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STECIŠTE NAUKE I PRAKSE U OBLASTIMA KOROZIJE, ZAŠTITE MATERIJALA I ŽIVOTNE SREDINE

PROCEEDINGS

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Under the auspicies of the
MINISTRY OF EDUCATION, SCIENCE AND TECHNOLOGICAL DEVELOPMENT OF THE REPUBLIC OF SERBIA

Pod pokroviteljstvom
MINISTARSTVO PROSVETE, NAUKE I TEHNOLOŠKOG RAZVOJA REPUBLIKE SRBIJE

September 17-20, 2019 : : Tara Mountain, Serbia

CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

620.193/.197(082)(0.034.2)
621.793/.795(082)(0.034.2)
667.6(082)(0.034.2)
502/504(082)(0.034.2)
66.017/.018(082)(0.034.2)

МЕЂУНАРОДНА конференција ЈУКОР (21 ; 2019 ; Тара)
Stecište nauke i prakse u oblastima korozije, zaštite materijala i životne sredine [Elektronski izvor] : knjiga radova = Meeting point of the science and practice in the fields of corrosion, materials and environmental protection : proceedings / XXI YuCorr [Jugoslovenska korozija] Međunarodna konferencija = XXI YuCorr International Conference, September 17-20, 2019, Tara Mountain, Serbia ; [organizatori Udruženje inženjera Srbije za koroziju i zaštitu materijala ... [et al.] = [organized by] Serbian Society of Corrosion and Materials Protection ... [et al.] ; urednici, editors Miomir Pavlović, Miroslav Pavlović]. - Beograd : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM, 2019 (Beograd : Udruženje inženjera Srbije za koroziju i zaštitu materijala UISKOZAM). - 1 USB fleš memorija ; 12 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 200. - Bibliografija uz većinu radova. - Abstracts. - Registar.

ISBN 978-86-82343-27-1
а) Премази, антикорозиони -- Зборници б) Превлаке, антикорозионе -- Зборници в) Антикорозиона заштита -- Зборници г) Животна средина -- Заштита -- Зборници д) Наука о материјалима -- Зборници
COBISS.SR-ID 279136012

XXI YUCORR – International Conference | *Međunarodna konferencija*

PUBLISHED BY | *IZDAVAČ*
SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION (UISKOZAM)
UDRUŽENJE INŽENJERA SRBIJE ZA KORZIJU I ZAŠTITU MATERIJALA (UISKOZAM),
Kneza Miloša 7a/II, 11000 Beograd, Srbija, tel/fax: +381 11 3230 028, office@sitzam.org.rs; www.sitzam.org.rs

FOR PUBLISHER | *ZA IZDAVAČA* *Prof. dr MIOMIR PAVLOVIĆ, predsednik UISKOZAM*

EDITORS | *UREDNICI:* *Prof. dr Miomir Pavlović, Dr Miroslav Pavlović*

SCIENTIFIC AREA | *OBLAST:* CORROSION AND MATERIALS PROTECTION **|** *KOROZIJA I ZAŠTITA MATERIJALA*

PAGE LAYOUT | *KOMPJUTERSKA OBRADA I SLOG:* *Marijana Pantović Pavlović, M.Sc.*

CIRCULATION | *TIRAŽ:* **200** copies **|** *primeraka*

ISBN 978-86-82343-27-1

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ORGANIZATORI XXI YUCORR-a

SERBIAN SOCIETY OF CORROSION AND MATERIALS PROTECTION

Udruženje Inženjera Srbije za Koroziju i Zaštitu Materijala

INSTITUTE OF CHEMISTRY, TECHNOLOGY AND METALLURGY, UNIVERSITY OF BELGRADE

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SAVEZ INŽENJERA I TEHNIČARA SRBIJE, Beograd

Speciation and contamination assessment of potentially toxic elements in soils from three urban parks in Serbia

Dragana Pavlović, Marija Pavlović, Dragan Čakmak, Olga Kostić, Zorana Mataruga, Miroslava Mitrović, Pavle Pavlović

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Abstract

The main objectives of this study were determination of concentration of five potentially toxic elements (Cr, Cu, Ni, Pb and Zn) and investigation of their distribution and environmental impact in soils, collected from urban parks in Belgrade, Smederevo and Pančevo. The optimized four-step BCR sequential extraction technique was used for element fractionation. Risk assessment code (RAC), individual contamination factors (ICF) and global contamination factors (GCF) were used to assess the environmental impacts of elements in soil samples. The study revealed that content of Cu and Ni at all localities, Pb in Belgrade and Smederevo and Zn in Smederevo exceed the limits established by local regulations, which may represent an environmental threat. Sequential extraction results showed that major portion of Cr existed in the residual fraction. The highest content of Cu and Ni from Belgrade and Pančevo was found in the first three fractions, while a large portion of Pb and Zn were found in reducible fraction, indicating that these elements may pose a great threat to environment in case of any change in environmental condition. According to the computed RAC, ICF and GCF the highest risk was found in Belgrade for Zn and Pb.

Key words: *Urban soils, Sequential extraction, Potentially toxic elements, Risk assessment code, Contamination factors*

Introduction

Urbanization and industrialization in the past few decades have resulted in serious pollution by harmful substances, in particular potentially toxic elements (PTEs) [1,2]. This is especially evident in urban areas where various stationary and mobile sources release large quantities of pollutants and other persistent toxic substances, leading to the degradation of environmental conditions [3,4]. Most of PTEs in urban areas are emitted from various anthropogenic sources like transport sources (motor exhausts, brake pads, tire wear), commercial and industrial emissions (energy production, metallurgical industry, electronics, chemical plant, fuel combustion, incinerators) and domestic activities (construction and demolition, waste disposal, wastewater) [2]. Urban soils act as a net accumulator of PTEs but they also serve as a source of different pollutants when there is natural or anthropogenic disturbance [2,5]. Pollution by PTEs has attached significant attention by many researchers due to the fact that they present toxic and persistent pollutants that can deposit and accumulate on urban surfaces and then transport among various mediums [5]. Although estimation of the total metal concentrations in soils can provide valuable information on overall contamination levels, it is not suitable for determination of their mobility, availability or toxicity [6,7]. The potential availability and toxicity of the PTEs depends on their chemical forms and binding state, which is why sequential extraction technique represents useful tool that provides information about the strength at which metals bind to particles and the phase associations of metals in a solid matrix [1]. One of the most widely applied sequential extraction protocols is BCR protocol which has also been widely applied to PTEs fractionation in different types of environmental media [6,8,9,10].

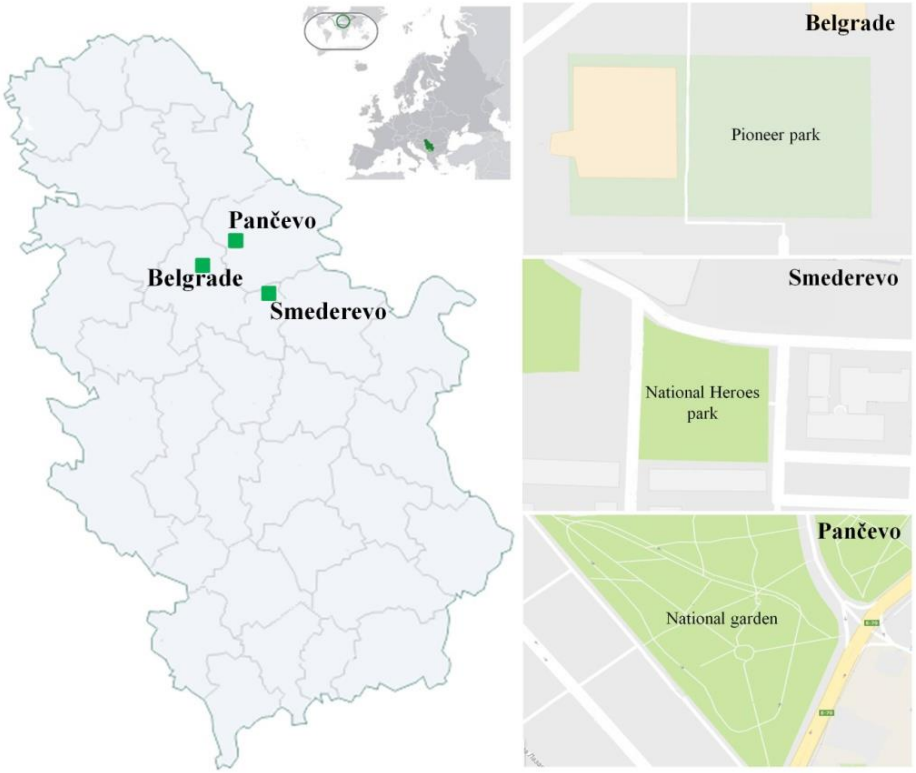
The main objectives of this study were (1) to determinate the pseudo-total concentrations of five potentially toxic elements (Cr, Cu, Ni, Pb and Zn) in selected soil samples collected in urban parks in Belgrade, Smederevo and Pančevo (2) to provide a better understanding of their mobility and

bioavailability in soil using optimized four-step BCR sequential extraction technique and (3) to provide a preliminary assessment of the environmental risk caused by PTEs.

Materials and methods

The study area and soil sampling

The study was conducted at urban parks in three Serbian cities exposed to different sources of pollution: in Pančevo, Smederevo and Belgrade (Figure 1). At all localities, soil samples were collected at five points from a depth of 0 - 20 cm and then mixed into a composite sample [11; LUCAS: Land use/ Cover Area frame Statistical Survey]. Collecting was done with stainless-steel tool. Small stones, plants and other foreign objects from soil samples were removed by hand, after which they were delivered to the laboratory. In the laboratory each soil sample was air dried at room temperature to constant mass and then grounded with an inert steel crusher with a 2-mm mesh. The prepared samples were then used for analysis.



Locality	Principal sources of pollution	Sampling sites and their labelling with capital letters
Pančevo	Oil Refinery Pančevo; Nitrogen Fertilizer Plant Pančevo; Petrochemical Complex Pančevo	National Garden (Narodna Bašta) (44°51'54" N, 20°39'23" E); P-1, P-2, P-3
Smederevo	'Železara Smederevo' Steelworks	National Heroes Park (park Narodnih heroja) (44°40'22" N, 20°55'67" E); S-1, S-2, S-3
Belgrade	Car exhaust pollution	Pioneer Park (Pionirski park) (44°48'53" N, 20°29'70" E); B-1, B-2, B-3

Figure 1 Map of the selected urban sampling sites in Serbia: a) Pančevo, b) Smederevo and c) Belgrade

Sequential extraction

Chemical partitioning of Cr, Cu, Pb, Ni and Zn was carried out by the modified BCR sequential extraction procedure [12,13,14]. The content of tested elements was analyzed using inductively coupled plasma optic emission spectrometry (ICP-OES, Spectro Genesis, Spectro Analytical

Instruments GmbH, Kleve, Germany). The operating conditions and chemicals required in optimized BCR sequential extraction are presented at Figure 2.

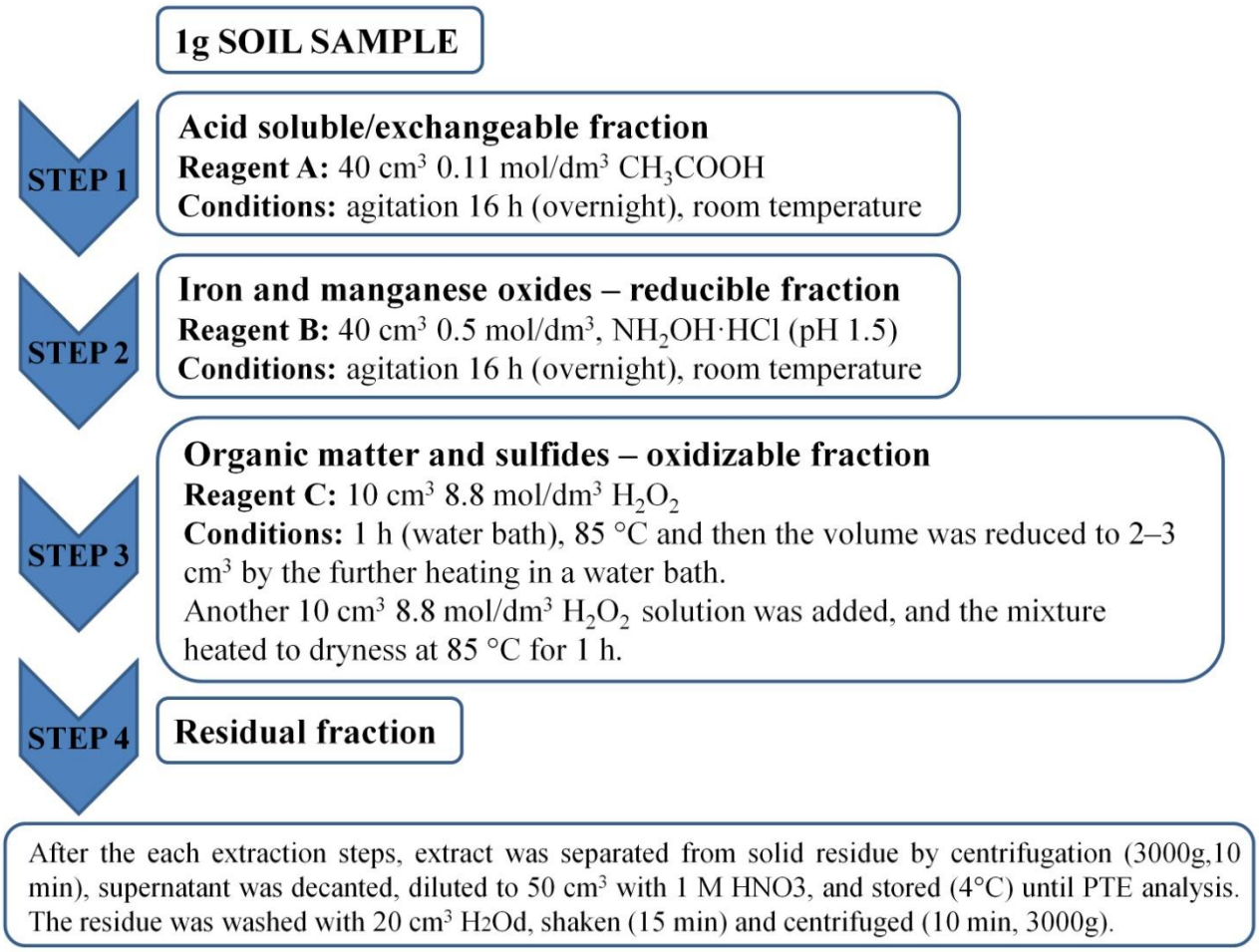


Figure 2 Scheme of the reagents and operating conditions

The pseudo-total PTE concentrations in soil samples were calculated as the sum of the element concentrations in all four fractions.

$$C_{PTE} = \sum F1 + F2 + F3 + F4 \quad (1)$$

Quality Control

Quality control and quality assurance of the analytical data was performed by using the certified reference material for soil - BCR-701, obtained by IRMM, Institute for Reference Materials and Measurements, Geel, Belgium, as well as by analysis of both reagent blanks and replicates. The recovery values found were within 87.3–109.4%, demonstrating a good accordance between the measured and certified values. The relative standard deviations of duplicate measurement were less than 10 %. The detection limits for the analyzed elements in the soil samples were as follows (mg kg^{-1}): Cr-0.011, Cu-0.007, Ni-0.029, Pb-0.001 and Zn-0.006.

Determination of Risk Assessment Code (RAC)

The risk assessment code (RAC), defined as the fraction of the PTE exchangeable and/or associated with carbonates (% F1), was determined for the studied elements, and the values were interpreted in accordance with the RAC classifications. This classification is described by Perin et al. [15]. If the percentage of the carbonate and exchangeable fractions is less than 1%, there is no risk (NR). For a

range of 1-10%, there is low risk (LR), medium risk (MR) for a range of 11-30%, high risk (HR) for 31-50% and very high risk (VHR) for 51-100%.

$$RAC = \frac{F1}{\sum F1+F2+F3+F4} \times 100 \quad (2)$$

Determination of individual and global contamination factor

Individual contamination factors (ICFs) and the global contamination factor (GCF) evaluates the degree of toxicity or risk to the environment and the bioavailability of trace metals in the soil relative to its retention time. In this study, ICFs were calculated for the top layer (0-20 cm depth) at all localities as the sum of the concentrations of PTEs extracted in the first three steps (acid soluble/exchangeable, reducible, and oxidizable fraction) divided by the concentration in the residual fraction [16,17,18]. The GCF was calculated by summing the ICFs of PTEs [16,18].

$$ICF_{PTE} = \frac{\sum F1+F2+F3}{F4} \quad (3)$$

$$GCF = \sum ICF_{PTE} \quad (4)$$

Results and discussion

Pseudo total concentrations and fractionation of PTEs in selected soils

The pseudo-total concentrations of PTEs in the urban park soils from Belgrade, Smederevo and Pančevo and their fractionation profile are presented in Figure 3 and Figure 4. The pseudo-total concentrations of five PTEs (Cr, Cu, Ni, Pb and Zn) generally decreased in the order Zn > Pb > Ni > Cr ≥ Cu.

Chromium concentrations ranged from a minimum of 36.48 mg kg^{-1} measured in Smederevo, to a maximum of 45.55 mg kg^{-1} in Belgrade. Levels were below the standard values established by local regulations (100 mg kg^{-1}, [19]) and below background values for European soils (50-100 mg kg^{-1}, [20,21]) at all localities. Chromium concentrations obtained in this study are comparable to those determined for urban soils in Belgrade (38.72-61.51 mg kg^{-1}, [22], and are lower than those reported for Madrid (10.4-211 mg kg^{-1}, [23]) and Palermo (12-100 mg kg^{-1}, [24]). The main source of Cr in natural soils is weathering of the parent material, however contamination of soil by Cr originates mainly from the industrial emissions, since Cr is used in many industrial processes in production of paints and pigments, wood preservation and metallurgy [25]. Given the fact that Cr concentrations in studied soils were within limits established for European soils, it can be assumed that total Cr concentrations in soils do not represent an environmental burden, a fact which was also supported by the obtained minimal RAC (Figure 4). Fractionation profile for Cr confirmed its natural origin; namely the highest portion of Cr has been bound to the silicate lattice and crystallized oxide minerals (70.16-79.00 %), while the rest is mainly associated with organic matter and sulphides (15.75-25.00 %) and iron and manganese oxides (4.84-9.73 %). The content of Cr in the acid soluble/exchangeable fraction was very low (< LoQ). Such fractionation profile suggests that Cr is chemically stable and unavailable for plants uptake [26].

Concentrations of Cu in soils of the investigated urban parks ranged from 37.43 to 45.55 mg kg^{-1} and exceeded the standard values established by local regulations (36 mg kg^{-1}, [19]). The most important natural source of Cu is the geological parent material, but fuel combustion (industrial and domestic heating, power production) and traffic (corrosion of overhead wires) are responsible for the majority of Cu inputs in urban soils [25,27,28]. However, these Cu concentrations were below background values for European soils established by directive of European Communities (50-140 mg kg^{-1}, [20,21]) and do not constitute a threat to the environment. Copper concentrations in soils were similar to those found in urban soils from parks and green areas in Belgrade (46.3 mg kg^{-1}, [29]), but lower than those reported for Madrid (71.7 mg kg^{-1}, [23]) and Sopron (118.38 mg kg^{-1},

[30]). According to results of sequential BCR extraction, the great amounts of Cu were extracted in the first three fractions (45.98 – 55.95 %), while the rest was strongly associated to the crystalline structures of the soil minerals (44.05 – 54.02 %). This result indicates that Cu could potentially be available for plant uptake in case of any change in environmental condition [31,32]. From a plant standpoint, this is very important, given the fact that Cu is an essential micronutrient involved in many physiological processes [33].

In this study, Ni concentrations ranged from 55.61 mg kg^{-1} in Smederevo to 65.26 mg kg^{-1} in Belgrade, and were generally higher than the standard values established by local regulations (35 mg kg^{-1}, [19]) and within range of background values described for European soils (30-75 mg kg^{-1}, [21,21] at all localities. Generally, this study revealed higher concentrations of Ni than those found in urban soils from Ljubljana (26 mg kg^{-1}, [34]) and Sopron (25.74 mg kg^{-1}, [30]), but lower than those reported for Torino (300 mg kg^{-1}, [35]). However, results obtained from current study suggest that Ni content in soil does not constitute a threat to the environment, since all values were in line with average concentrations for Serbian soils (58 mg kg^{-1}, [36,37]). Nickel was found in all four soil phases. The highest portion of Ni was obtained in residual fraction (36.04-57.23 %), while the rest was distributed between reducible (19.50-40.67 %), oxidizable (13.00-18.59 %) and the acid soluble/exchangeable fraction (4.69-5.54 %). However, Ni showed different fractionation profile in soils from Belgrade (54.48 %) and Pančevo (63.96 %), were it was predominantly extracted in the first three fractions (54.48 and 63.96 %, respectively), suggesting that Ni could be available for plant uptake under suitable conditions (salinity, pH and redox potential [31]), which is in good agreement with findings of Mahanta et al. [38]. However, results obtained from other urban soil studies showed that residual Ni is the dominant fraction [39,40,41], results that coincide for soil in Smederevo.

The pseudo-total concentrations of Pb in the present study varied from 74.19 mg kg^{-1} in Pančevo to 117.76 mg kg^{-1}in Smederevo, and were higher compared to the standard values established by local regulations (85 mg kg^{-1}, [19]) in Belgrade and Smederevo, but still within background values for European soils (50-300 mg kg^{-1}, [20,21]) at all localities. Lead concentrations measured in this study were lower than those obtained for Glasgow (389 mg kg^{-1}, [39]), Palermo (202 mg kg^{-1}, [24]) and Belgrade (252.90 mg kg^{-1}, [42]), and were similar to those obtained for Sopron (124.55 mg kg^{-1}, [30]). The elevated content of Pb measured in Belgrade and Smederevo are most probably the result of emissions from traffic, since leaded petrol was used in Serbia until 2010 [43], as well as from lead particulate matter emitted from industrial activities [8,28]. Fractionation profile of Pb confirmed its anthropogenic origin. Namely, the highest proportion of Pb was bound to Fe and Mn oxides (42.29-76.95 %), while residual (12.72-21.28 %), oxidizable (5.61-26.06 %) and acid soluble/exchangeable (4.72-10.37 %) fractions were almost equally represented in profile. Such distribution of Pb indicates that it can be easily released from soil if there is a change of oxidation state of Fe and Mn [44].

Concentration of Zn in the soil ranged from a minimum of 106.31 mg kg^{-1} measured in Pančevo, to a maximum of 144.82 mg kg^{-1} in Smederevo. All measured concentrations were below the standard values established by local regulations (140 mg kg^{-1}, [19]) and below background values for European soils established by directive of European Communities (150-300 mg kg^{-1}, [20,21]), except in Smederevo (144.82 mg kg^{-1}) where they were above standard values established by local regulations. However, concentrations of Zn in the studied soils were in line with previously reported for urban soils in Belgrade (118 mg kg^{-1}, [45] and Seville (105 mg kg^{-1}, [34]), but lower than those measured in Torino (182 mg kg^{-1}, [34]), Glazgow (177 mg kg^{-1}, [39] and Madrid (210 mg kg^{-1}, [23]. High content of Zn in Smederevo is mostly related to the anthropogenic factors, given the fact that suspended particles produced during iron and steel production process contain Zn, as previously expalined by Dragović et al. [46]. The distribution of various Zn fractions showed that the highest portion of Zn is associated with iron and manganese oxides (39.17-55.88 %) and in percentage terms, this is followed by the residual (22.70-30.39 %), oxidizable (10.25-19.65 %) and

acid soluble/exchangeable fraction (3.55-18.64 %). It should be mentioned that higher content of extracted Zn in the acid soluble/exchangeable fraction (18.64 %), as well as an elevated pseudo-total content of Zn, was observed in Smederevo, indicating its high mobility and anthropogenic origin.

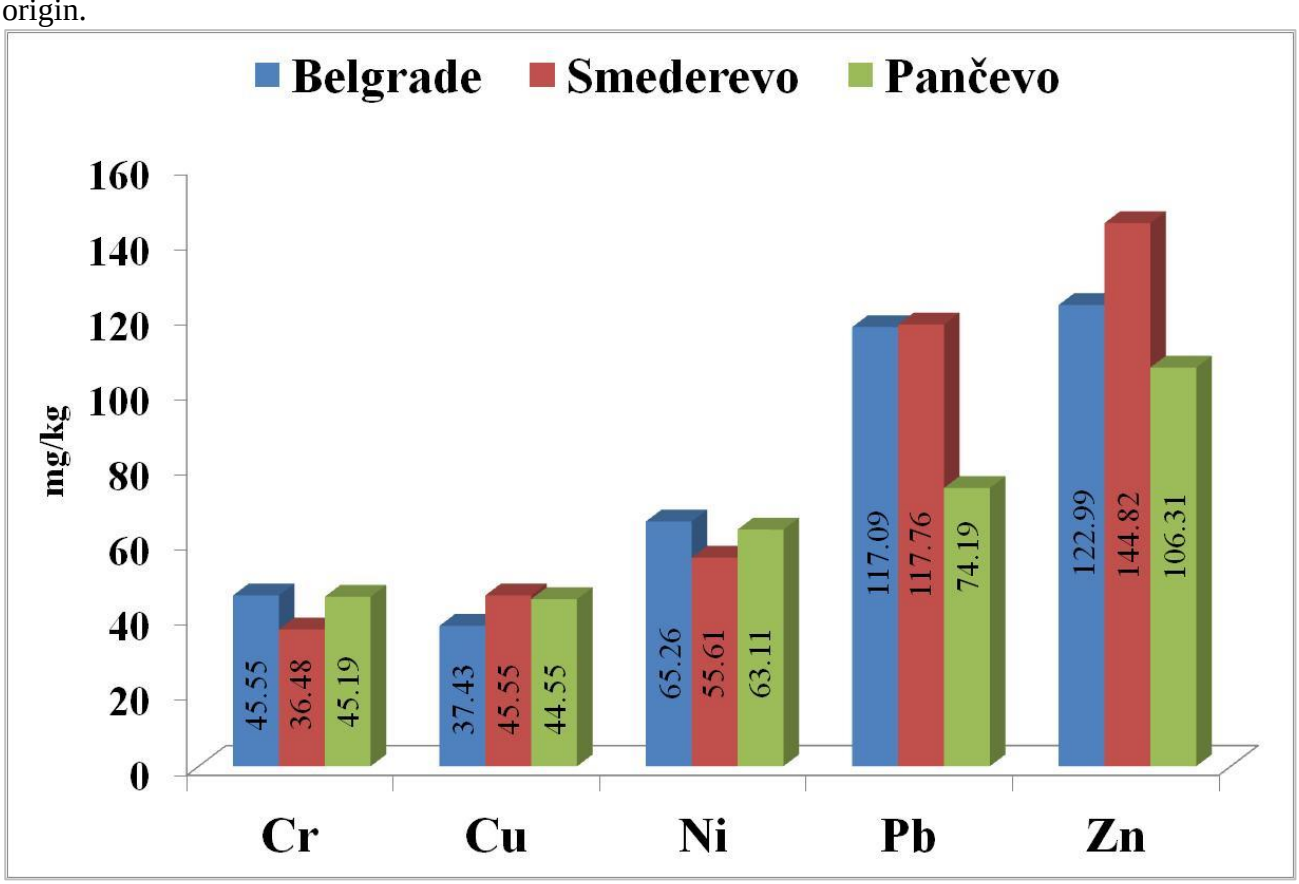


Figure 3 Pseudo-total concentrations of PTEs in selected urban soils (mg kg^{-1} d.w.)

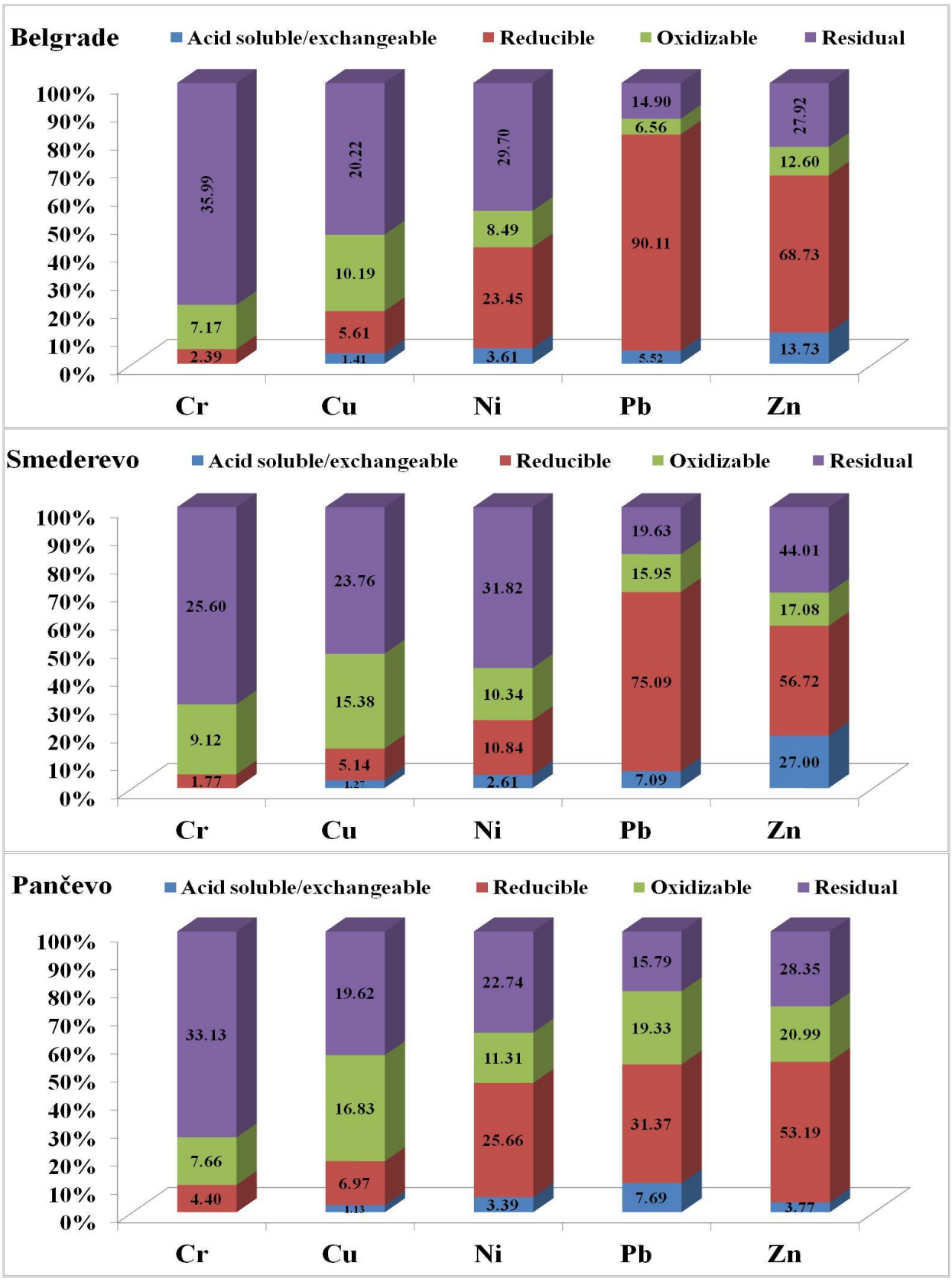


Figure 4 Partitioning of PTEs in selected urban soils from Belgrade, Smederevo and Pančevo

Assessment of the environmental risk

Risk assessment code (RAC)

It is well known that the PTEs in soil are bound to different soil geochemical phases with different strengths. Calculation of RAC provides significant and useful information about mobility and environmental implication of PTEs. It represents the percentage of metals in the acid soluble/exchangeable fraction [47], i.e. the fraction of metals with the most labile bond in soil and, therefore, the most dangerous for the environment [48].

According to RAC analysis, examined urban soils showed low risk for Cr, Cu, Ni and Pb, with RAC values below 10 % (RAC < 10 %, Figure 5), indicating no significant mobility for these elements. However, Zn showed medium risk (RAC > 10) in soils from Belgrade and Smederevo, indicating its higher mobility in relation to other elements, which could be also attributed to anthropogenic origin at these localities (intensive industrial and traffic activities) [5,28,46].

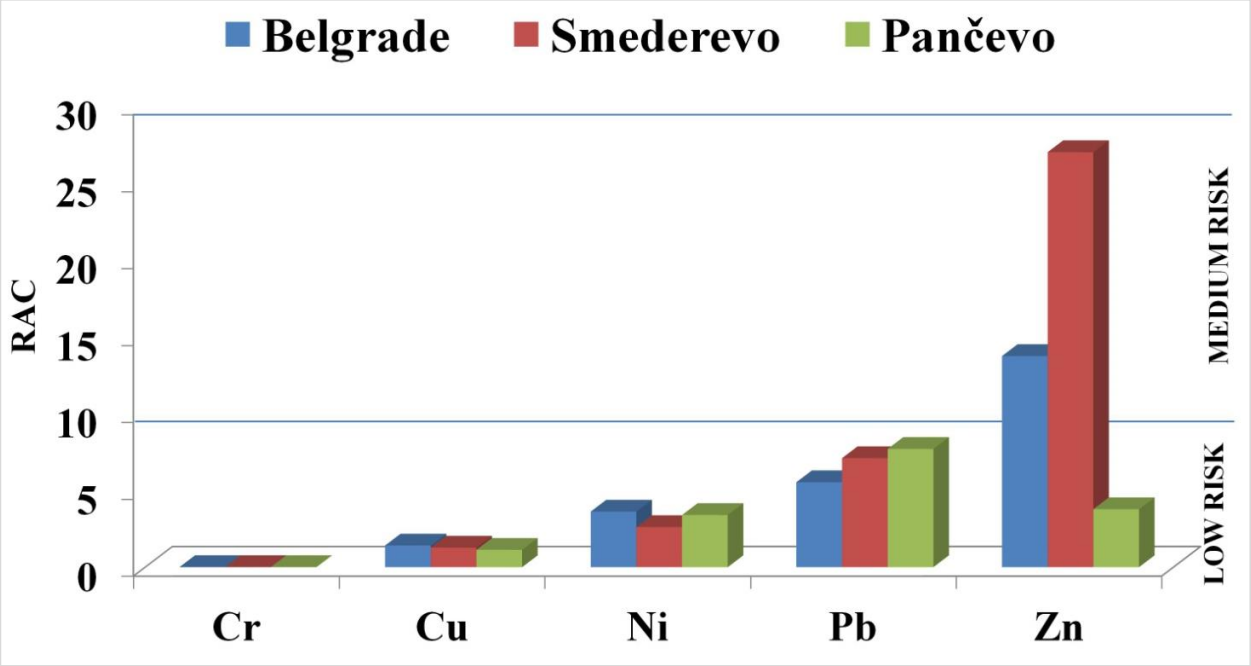


Figure 5 Risk assessment code for PTEs in selected urban soils. The lines indicate critical RAC values, medium and low risk

Individual and Global contamination factor (ICF and GCF)

The ICF reflects the risk of soil contamination by a pollutant, while the GCF reflects the overall potential risks posed by the PTEs to the environment. These two factors were often used as a relative measure of PTE retention in soils. The lower the ICF values, the higher relative PTE retention and lower risk of the environment [16, 47].

In studied urban soils, the highest ICF values for Cr were found in Smederevo, for Cu and Ni in Pančevo and for Pb and Zn in Belgrade. The calculated ICF reveal the highest ICF for Pb (13.70-6.86) and Zn (2.29-3.40), while Cr (0.27-0.43), Cu (0.85-1.27) and Ni (0.75-1.78) showed the lowest.

The highest values for GCF were determined in Belgrade, while in Smederevo and Pančevo they were almost the same (Table 1), indicating that traffic has the highest impact on pollution of soils. Baring in mind that the content of tested PTEs was in the range of background values for European soils, it is evident PTEs do not represent potential risk to the examined urban soils.

Table 1 The individual and the global contamination factors for PTEs in selected urban soils

ICF	Belgrade	Smederevo	Pančevo
Cr	0.27	0.43	0.36
Cu	0.85	0.92	1.27
Ni	1.20	0.75	1.78
Pb	6.86	5.00	3.70
Zn	3.40	2.29	2.75
GCF	12.58	9.38	9.86

Conclusions

Current study investigated the pseudo-total content of PTEs (Cr, Cu, Ni, Pb and Zn), as well as their fractionation profile in urban soils collected from urban parks in three Serbian cities. The results obtained showed that Cu and Ni concentrations at all localities, Pb in Belgrade and Smederevo and Zn in Smederevo exceed the limits established by local regulations. Optimized BCR sequential extraction showed that major portion of Cr was extracted in the residual fraction, unlike Cu and Ni from Belgrade and Pančevo, where the largest share was extracted in the first three fractions. As for Pb and Zn, noticeable percentage was found in reducible fraction, which indicates that these elements may be released to the surroundings under changed environmental conditions, and might alter the ecological balance.

According to the computed pollution factors (RAC, ICF and GCF) the highest risk was revealed in Belgrade for Zn and Pb, followed by slightly lower values in Smederevo and Pančevo. These results imply that traffic has the highest impact on pollution of soil. Baring in mind, however, that the content of tested PTEs was in the range or below the background values for European soils, it is evident PTEs do not represent potential risk to the examined urban soils.

Acknowledgement This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (grant no. 173018).

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