University of Belgrade, Technical Faculty in Bor

30 ECOTER

30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

Editor
Prof. Dr Snežana Šerbula

University of Belgrade, Technical Faculty in Bor

30th International Conference Ecological Truth & Environmental Research 2023

Proceedings

Editor
Prof. Dr Snežana Šerbula

PROCEEDINGS

30th INTERNATIONAL CONFERENCE

ECOLOGICAL TRUTH AND ENVIRONMENTAL RESEARCH – EcoTER'23

Editor:

Prof. Dr Snežana Šerbula

University of Belgrade, Technical Faculty in Bor

Editor of Student section:

Prof. Dr Maja Nujkić

University of Belgrade, Technical Faculty in Bor

Technical editors:

Jelena Milosavljević, PhD, University of Belgrade, Technical Faculty in Bor

Asst. prof. Dr Ana Radojević, University of Belgrade, Technical Faculty in Bor

Sonja Stanković, **MSc**, University of Belgrade, Technical Faculty in Bor

Cover design:

Aleksandar Cvetković, **BSc**, University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor

For the publisher: Prof. Dr Dejan Tanikić, Dean

Printed: University of Belgrade, Technical Faculty in Bor, 100 copies, electronic edition

Year of publication: 2023

ISBN 978-86-6305-137-9

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

502/504(082)(0.034.2)
574(082)(0.034.2)

INTERNATIONAL Conference Ecological Truth & Environmental Research (30 ; 2023)
Proceedings [Elektronski izvor] / 30th International Conference Ecological Truth & Environmental Research - EcoTER'23, 20-23 June 2023, Serbia ; organized by University of Belgrade, Technical faculty in Bor (Serbia) ; co-organizers University of Banja Luka, Faculty of Technology – Banja Luka (B&H) ... [et al.] ; [editor Snežana Šerbula]. - Bor : University of Belgrade, Technical faculty, 2023 (Bor : University of Belgrade, Technical faculty). - 1 elektronski optički disk (CD-ROM) ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Preface / Snežana Šerbula. - Tiraž 100. - Bibliografija uz svaki rad.

ISBN 978-86-6305-137-9

а) Животна средина -- Зборници б) Екологија – Зборници

COBISS.SR-ID 118723849

30th International Conference
Ecological Truth and Environmental Research – EcoTER'23

is organized by:

UNIVERSITY OF BELGRADE
TECHNICAL FACULTY IN BOR (SERBIA)

Co-organizers of the Conference:

University of Banja Luka, Faculty of Technology, Banja Luka (B&H)

University of Montenegro, Faculty of Metallurgy and Technology, Podgorica (Montenegro)

University of Zagreb, Faculty of Metallurgy, Sisak (Croatia)

University of Pristina, Faculty of Technical Sciences, Kosovska Mitrovica

Association of Young Researchers Bor (Serbia)

HONORARY COMMITTEE

Dr. Petar Paunović
(Zaječar, Serbia)
Prof. Dr Zvonimir Stanković
(Bor, Serbia)
Prof. Dr Velizar Stanković
(Bor, Serbia)
Prof. Dr Milan Antonijević
(Bor, Serbia)
Dragan Ranđelović, Association of Young Researchers Bor
(Bor, Serbia)
Toplica Marjanović, Association of Young Researchers Bor
(Bor, Serbia)
Mihajlo Stanković, Special Nature Reserve Zasavica
(Sremska Mitrovica, Serbia)

SCIENTIFIC COMMITTEE

Prof. Dr Snežana Šerbula, ***President***

Prof. Dr Alok Mittal
(India)
Prof. Dr Jan Bogaert
(Belgium)
Prof. Dr Aleksandra Nadgórska-Socha
(Poland)
Prof. Dr Luis A. Cisternas
(Chile)
Prof. Dr Wenhong Fan
(China)
Prof. Dr Martin Brtnický
(Czech Republic)
Prof. Dr Isabel M. De Oliveira Abrantes
(Portugal)
Prof. Dr Shengguo Xue
(China)
Prof. Dr Tomáš Lošák
(Czech Republic)
Prof. Dr Maurice Millet
(France)
Prof. Dr Murray T. Brown
(New Zealand)
Prof. Dr Xiaosan Luo
(China)
Prof. Dr Daniel J. Bain
(United States of America)
Prof. Dr Che Fauziah Binti Ishak
(Malaysia)
Prof. Dr Richard Thornton Baker
(United Kingdom)
Prof. Dr Mohamed Damak
(Tunisia)
Prof. Dr Jyoti Mittal
(India)
Prof. Dr Miriam Balaban
(United States of America)

Prof. Dr Yeomin Yoon
(United States of America)
Prof. Dr Chang-min Park
(South Korea)
Prof. Dr Faramarz Doulati Ardejani
(Iran)
Prof. Dr Ladislav Lazić
(Croatia)
Prof. Dr Natalija Dolić
(Croatia)
Prof. Dr Milutin Milosavljević
(Kosovska Mitrovica)
Prof. Dr Nenad Stavretović
(Serbia)
Prof. Dr Ivan Mihajlović
(Serbia)
Prof. Dr Milovan Vuković
(Serbia)
Prof. Dr Nada Blagojević
(Montenegro)
Prof. Dr Darko Vuksanović
(Montenegro)
Prof. Dr Irena Nikolić
(Montenegro)
Prof. Dr Šefket Goletić
(B&H)
Prof. Dr Džafer Dautbegović
(B&H)
Prof. Dr Borislav Malinović
(B&H)
Prof. Dr Slavica Sladojević
(B&H)
Prof. Dr Nada Šumatić
(B&H)
Prof. Dr Snežana Milić
(Serbia)

ORGANIZING COMMITTEE

Prof. Dr Snežana Šerbula, *President*

Prof. Dr Snežana Milić, *Vice President*

Prof. Dr Đorđe Nikolić, *Vice President*

Prof. Dr Marija Petrović Mihajlović

Prof. Dr Milan Radovanović

Prof. Dr Milica Veličković

Prof. Dr Danijela Voza

Prof. Dr Maja Nujkić

Prof. Dr Žaklina Tasić

Dr Ana Simonović

Dr Tanja Kalinović

Dr Ana Radojević

Dr Jelena Kalinović

Dr Jelena Milosavljević

Sonja Stanković, MSc

Miljan Marković, MSc

Vladan Nedelkovski, MSc

Aleksandar Cvetković, BSc

DETERMINATION OF PTEs CONTENT IN LIVESTOCK FODDER AND SOIL IN THE VICINITY OF THERMAL POWER PLANTS AND ASH DISPOSAL SITES

Marija Matić[1*], Dragana Pavlović[1], Veljko Perović[1], Dimitrije Sekulić[1], Natalija Radulović[1], Miroslava Mitrović[1], Pavle Pavlović[1]

[1]Department of Ecology, Institute for Biological Research "Siniša Stanković" – National Institute of Republic of Serbia, University of Belgrade, Bulevar Despota Stefana 142, 11060 Belgrade, SERBIA

[*]*marija.pavlovic@ibiss.bg.ac.rs*

Abstract

Potentially toxic elements (PTEs) are present in the environment as a result of natural processes, but also numerous anthropogenic activities. A large part of PTE in the soil originates from industrial plants or from contaminated water used to irrigate agricultural fields. Thus, they are taken up by plants used for human consumption or by plants grown to feed domestic animals (fodder). In order to determine the presence of B, Cu and Ni in the food chain and to evaluate and reduce the risk of growing plants for livestock feed on potentially contaminated soils in the immediate vicinity of coal mines and thermal power plants, samples of alfalfa (Medicago sativa L.) and soil were collected from the territory of municipalities of Obrenovac (village Krtinka) and Lazarevac (village Sokolovo), while the territory of the municipality of Surčin (village Jakovo) was chosen as the control site. Furthermore, the bioconcentration factor (BCF) was calculated, which can provide information about the potential efficiency of the removal of elements from the soil by the plant. The results of the content of the studied elements in fodder were within the usual concentrations for conventional production. However, Ni content in the soil was above the proposed MAC for soils according to the regulations of the Republic of Serbia (50 mg kg^{-1}) and higher than the limit values proposed by the Council Directive of the European Community (30–75 mg kg^{-1}). These results urge caution in the cultivation of fodder at investigated sampling sites.

Keywords: potentially toxic elements, *Medicago sativa*, soil contamination, bioconcentration factor.

INTRODUCTION

Intensive urbanization and industrialization led to the development of new and the expansion of existing cities and industrial areas, the main problem being the pollution of air, water, soil and vegetation. The main sources of pollution in such environments are combustion products from industry, traffic, urban heating plants, domestic heating, construction activities, and improper storage of industrial and municipal waste. Potentially toxic elements (PTEs) are present in the environment, both as a result of natural processes and numerous anthropogenic activities. A large proportion of PTEs and other pollutants in soil and water originate from industrial facilities, as a result of the use of pesticides and mineral fertilizers or from contaminated water used to irrigate agricultural fields. Thus, elements are taken up by plants grown for human consumption or to feed domestic animals. Sometimes these concentrations can rise to levels that are toxic to plants, animals, and thus to humans who consume food produced on such soils, as they are incorporated into the food chain [1-4].

Regardless of the origin of PTEs in the soil, their concentration, mobility and potential availability to plants depend on the parent substrate, the pH reaction, the proportion of organic matter and clay in the soil, the physical properties of the soil, moisture, the presence of other chemical substances and other factors [4–6].

In order to determine the presence of B, Cu and Ni in the food chain, to assess and reduce the risk of growing plants for animal feed on soils in the immediate vicinity of coal mines and thermal power plants, samples of alfalfa (*Medicago sativa* L.) and soils were collected on the territory of the municipalities of Obrenovac (village Krtinka) and Lazarevac (village Sokolovo). The area of Surčin municipality (village Jakovo) was chosen as the control site without direct industrial activity. In addition, the bioconcentration factor (BCF) was calculated, which can provide information about the potential efficiency of the removal of chemical elements from the soil by the plant.

Medicago sativa is a perennial herb that is one of the most important fodder crops. Apart from feeding livestock, it is also important for improving the physical, chemical and microbiological properties of the soil, as its harvest leaves significant amounts of organic matter in the soil, which is further decomposed. Owing to its deep root system, it helps improve the nitrogen fertility of the soil and protect it from soil erosion. The depth of root system makes it very resistant, especially to droughts [7].

MATERIALS AND METHODS

Sample collection and preparation

Sampling was conducted in three municipalities – Obrenovac (village Krtinka), Lazarevac (village Sokolovo) and Surčin (village Jakovo), in gardens located in the vicinity of the fly ash disposal site of the “Nikola Tesla-A” thermal power plant. At each of the three villages, three sampling sites (gardens) were randomly selected for plant and associated soil sampling. *Medicago sativa* was sampled in the form of hay for livestock feed in the amount of approximately 2 kg. Samples of plant material were dried for 10 days at room temperature, and then in a drying chamber (Binder, Tuttlingen, Germany) to a constant weight. Dried samples were grounded with a stainless-steel mill and sieved through 1.5 mm stainless-steel sieve (Polymix, Kinematica AG). The associated soil at each sampling site was also sampled from three individual sampling points at the depth of 0–20 cm following a harmonised sampling regime. These were then mixed into a composite sample with the total weight of approximately 2 kg. Soil samples were dried at 105 ºC to a constant mass and homogenized. The surface layer of soil was chosen for analysis because PTE deposition in soil mostly occurs in top soil [8].

PTEs and statistical analysis

The concentration of B, Cu and Ni in the collected plant material was measured after digestion with HNO_3 and H_2O_2 (USEPA 3052). Element concentrations were measured by the method of optical emission spectrometry for simultaneous multielemental analysis (ICP-OES, Spectro Genesis), using the reference material beech leaves (BCR-100) for validation of the analytical procedure and quality control of the laboratory protocol. The analysis was performed in six replicates (n=6). The detection limits (mg kg^{-1}) are as follows: B-0.001, Cu-0.007 and Ni-0.089. The element content in the soil was determined in the same manner as for the plant material, using the USEPA method (3052) and the standard reference material (Loam soil - ERM - CC141) to validate the analytical procedure, with detection limits identical to those of the plant material.

The data from this study was analysed using statistical analysis (ANOVA) and means were separated with a Bonferroni test at a level of significance of $p<0.05$, using the Statistica software package (StatSoft In., Tulsa, USA, 2007).

Based on the obtained element concentrations in soil and plant material, the bioconcentration factor (BCF) was determined, which indicates the potential efficiency of removal of chemical element from soil by plants. This factor defines the ratio between the available amount of a chemical element in the soil and the amount in the plant material ($[Element]_{leaf\ or\ bark}/[Element]_{soil}$) [9,10]. A value of BCF > 1 indicates the potential of plant for phytostabilization of certain soil element.

RESULTS AND DISCUSSION

The concentrations of PTEs in plant material were compared with reference values for the leaves of most herbaceous plants [11], and the maximum allowable concentration of certain elements in fodder that do not adversely affect the diet of domestic animals (Table 1) [12,13].

Table 1 *Limit values of PTEs in plants and fodder (mg kg^{-1})*

	B	Cu	Ni
TL[a]	50–200	20–100	10–100
MAC[b]	/	12–200	50

[a] Critical or toxic levels in leaf tissue for various species [11]; [b] maximum allowable concentration in fodder [13].

The concentrations of PTEs in fodder and associated soil at the investigated sampling sites are shown in Figure 1.

Boron is an essential trace element for higher plants, and its requirement varies from species to species (10–100 mg kg^{-1}, [11]), so the range between B deficiency and its toxicity is smaller than for any other element. Its uptake in plants depends directly on the physical and chemical properties of the soil, but also on the form of B and on plant transpiration [14]. In the literature, B is often cited as one of the most toxic phytonutrients due to its high solubility [15]. In the examined *Medicago sativa* samples normal concentrations of B were measured (18–25 mg kg^{-1}, [11]) (Figure 1a), with statistically significant differences in accumulation capacity determined between all sampling sites (Table 2). Regulation on maximum allowable concentrations of harmful substances and ingredients in livestock fodder does not set permissible concentration for this element (Table 1). Soil boron content ranged from 130–155 mg kg^{-1} (Figure 1b), with the highest values measured in soil samples from Surčin.

Statistically significant differences in B content ($p<0.05^*$) were found between the control site in Jakovo and Obrenovac (Table 2).

a) *b)*

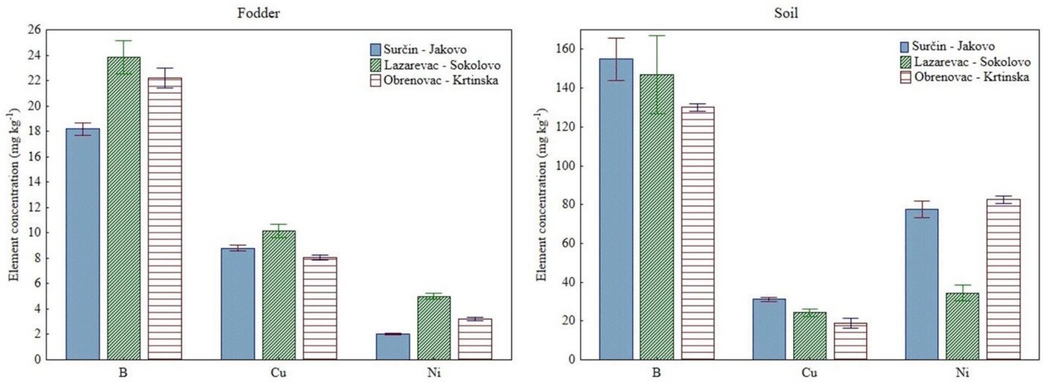

Figure 1 *Potentially toxic elements content in a) fodder and b) associated soil at examined sampling sites (mean values and standard deviation)*

The B content was above the MAC set by the regulations of the Republic of Serbia (50 mg kg^{-1}), at all sites examined, and its increased concentration may be related to coal combustion and ash formation, considering the proximity of thermal power plants [15]. Ash from thermal power plants is characterized by high content of macro and microelements, especially B, which is one of the most important environmental pollutants in the vicinity of thermal power plants and ash landfills due to its high mobility [16]. However, high B content in soil does not necessarily imply a potential risk to the environment, as its transport is affected by numerous soil parameters (texture, organic matter content, $CaCO_3$, type of parent substrate, etc.), but mainly by the pH reaction [17].

Average Cu concentrations in leaves range from 5 to 30 mg kg^{-1} [11], whereas in fodder they can vary from 2 to 69 mg kg^{-1} [12,18]. The Cu content of the studied fodder was in the normal range (8.06–10.16 mg kg^{-1}, Figure 1a), but statistically significant differences were found between all the examined sites (Table 2). Copper content in the examined soils did not exceed the MAC in soil set by regulations of the Republic of Serbia (100 mg kg^{-1}) [19,20] and the limits set by the Council Directive of the European Community (50–140 mg kg^{-1}) [21] and ranged from 18.87 mg kg^{-1} in Obrenovac to 31.2 mg kg^{-1} in Surčin. Statistically significant differences were found between all sampling sites (Table 2).

The lowest Ni content in fodder was measured in Surčin (2.04 mg kg^{-1}) and the highest in Lazarevac (5 mg kg^{-1}) and was within the normal range for plants and below the value specified for animal food ingredients MAC (Table 1). Nickel is accumulated mainly in the roots of plants, and its uptake depends primarily on the characteristics of the soil (OM content, clay, pH), the origin of Ni, and the characteristics of the plant itself. Statistically significant differences were found between all sampling sites in fodder (Table 2). Nickel content in the studied soils was higher than the MAC values for soils according to the regulations of the Republic of Serbia (50 mg kg^{-1}), except at the Lazarevac site (34.37 mg kg^{-1}, Figure 1b), and higher than the limit values proposed by the Council Directive of the European Community (30–75 mg kg^{-1}) [21]. These results are not unexpected, considering that soils in the Republic of Serbia are characterized by high Ni content due to their geological origin [22,23], but contamination of soils by Ni is possible due to the influence of industry [24].

Table 2 *Difference in PTEs content between sampling sites in fodder and associated soil*

	Fodder			**Soil**		
B (mg kg^{-1})	Surčin	Lazarevac	Obrenovac	Surčin	Lazarevac	Obrenovac
Surčin Jakovo	/	***	***	/	ns	*
Lazarevac Sokolovo	***	/	*	ns	/	ns
Obrenovac Krtinska	***	*	/	*	ns	/
Cu (mg kg^{-1})						
Surčin Jakovo	/	***	**	/	***	***
Lazarevac Sokolovo	***	/	***	***	/	***
Obrenovac Krtinska	**	***	/	***	***	/
Ni (mg kg^{-1})						
Surčin Jakovo	/	***	***	/	***	ns
Lazarevac Sokolovo	***	/	***	***	/	***
Obrenovac Krtinska	***	***	/	ns	***	/

ANOVA, n=5, *$p<0.05$; **$p<0.01$; ***$p<0.001$; ns – no statistical significance.

Phytostabilization is the formation of chemical compounds by plants and the immobilization of pollutants, which reduces their availability. The investigated *Medicago sativa* did not prove to be effective in immobilizing the examined PTEs, as all obtained values for BCF were below 1.

CONCLUSION

The concentration of the studied PTEs measured in livestock fodder from the selected sampling sites was within the usual concentrations for conventional production. *Medicago sativa* was found not to be a significant accumulator of B, Cu and Ni, as the values of the bioconcentration factor were below 1, indicating that fodder is not suitable for phytostabilization of these elements in the studied soils. It was found that the highest content of all elements in fodder was measured in the Sokolovo village (Lazarevac) and the lowest in the control site in Jakovo (Surčin). In contrast, the highest concentrations of the examined elements in the soil were measured at the control site, where the Ni values were above the MAC values for soils according to the regulations of the Republic of Serbia (50 mg kg^{-1}) and above the limit values proposed by the Council Directive of the European Community (30–75 mg kg^{-1}). Such results for Ni are not unexpected, considering that soils in the Republic of Serbia are characterized by high Ni content of geological origin, but soil contamination is also possible due to the influence of industry.

Despite the common concentrations of the studied elements in fodder, caution should be exercised in their use, as certain elements are present in the soil in high concentrations. Soil is a dynamic system in which, under suitable conditions (change in pH, redox potential and salinity), elements can be easily transported to above-ground plant parts, which could lead to significant accumulation.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia, grant No. 451-03-47/2023-01/200007.

REFERENCES

[1] Madrid F., Biasioli M., Ajmone-Marsan F., Arch. Environ. Contam. Toxicol. 55 (2008) 21–32.

[2] Bielicka-Giełdoń A., Rylko E., Zamojc K., Pol. J. Environ. Stud. 22 (4) (2013) 1013–1021.

[3] Pan L., Ma J., Hu J., *et al*., Environ. Sci. Pollut. Res. 23 (19) (2016) 19330–19340.

[4] Pavlović P., Mitrović M., Degradacija i zaštita zemljišta, Tematski zbornik, Univerzitet u Beogradu, Šumarski fakultet (2016), p.173, ISBN: 978-86-7299-242-7.

[5] Ghrefat H. A., Yusuf N., Jamarh A., *et al*., Environ. Earth Sci. 66 (2012) 199–208.

[6] Gržetić I., Ghariani R. H. A., J. Serb. Chem. Soc. 73 (8-9) (2008) 923–934.

[7] Latrach L., Farissi M., Mouradi M., *et al*., Turk. J. Agric. For. 38 (3) (2014) 320–326.

[8] Pavlović D., Pavlović M., Perović V., *et al*., Int. J. Environ. Res. Public Health. 18 (2021) 9412.

[9] Migeon A., Richaud P., Guinet F., *et al*., Water Air Soil Pollut. 204 (2009) 89–101.

[10] Chen M., Tang Y. L., Ao J., *et al*., Russ. J. Plant Physiol. 59(6) (2012) 772–780.

[11] Kabata-Pendias A., Pendias H., Trace elements in soils and plants, CRC Press, Boca Raton, FL, USA (2001), p.331, ISBN: 0-8493-1575-1

[12] Adams R. S., J. Dairy Sci. 58 (1975) 1538–1548.

[13] Official Gazette of Social Federative Republic of Yugoslavia, No. 2/90 and No. 27/90.

[14] Goldberg S., Lesch S. M., Suarez D. L., Soil Sci. Soc. Am. J. 64 (2000) 1356–1363.

[15] Adriano D. C., Trace elements in terrestrial environments, Springer, New York (2001), p.867, ISBN: 978-1-4684-9505-8.

[16] Pavlović P., Mitrović M., Đurđević L., Environ. Manage. 33 (2004) 654–663.

[17] Padbhushan R., Kumar D., J. Agric. Sci. 155 (7) (2017) 1023–1032.

[18] Simić A., Dželetović Ž., Vučković S., *et al*., Hem. Ind. 69 (5) (2015) 459-467.

[19] Official Gazette of the Republic of Serbia, No.23/94.

[20] Official Gazette of the Republic of Serbia, No. 88/10.

[21] Directive 86/278/EEC, Off. J. Eur. Communities. 1986 (181) 6–12.

[22] Mrvić V., Zdravković M., Sikirić B., *et al*., Harmful and hazardous elements in soil *in* The Fertility and Content of Hazardous and Harmful Substances in the Soils of Central Serbia, Editors: Mrvić V., Antonović G., Martinović L., Institute of Soil Science, Belgrade (2009) 75–144, ISBN: 978-86-911273-1-2.

[23] Kuzmanoski M. M., Todorović M. N., Aničić-Urošević M. P., *et al.*, Hem. Ind. 68 (2014) 643–651.

[24] Wei B., Yang L., Microchem. J. 94 (2010) 99–107.