectroGenesis EOP II, Spectro Analytical Instruments GmbH, Kleve, Germany).

Five frequent wild plant species were collected as composite samples from the overburden area. They were rinsed with tap water and carefully washed with distilled water, after which thez were separated to root and shoot parts. Three parts were microwave digested with HNO_3 i H_2O_2 and their manganese concentrations were determined by ICP-OES. In order to determine phytoremediation potential of selected plants, biological concentration factor (BCF) was calculated as ratio of metal concentration in plant roots to that in soil, biological accumulation factor (BAC) was calculated as ratio of heavy metal in shoots to that in soil, and translocation factor (TF) was described as ratio of heavy metals in plant shoot to the content in plant root [15].

Box-Cox transformation was conducted prior to statistical analysis in order to normalize data. Analysis of variance (ANOVA) and calculation of Pearson correlation coefficient was conducted in statistical package StatSoft 8.0.

RESULTS AND DISCUSSION

Average content of manganese in soils of Bor mine overburden (X_{invBC}=383 ppm) is lower than the European soil's natural background value [16], having enrichment factor of 0.76. Average content of available manganese Bor mine overburden soils exhibits 17.4 % of their total manganese content (ranging from 15.4 % at rhizosphere soil of *A. stolonifera*, up to 19.4 % for rhizosphere soil of *L. genistifolia*). Average levels of manganese in root and shoot of sampled plant species are generally low, having values of 24.7 and 26.2 ppm, which places them close to deficiency levels [5].

Table 1. Average pseudototal and EDTA-available manganese content in rhizosphere soils and roots and shoots of wild plants at Bor overburden site

Species	$Mn_{pseudototal\ XBc(inv)}$	$Mn_{EDTA\text{-}available\ XBc(inv)}$	$Mn_{rootXBc(inv)}$	$Mn_{shoot\ XBc(inv)}$
Linaria genistifolia	607	112	2.67	14.1
Epilobium dodonaei	556	108	6.27	5.01
Calamagrostis epigejos	277	42.8	87.2	119
Sanguisorba minor	452	87.4	1.37	N.D.
Agrostis stolonifera	214	33	256	158

Manganese content in plants varies greatly depending on the species. According to the results of analysis of variance (ANOVA), wild plant species show significant differences between their rizosphere soil Mn levels (F_{edta}=3 , p_{edta}=0.03 ; F_{pt}=8.02 , p_{pt}=0.00), as well as their root (F_r= 22.84, p_r=0.00)and shoot (F_s= 28.77, p_s= 0.00) Mn content. As presented in table 1, average content of Mn in plants tends to be higher in shoots then in roots of species *L. genistifolia* and *C. epigejos*, while the other wild species exhibit the opposite trend. The content of Mn in species *L. genistifolia*, *E. dodonaei and S. minor* is beyond deficiency limit. Species *C. epigejos* and *A. stolonifera* show highest concentration of Mn in their roots and shoots, while contents of Mn in their rhizosphere soil are lower compared to the rhizosphere soil of other investigated species.

Results presented in table 2 show high ranges of soil pH values, electrical conductivity, organic material content, available potassium and phosphorous , S_{EDTA} i S_{PT} content. Further, table xz shows main correlations of manganese content in soil and plants with physico-chemical mine soil properties and the content of soil sulfur.

Table 2. Range of main physico-chemical characteristics and correlation coefficients of manganese content in soil and plants with Bor mine overburden soil physico-chemical properties and content of sulfur (Eh – oxido'reduction potential, EC-electrical conductivity, OM – organic material, N_tot – total nitrogen content, K_2O – available potassium content, P_2O_5 – available phosphorous content, S_{EDTA} – EDTA available sulphur, S_{PT} -pseudototal content of sulphur, significant correlations are given with *)

Variable	Interval	Mn_{Root}	Mn_{Shoot}	$Mn_{EDTA\ available}$	$Mn_{pseudo-total}$
Silt (%)	0.2-2.49	-0.26	-0.29	-0.01	0.05
Clay (%)	0.33-3.12	-0.15	-0.13	0.10	0.12
pH (H_2O)	3.45-8.4	*-0.77	*-0.83	*0.52	*0.64
pH (KCl)	2.65-6.94	*-0.75	*-0.80	*0.57	*0.67
Eh (mV)	202-363	*0.72	*0.80	*-0.45	*-0.56
EC (µS)	76.9-2310	*0.54	*0.58	-0.11	-0.27
OM (%)	0.01-9.3	-0.24	-0.30	0.22	0.31
K_2O (%)	2.65-37	-0.44	-0.57	*0.49	*0.50
N_Tot (%)	0.01-0.08	-0.60	-0.63	0.35	0.38
P_2O_5 (%)	0.05-24	*-0.72	*-0.74	0.15	0.22
S_{EDTA}	121-13264	*0.58	*0.60	-0.13	-0.27
S_{PT}	1171-22719	*0.61	*0.59	0.15	0.01

Content of pseudototal and available Mn in rizosphere soil, as well as level of Mn in root and shoot of plant species strongly correlates with pH and Eh of mine overburden soil, confirming the known dependence of manganese mobility and soil Eh–pH conditions [5]. Observed correlation of Mn plant levels and available soil P in Bor overburden mine soils is in the accordance with the researches that have spotted negative correlation with available P content in soil and level of Mn accumulation in plants [17]. Although the exact mechanisms of the Mn–P interaction so far remained unknown, it has been suggested that P interferes directly with Mn at the uptake and translocation level [17], [18] ,[19].

Relation of electrical conductivity and plant manganese levels has been observed in some investigations, where both antagonistic and synergistic effects were recorded depending on the plant species and soil conditions, as well as the type of salt [20]. However, the impact of decreased or increased uptake of Mn under salinity stress is a phenomenon that requires further study (Han et al, 2014 [21]).Increased salinity in Bor mine overburden soils is a result of soluble sulphate salts in surface overburden layers, which is reflected through high correlation coefficient of sulfur levels and measured EC (r_{EDTA}=0.87, r_{PT}=0.80). Therefore, observed correlation of Mn plant content and measured EC as well as the correlation with levels of S could be in accordance with processes of soil acidification during dissolution of sulphur salts.

Table 3. Manganese concentration and accumulation factors of wild plants

Species	BCF_{PT}	BCF_{EDTA}	BAF_{PT}	BAF_{EDTA}	TF
Linaria genistifolia	0.04	0.02	0.02	0.12	5.28
Epilobium dodonaei	0.01	0.06	0.009	0.046	0.8
Calamagrostis epigejos	0.31	2.04	0.43	2.78	1.36
Sanguisorba minor	0.003	0.01	-	-	-
Agrostis stolonifera	1.19	7.75	0.74	4.79	0.62

Results presented in table 3 show high variability of concentration, accumulation and transfer factors for Mn between the selected wild species. Species *S. minor* showed lowest efficiency in accumulating and transporting Mn from overburden soil, while *A. stolonifera* had highest efficiency for concentration and accumulation of this element. However, higher transfer efficiency of this element belongs to *L. genistifolia* and *C.epigejos*.

Concerning the phytoremediation potential, species *A. stolonifera* showed potential for phytostabilization of manganese in Bor overburden mine soils, while species *C. epigejos* showed phytoaccumulation abilities for bioavailable content of Mn. Genus *Agrostis* has been recognized for their ability to accumulate Mn, e.g. grass *Agrostis gigantea* was used and has further been proposed for restoration of Mn-contaminated sites, due to its high threshold values for Mn toxicity [22], [23]. Some species of genus *Calamagrostis* (such as *Calamagrostis arundinacea*) have also been recognized for accumulating higher concentrations of Mn in roots and shoots [24].

CONCLUSION

Average content of manganese in soils of Bor mine overburden is generally lower than the European soil's natural background value. Content of manganese in root and shoot of wild plants growing on the Bor mine overburden mainly depends on pH-Eh soil system, content of available phosphorous and electrical conductivity. Manganese level in soils also corresponds to pH-Eh soil regime, as well as the content of available potassium.

Average Mn content of wild plants in Bor overburden significantly varies among the plant species. While the content of Mn in species *L. genistifolia*, *E. dodonaei and S. minor* is beyond deficiency limits, species *C. epigejos* and especially *A. stolonifera* show higher concentration in their roots and shoots, as well as the phytoremediation potential for this element.

For gaining stronger insight into geochemical and biogeochemical behavior of manganese in mine soils of Bor overburden, further investigations should take into account speciation of manganese in overburden soil, as well as synergistic and antagonistic relation of Mn behavior and uptake with other important chemical elements from Bor overburden, such as cooper, arsenic, lead and zinc.

Acknowledgement

This study was supported by the Serbian Ministry of Education, Science and Technological Development (Project No. 176016)

REFERENCES

1. Marschner, P.: Marschner's Mineral Nutrition of Higher Plants. Third Edition. Elsevier, London,UK, 2012.
2. Nadaska, G., Lesny, J., Michalik, I.: Environmental Aspect of Manganese Chemistry, http://heja.szif.hu/ENV/ENV-100702-A/env100702a.pdf, 2012.

3. Mayanna, S., Peacoc, C.L., Schäffner, F., Grawunder, A., Merten, D., Kothe, E., Büchel, G.: Biogenic precipitation of manganese oxides and enrichment of heavy metals at acidic soil pH, Chemical Geology, 402 : 6-17., Elsevier, 2015.
4. Burnell, J. N.: The biochemistry of manganese in plants. In Manganese in Soils and Plants (R. D. Graham, R. J. Hannam and N. C. Uren, eds.), pp. 125–137. Kluwer Academic Publ. Dordrecht, 1988.
5. Kabata-Pendias, A.: Trace elements in soils and plants 4th ed. Boca Raton, CRC Press, 2011.
6. Khabaz-Saberi, H., Rengel, Z., Wilson, R., Setter, T.L.: Variation of tolerance to manganese toxicity in Australian hexaploid wheat. Journal of Plant Nutrition and Soil Science, 173: 103-112., Wiley-VCH, 2010.
7. Foy, C, Scott, B., Fisher, J.: Genetic differences in plant tolerance to manganese toxicity. In: R.D. Graham, R.J. Hannam, N.J. Uren. (eds). Manganese in Soil and Plants., pp. 293-307. Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.
8. Wissemeier, A., Horst, W.: Simplified methods for screening cowpea cultivars for manganese leaf-tissue tolerance. Crop Science, 31: 435-439., Crop Science Society of America, 1991.
9. Rengel, Z., Marschner, P.: Nutrient availability and management in the rhizosphere: exploiting genotypic differences. New Phytologist, 168: 305-312., Wiley-VCH, 2005.
10. Adriano, D.C.: Trace elements in terrestrial environments: Biogeochemistry, bioavailability, and risks of metals, 2nd ed., pp. 867. Springer, New York, 2001.
11. American Public Health Association: Standard methods, 20th edition, Washington DC, 1998.
12. Tjurin, I.: Agrochemical methods of soil analysis. Nauka, Moscow, 1965.
13. Benton Jones, B.: Laboratory Guide for Conducting Soil Tests and Plant Analysis. CRC Press, 2001.
14. Egner, H., Riehm, H., Domingo, W.: Untersuchungen uber die chemische Bodenanalyse als Grundlage fur die Beurteilung des Nahrstoffzustandes der Boden II. Chemische Extractionmetoden zu Phosphor- und Kaliumbestimmung. – K. Lantbr., 26: 199-215., Hogsk. Annlr. W.R , 1960.
15. Yoon, J., Cao, X., Zhou, Q., Ma, L.: Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site, Science of the Total Environment, 368: 456–464., Elsevier, 2006.
16. Salminen, R. (chief ed.) et al. : Geochemical Atlas of Europe. Part 1 - Background Information, Methodology and Maps. Geological Survey of Finland, 525 pp., Otamedia Oy, Espoo, 2005.
17. Pedas, P., Husted, S., Skytte, K., Schjørring, J. K.: Elevated phosphorus impedes manganese acquisition by barley plants, Frontiers in Plant Science, 37 (2)., Frontiers, 2011.
18. Neilsen D., Neilsen G. H., Sinclair A. H., Linehan D. J.: Soil phosphorus status, pH and the manganese nutrition of wheat. Plant and Soil , 145 (1): 45-50, Elsevier, 1992.

19. Zhu Y. G., Smith F. A., Smith S. E.: Phosphorus efficiencies and their effects on Zn, Cu, and Mn nutrition of different barley (*Hordeum vulgare*) cultivars grown in sand culture, Australian Journal of Agricultural Research, 53(2): 211 – 216.,Csiro Publishing, 2002.
20. Cooper, A.: A comparative study of the tolerance of salt marsh plants to manganese, Plant and Soil, Volume 81(1): 47-59., Springer, 1984.
21. Han, L., Gao, Y., & Li, D.: Ion Uptake in Tall Fescue as Affected by Carbonate, Chloride, and Sulfate Salinity. Plos One, 9(3), e91908. http://dx.doi.org/10.1371/journal.pone.0091908, 2014.
22. Muncy, Jack A.: Reclamation of abandoned manganese mines in southwest Virginia and northeast Tennessee. In: Walker, D. G.; Powter, C. B.; Pole, M. W., compilers. Reclamation, a global perspective: Proceedings of the conference; 1989 August 27-31; Calgary, AB. Edmonton, AB, p. 199-208. Alberta Land Conservation and Reclamation Council, 1989.
23. Paschke, M.W. Valdecantos,A., Redente, E.F.: Manganese toxicity thresholds for important restoration grass species of the Western United States, Environmental Pollution, 135: 313-322, Elsevier, 2005.
24. Antosiewicz, D.M., Agnjeszka, S, Sowinski, P.: Trace Elements as Contaminants and Nutrients: Consequences in Ecosystems and Human Health, John Wiley & Sons, 2008.