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Zrenjanin, Republic of Serbia

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INTRODUCTION

Department of Mechanical Engineering and Department of Environmental Protection of Technical Faculty "Mihajlo Pupin" Zrenjanin have organized the XIII International Conference Industrial Engineering and Environmental Protection – IIZS 2023. The first international conference IIZS was organized in October 2011, and since October 2017, two departments have jointly participated in organizing this event. The topics of the scientific conference cover the fields of Industrial engineering and Environmental protection: Mechanical engineering, Energetics and Process Technique, Design and Maintenance, Oil and Gas Engineering, Health and Environmental Protection, Environmental Management, Occupational Safety, and Engineering management.

This year, IIZS was organized in a hybrid manner. Received and accepted papers were presented orally on the premises of the Technical faculty "Mihajlo Pupin" Zrenjanin and online using the Zoom platform. A specific number of papers was presented through posters. The Proceedings of IIZS 2023 contains 69 papers from 198 participants, among whom 49 are foreign authors. Besides Serbia, the authors come from 12 countries: Croatia, Bosnia and Herzegovina, Romania, India, Iran, Turkey, Bulgaria, Denmark, China, Montenegro, Slovenia, Austria, and Slovakia.

The main objectives of the IIZS 2023 conference are to innovate and expand engineering knowledge from industry and environmental protection, provide support to researchers in presenting their research results, establish new contacts with leading national and international institutions and universities, popularize the faculty and its leading role in our society and its immediate environment, draw the attention of diligent young researchers to study at our faculty, cooperate with other organizations, public companies, and industry, initiate collection of new ideas in solving specific practical problems, introduce professional and business organizations to results of scientific and technical research, present scientific knowledge and exchange experiences regarding the topics of the conference program.

We wish to express our gratitude to our long-term partners of the conference – „Aurel Vlaicu" the University of Arad, Faculty of Engineering, Arad, Romania, University "St. Kliment Ohridski," Technical faculty, Bitola, Macedonia, University Politehnica Timisoara, Faculty of engineering, Hunedoara, Romania, University of East Sarajevo, Faculty of mechanical engineering East Sarajevo, B&H, Republic of Srpska, and University of Giresun, Faculty of Engineering, Giresun, Turkey for supporting the organization of IIZS 2023. We are also grateful to all the authors who have contributed with their papers to organizing the scientific meeting IIZS 2023.

We want to extend our special thanks to the Technical faculty "Mihajlo Pupin" Zrenjanin and Dean Prof. Ph.D. Milan Nikolic for their active support concerning the organization of IIZS 2023. Also, our gratitude goes to the Ministry of Education, Science and Technological Development, Republic of Serbia, for providing financial support to organize this event.

The IIZS Conference became a traditional meeting of researchers from all over the world every year. We are open to and thankful for all valuable suggestions that could contribute to the next International Conference on Industrial Engineering and Environmental Protection organizationally and technically.

Chairman of the Organizing Committee
Assist. Prof. Mića Đurđev, PhD

Zrenjanin, October 5-6, 2023.

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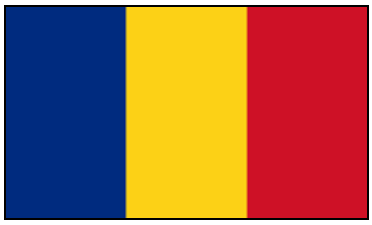

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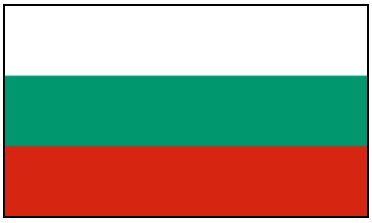

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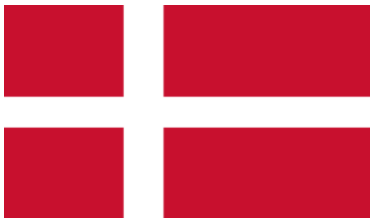

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CONTENT OF POTENTIALLY TOXIC ELEMENTS IN SOIL OF URBAN PARKS IN NOVI SAD

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Abstract: This paper reports on the presence of potentially toxic elements in the soil of urban parks in in the city of Novi Sad, Serbia. The surface soil samples (0-10 cm depth) were collected in seven urban parks. The chemical properties of the soil, as well as the particle size distribution of the 2 mm fraction, were determined. Pseudo-total concentrations and available (in EDTA) content of As, Cd, Co, Cr, Cu, Ni, Pb, and Zn were measured using an ICP-OES device. The samples were analyzed for total Hg content using Direct Mercury Analyzer. The limit value was exceeded by two soil samples, one for Cu (44.9 mg/kg) and one for Ni (50.4 mg/kg).
Keywords: PTEs, soil, urban parks, risk assessment

INTRODUCTION

Trace elements in the soil that are most often associated with environmental toxicity are cadmium, chromium, cobalt, copper, iron, lead, mercury, nickel, silver, tin, and zinc, as well as the lighter elements aluminium, arsenic, and selenium. These elements occur naturally in many soils in different concentrations, but the most significant concern is accumulating the elements from anthropogenic sources. Based on recent literature, an adequate term for the nonorganic observed pollutants in the soil is: "potentially toxic elements" (PTEs) since they can have a natural geochemical origin and the role of nutrients, and at the same time, they can also be toxic if they are found in excessive concentration. They all have an essential role in the relationship between soil plants and animal organisms, either as nutrients or toxicants.
The soil is a complex heterogeneous medium comprising mineral constituents, organic matter, living organisms, and aqueous and gaseous components [1]. It is a significant component of urban ecosystems, contributing directly or indirectly to the general quality of life of city residents. Compared to rural areas, urban areas have a higher population density, which results in more intense traffic. They are located closer to industrial plants and other sources of anthropogenic pollution [2]. As a result, the soil in urban areas is more susceptible to the adverse effects of these factors. Potentially toxic elements in urban areas are of great concern due to their nonbiodegradability, long residence time and long biological half-lives for elimination from the body. PTEs can accumulate in plants and thus enter the food chain. Humans can also be exposed to these elements in the soil more directly through inhalation, dermal contact absorption and ingestion through the mouth with dirty hands, which puts children at particular risk [3]. Based on previous surveys in Novi Sad, high concentrations of certain pollutants were detected in several urban zones, so it is essential to conduct a comprehensive analysis to assess and reduce the population's health risk. The observed soil was sampled from a depth of 0-10 cm to determine the danger of PTEs direct entering the human body via inhalation, ingestion, and dermal contact.
The economic mismanagement in the last decades has led to the decay or demise of once large industrial combines in the city of Novi Sad. It is considered that the primary pollution sources in the area studied in this work may be traffic, oil refining and combustion from home

heating in some parts of the city. The aim of the study was: (1) to determine the pseudo-total and available (in EDTA) concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, Zn, and total mercury content (THg) in the soil in urban parks of Novi Sad, Serbia; (2) to estimate pollution sources; (3) to assess health risk associated with the pollutants.

Soil pollution by potentially toxic elements is a widespread problem posing a significant risk to human health or the environment. The criteria presented in 2005 based on the average values of a large number of data for the concentration of potentially toxic elements in the soils of the Mediterranean, Central Europe, and Eurasia are shown in Table 1.

Table 1. *The content of metals in the soils of Europe (The European Soil Database, version V2.0, EUR 19945 EN) [4]*

Element mg/kg	Background - Natural Values	Slightly Higher Values	Contamination	High Contamination
As	< 29	29 – 30	30 – 50	> 50
Co	< 20	21 – 50	50 – 300	> 300
Cd	< 0.8	0.8 – 5.0	5 – 20	> 20
Cr	< 130	130 – 250	250 – 800	> 800
Cu	< 36	36 – 100	100 – 500	> 500
Ni	< 35	35 – 100	100 – 500	> 500
Pb	< 85	85 – 150	150 – 600	> 600
Zn	< 140	140 – 500	500 – 3000	> 3000
Hg	< 0.3	0.3 – 2	2 – 10	> 10

MATERIAL AND METHODS

Ten surface soil samples (0 -10 cm) depth were collected in seven urban parks of the city of Novi Sad, according to the methodology of the reference sample (circle method). One sample represents the average value of several individual soil samples taken in concentric circles around one central point. (Figure 1). The soil samples were air-dried at room temperature and milled to a particle size of < 2 mm. All laboratory analyses were performed at the Laboratory for Soil and Agroecology of the Institute of Field and Vegetable Crops, Novi Sad, accredited according to the standard ISO/IEC 17025 (2005). Particle size distribution of the soil was determined by the internationally recognized pipette method. The size fractions were defined as coarse sand (2 – 0.2 mm), fine sand (0.2 – 0.02 mm), silt (0.02 - 0.002 mm) and clay (< 0.002 mm). The pH value in 1:5 (V/V) suspension of soil in 1 mol/L KCl was determined using a glass electrode according to ISO 10390 (2010). The carbonate content, as free $CaCO_3$ content, was determined according to the ISO 10693 (1995) volumetric method. Oxidation using the sulfochromic oxidation method specified in ISO 14235 (1998) was used to determine the amount of organic matter (OM). The samples were analyzed for pseudo-total contents of As, Cd, Co, Cr, Cu, Ni, Pb and Zn after microwave digesting the soil in concentrated HNO_3 and H_2O_2 (5 HNO_3:1 H_2O_2, and 1:12 solid: solution ratio) by stepwise heating up to 180^{o}C using a Milestone Vario EL III for 55 min. The concentration of the elements was determined by ICP-OES (Vista Pro-Axial, Varian) by US EPA method 200.7:2001. The samples were analyzed for total mercury content using the Direct Mercury Analyzer DMA 80 Milestone, which combines techniques of thermal decomposition, catalytic conversion, amalgamation, and atomic absorption spectrophotometry (λ = 253.65 nm) in solid soil samples. The samples were analyzed for available metal content after extraction with 0.05 mol/l EDTA (pH = 7.00). The concentrations of metals were determined by ICP-AES (Vista Pro-Axial, Varian) by US EPA method 200.7:2001.

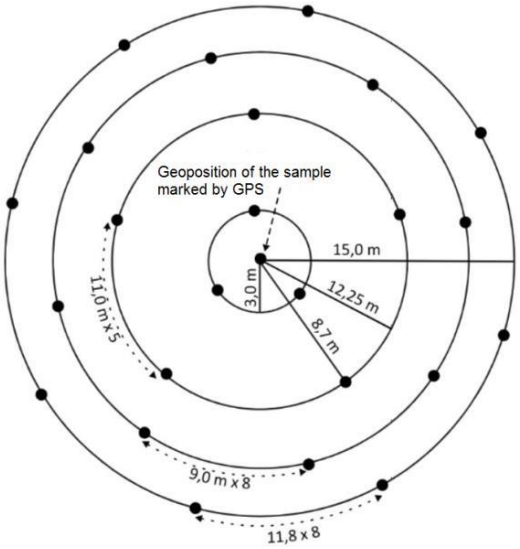

Fig. 1. *Circle method of sampling*

RESULTS AND DISCUSSION

The chemical and physical characteristics of the topsoil in seven urban parks of Novi Sad are summarized in Table 2. The pH value of the soil ranged from 5.98 to 7.87, with an average value of 7.34. All samples are slightly alkaline except one, which is moderate acid (5.98). According to the content of total $CaCO_3$, most of the samples are found to contain high levels of $CaCO_3$. One-third of the samples belong to the class of medium-carbonated soils. Only one sample (the value of 0.17 %) belongs to non-calcareous soil. It is interesting to note that this sample of carbonate-free soil has an acidic pH value (5.98). The organic matter content ranged from 1.77 to 3.47, with an average value of 2.69, which means that the soils are weakly to moderately fortified with organic matter. A value greater than 3 % was recorded only for one sample. The pH value, content of $CaCO_3$ and OM content have a significant influence on the binding and accessibility of potentially toxic elements in the soil. The soils of the study area show a sandy texture. Half of the soil samples (55.1 %) correspond to the mechanical composition of fine sand (Figure 2). The mean values of silt and clay are 22.7 % and 13.8 %, respectively. The fraction of coarse sand is the least represented, with a value of 8.45 %.

Table 2. *Average values of main physical and chemical characteristics of the soil in urban parks*

	Coarse sand %	**Fine sand** %	**Silt** %	**Clay** %	**pH (KCl)**	**Tot $CaCO_3$** %	**OM** %
Mean	8.45	55.1	22.66	13.79	7.34	10.18	2.69
Median	7.1	53.89	21.82	13.56	7.43	11.32	2.68
Range	2.60-18.27	36.87-79.37	13.44-31.6	3.88-25.6	5.98-7.87	0.17-16.47	1.77-3.47
SD	5.7	14.71	6.06	8.28	0.53	5.34	0.46

Soil quality standards have been established in many countries to evaluate the contamination and risk assessment for PTEs in soils. The results were compared with the values given by Serbian Official Gazette: Regulation on limit values of polluting, harmful and dangerous substances in soil [5].

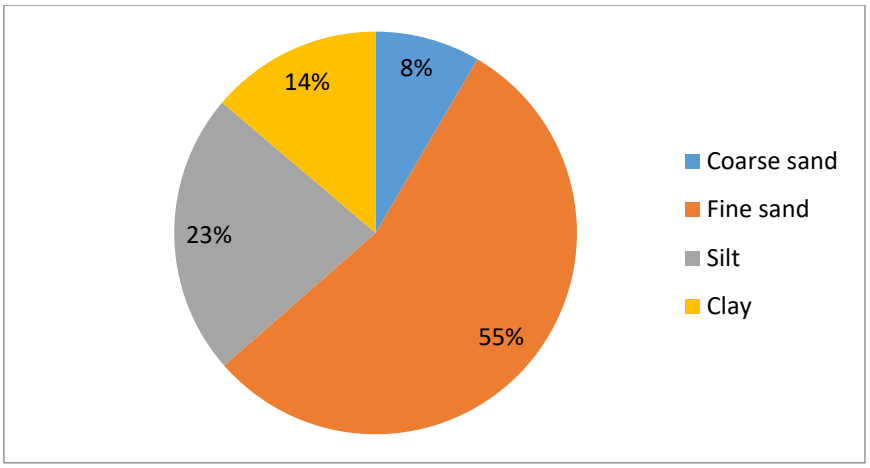

Fig. 2. *Particle size distribution in the soil*

The pseudo-total amount of potentially toxic elements in the soils of seven urban parks in Novi Sad and some basic statistical parameters are presented in Table 3. The available content of PTEs is shown in Table 4. The maximum value of arsenic concentration was 8.21 mg/kg (Table 3), and none of the tested soil samples exceeded the target value (29 mg/kg). Based on the criteria listed in Table 1, the arsenic content in this research is at the level of background concentrations in Europe. Stajic et al. [6] reported similar results for arsenic concentration in soils of urban parks in Kragujevac. Cadmium was not detected in this study (the detection limit was 1.5 mg/kg), as in the research of Pavlovic et al. carried out for soils in urban parks in four cities in Serbia [7]. The median value obtained for Co was about 6 mg/kg, corresponding to the average background concentration level in Europe. The cobalt concentration was close to the limit value only for one sample (9.1 mg/kg) in Kamenički Park, located on Fruška Gora's slopes. Gulan et al. [8] reported exceded content of Co and Ni (comparing to the limit values) for locations in urban parks in Belgrade and remnant forest in its surroundings. The values for pseudo-total chromium content range from 15.45 to 61.24 mg/kg, and none of the tested samples has a higher concentration than LV (100 mg/kg). The available content of Cr (in EDTA) was not detected in any sample, i.e. it was below the detection limit (0.5 mg/kg) of the applied analytical method. One sample in Dunavski park in total content (44.9 mg/kg) exceeds the prescribed limit value for copper (36 mg/kg). In this locality, the concentration of Cu is elevated, but signicantly lower than the remediation value of 190 mg/kg (Table 3). The available ratio of copper (AR = Cu_{EDTA}/Cu_{TOT}) in all locations is high (about 30 %), which can suggest anthropogenic pollution. Values for nickel content vary from 13.34 to 50.45 mg/kg (LV is 35 mg/kg). At one location, the concentration of 50.4 mg/kg is above the limit value for Ni (35 mg/kg), but the value is four-times lower than the remediation value (210 mg/kg) given by regulations. A similar result was obtained in the research within the poject ’’Program for monitoring the quality of agricultural and non-agricultiral land in the territory of the city od Novi Sad’’ in the period from 2006 to 2008 [9] when the elevated nickel concentration of 84 mg/kg was measured at the same location. This indicates the geochemical origin of nickel in Kamenički park because the soils of Fruška Gora have naturally elevated nickel content as a result of the parent material on which the soil was formed. The available Ni content of this sample is low (2.1 mg/kg) with an available ratio of Ni_{EDTA}/Ni_{TOT} = 0.042, which also confirms its natural origin. Lead (Pb) is one of the most common pollutants in urban areas. Mihailovic et al. [10] obtained 300 mg/kg for the mean value of pseudo total Pb content in roadside soils in Novi Sad. Vidojevic et al. [9] reported a range of 19.0 - 47.4 mg/kg. According to this study, the determined lead concentrations are at the background level for European soils (Table 1), probably because all locations were not near roads with intense traffic. The available content is relatively low, at the level where there is no risk of phytotoxicity. However, the available ratio for lead is relatively high (about 50%), which, as for Cu, implies the anthropogenic origin of Pb in the soils of urban parks in Novi Sad. The values of the total mercury content in this research vary

in the interval from 0.03 mg/kg to 0.18 mg/kg, and the result is most often cited for mercury content in soil without a known close source of pollution, which amounts to 0.01-1 mg/kg. The median value obtained for Zn is (72.97 mg/kg), which is about two times lower than the limit value for this element.

Table 3. *Statistical description of pseudo-total PTEs content and total mercury content (THg) in the soil of urban parks*

[mg/kg]	As	Co	Cr	Cu	Ni	Pb	Zn	THg
Mean	6.82	6.28	27.5	26.21	23.69	17.02	73.63	0.1
Median	7.13	6.16	23.33	24.69	21.2	15.3	72.97	0.09
Range	4.52-8.21	3.98-9.11	15.45-61.24	16.96-44.86	13.34-50.45	10.72-30.70	38.21-123.1	0.03-0.18
SD	1.18	1.77	13.66	8.21	10.54	5.53	25.23	0.06
LV	29	9	100	36	35	85	140	0.3
RV	55	240	380	190	210	530	720	10

SD – Stanard Deviation
LV – Limit Values [5]
RV – Remedation Values [5]

Table 4. *Statistics of available (in EDTA) PTEs content in the soil of urban parks*

[mg/kg]	As	Co	Cr	Cu	Ni	Pb	Zn
Mean	0.71	0.66	<MDL (0.5)	8.16	2.02	11.28	11.40
Median	0.68	0.25		8.84	1.36	9.86	6.73
Range	0.25-1.60	0.25-3.32		1.49-11.36	0.42-6.36	2.18-24.69	3.54-44.57
SD	0.43	0.99		2.75.	1.83	6.67	12.45

CONCLUSION

The pseudo-total and available concentrations of potentially toxic elements (As, Cd, Co, Cr, Cu, Ni, Pb, Zn and Hg) in the topsoil of seven urban parks in Novi Sad were determined using the ICP-OES technique and Direct Mercury Analyzer. Based on the content of toxic elements in relation to the criteria outlined in the Regulation on limit values of polluting, harmful and dangerous substances in soil in Serbia, none of the ten examined soil samples in the parks exceeded the limit values for arsenic (As), cobalt (Co), chromium (Cr), lead (Pb), zinc (Zn), and mercury (Hg). However, two soil samples, one from Dunavski park (for Cu) and one from Kamenički park (for Ni), exceeded the limit values. Maximum values for the available ratio for Pb and Cu were obtained, suggesting their anthropogenic origin. In general, the content of toxic elements in the city park soils falls within the permitted limits. Nonetheless, higher levels of certain harmful elements were detected in two locations, highlighting the need for ongoing research on soil quality in city parks.

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