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Fractionation, Mobility, and Contamination Assessment of Potentially Toxic Metals in Urban Soils in Four Industrial Serbian Cities

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Abstract

The main soil properties, concentrations of selected elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn), and the chemical speciation of each element were determined in urban soil samples taken from urban parks in four Serbian cities (Belgrade, Pančevo, Obrenovac, and Smederevo) exposed to different sources of pollution. Pollution indices (PI, PI_N) and factors (MF, ICF, GCF) also were evaluated. The study revealed As and Cd concentrations below the detection limit, whereas the content of Cr, Cu, Fe, Mn, Ni, Pb, and Zn at some sites exceeded the limits established by local regulations, as well as the background values, which may represent an environmental threat. Sequential extraction results show that Fe, Cr, Cu, and Ni were predominantly in the residual fraction at most sites; however, Ni from Pančevo and Smederevo also was bound to the reducible fraction. The presence of Pb at all sites and Zn in Smederevo and Belgrade was mainly associated with the reducible and residual fractions. The highest Mn content was found in the reducible fraction, followed by the acid soluble/exchangeable and residual fractions. Based on the obtained indices and factors, the overall soil status at the selected sampling sites was found to range from the warning limit to slightly polluted, whereby Smederevo had the highest risk, and Pančevo and the control site the lowest risk of contamination by toxic metals.

Rapid urbanisation and industrialisation, as well as high population densities in cities, has led to an increasing level of environmental pollution in urban settings. Human activities significantly affect the balance of the biochemical and geochemical cycles of some toxic metals (Wong et al. 2006). Due to the toxic, persistent, and nonbiodegradable properties of metals, pollution caused by them has become a serious and wide environmental problem, especially in urban areas (Tokalioğlu et al. 2010; Ghrefat et al. 2012; Yang-Guang et al. 2016). This has led to their increased content and a negative effect on the whole ecosystem (Imperato et al. 2003; Lu et al. 2007), particularly on the health of people through dust ingestion, dermal contact, or inhalation (Gržetić and Ghariani 2008; Benhaddya et al. 2016; Gabarrón et al. 2017).

Total metal concentration distribution and levels are useful indicators of the extent to which soil is contaminated (Tokalioğlu et al. 2010; You et al. 2016). However, because the risk from metals depends on their potential availability (Sutherland 2010; Relić et al. 2013), the total concentrations do not provide sufficient information on the possible environmental impact. Sequential extraction, which provides information on both the mobile and stable fractions of metals in soil, evaluates the actual and potential mobility of metals (Nemati et al. 2009). A few studies have determined metals in soils using different sequential extraction procedures (Wilcke et al. 1998; Olajire et al. 2002; Ghrefat et al. 2012; Osakwe 2013; Jiang et al. 2013; You et al. 2016). The data obtained from different sequential extraction schemes are difficult to compare, because the results depend heavily on the extraction procedure used (Ghariani et al. 2010). The Standards, Measurements and Testing Programme (SM&T), formerly known as the European Community Bureau of Reference (BCR), has proposed a sequential extraction procedure to harmonise and standardise the different techniques

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used to fractionate metals in soils and sediments (Ure et al. 1993). The BCR protocol fractionates metals into acid soluble/exchangeable, reducible, and oxidizable phases and has the advantage of simplicity and the availability of certified reference materials (BCR 701) for method validation (Davidson et al. 2006; Bielicka-Giełdoń et al. 2013). This method also has been widely accepted and applied to metal fractionation in different types of solid samples (Imperato et al. 2003; Davidson et al. 2006; Tokalioğlu et al. 2010; Bielicka-Giełdoń et al. 2013; Yang-Guang et al. 2016).

Concentrations of potentially hazardous toxic metals in urban soils have been reported for cities worldwide. These include Tianjin, Beijing, and Shenyang in China (Xia et al. 2011; Li et al. 2013; Zhao et al. 2014), Palermo and Torino in Italy (Manta et al. 2002; Biasioli et al. 2006), Seville and Madrid in Spain (De Miguel et al. 1998; Madrid et al. 2002), Novi Sad and Belgrade in Serbia (Kuzmanoski et al. 2014; Mihailović et al. 2015), and several cities in Montenegro (Mugoša et al. 2016). The availability and actual and potential mobility of metals also was evaluated in the urban soils of Naples (Imperato et al. 2003), Valcamonica (Borgese et al. 2013), Aveiro, Seville, Torino, Ljubljana, Glasgow (Davidson et al. 2006), Koszalin (Bielicka-Giełdoń et al. 2013), Guwahati (Mahanta and Bhattacharyya 2011), and Bangkok (Wilcke et al. 1998).

The main objectives of this study were to: (1) determine the pseudo-total concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn) in urban soils from public areas in four Serbian cities; (2) determine their mobility by the fractionation of these elements using the optimized BCR sequential extraction protocol; (3) provide a preliminary assessment of the environmental risk associated with toxic metal pollution; and (4) compare levels of pollution between the cities. The terms “metals” or “toxic metals” are used in their broadest sense in this paper. The nonmetallic trace element arsenic is included under these terms.

Materials and Methods

Study Area and Sampling

Soils from four Serbian cities were studied in following urban parks: (1) Pančevo (National Garden); (2) Smederevo (National Heroes Park); (3) Obrenovac (City Park); (4) Belgrade (Pioneer Hall Park); and (5) the Arboretum of the Faculty of Forestry, (University of Belgrade). The Arboretum of the Faculty of Forestry, created within a zone of natural forest of *Quercuetum frainetto cerris* Rud., was selected as the control site without direct source of pollution and a distance away from the city center. Every effort has been made to select sampling sites with different sources of air pollution and with similar baseline conditions within each city. All of the chosen cities have a moderate continental climate characterised by cold winters and hot summers with an average annual temperature of approximately 11.5 °C and mean annual precipitation of about 650 mm. A SE wind (Košava) is one of the most important winds that is characteristic for the whole study area, while less frequent are W and NW winds. All the cities are within 50 km of each other and the distance of each park from the main source of pollution is between 4 and 7 km.

The sampling sites are exposed to pollution from various anthropogenic activities: in Pančevo—Oil Refinery Pančevo, Nitrogen Fertilizer Plant Pančevo, Petrochemical Complex Pančevo, in Smederevo—‘Železara Smederevo’ Steelworks, in Obrenovac—a thermoelectric power plant and fly ash disposal site, and in Belgrade—car exhaust pollution. The locations of the sampling sites (urban parks) including these major sources of pollution are listed in Fig. 1.

A harmonized sampling regime was applied at all the sites. Soil was collected from three individual sampling points at each site (Pančevo: P1, P2, P3; Smederevo: S1, S2, S3; Obrenovac: O1, O2, O3; Beograd: B1, B2, B3; Control site: C1, C2, C3). At each sampling point, five subsamples were collected from the top 10-cm layer, within a 1-m^2 square and using a stainless steel shovel, and were mixed to obtain a bulk composite sample, making three bulk samples per sampling site. The surface soil was used for analysis because toxic metal deposition in soil in urban areas mostly occurs in top soil (De Miguel et al. 1998; Gabarrón et al. 2017). The total weight of the composite soil samples ranged from ~ 1.5–5 kg. All the samples were air-dried in a laboratory, ground in a stainless steel mill, sieved through a 2.0-mm stainless steel sieve, and kept in clean polypropylene bags before being analysed.

Chemical Analyses

The soil pH in an aqueous solution was measured using a WTW (Germany) inoLab® 7110 pH meter with a glass electrode (1:2.5 soil–water ratio) after agitating the samples to equilibrium for approximately 30 min. The pH was measured directly in the suspension. The total organic carbon (OC) in soil was measured using an elemental carbon, nitrogen and sulphur (CNS) analyser, Vario model EL III (Elemental Analysis systems GmbH, Hanau, Germany), by dry burning the samples at 1150 °C (Nelson and Sommers 1996). Soil granulometric composition was determined by the pipette method, whereas fractionation was performed according to Atterberg (1911). The pseudo-total metal concentrations in soil samples were calculated as the sum of the metal concentrations in all four fractions.

	Cities	Principal sources of pollution	Sampling sites and sampling points labelling with capital letters
①	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
②	Smederevo	'Železara Smederevo' Steelworks	National Heroes Park (park Narodnih heroja) (44°40'00'' N, 20°55'33'' E); S-1, S-2, S-3
③	Obrenovac	Thermoelectric power plant and fly ash disposal site	City Park (Gradski park) (44°39'16'' N, 20°12'50'' E); O1, O-2, O-3
④	Belgrade	Car exhaust pollution	Hall Pioneer Park (Park kod Hale Pionir) (44°48'51'' N, 20°28'58'' E); B-1, B-2, B-3
⑤	Belgrade-Control site	Area without a direct source of pollution	Arboretum of the Faculty of Forestry (44°46'57'' N, 20°25' 23'' E); C-1, C-2, C-3

Fig. 1 Map of the selected urban sampling sites in Serbia: **a** Pančevo, **b** Smederevo, **c** Obrenovac, **d** Belgrade, **e** Belgrade—control site

Sequential Extraction

To assess the mobility of As and toxic metals, as well as their availability or toxicity in soil, partitioning of As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn was performed by sequential extraction using the optimized BCR procedure (de Andrade Passos et al. 2010; Sutherland 2010; Sakan et al. 2016). Their contents were analysed using inductively coupled plasma optic emission spectrometry (ICP-OES, Spectro Genesis, Spectro-Analytical Instruments GmbH, Kleve, Germany). The optimized BCR sequential extraction scheme is presented in Table 1.

Quality Control

Quality control for soil was performed using the sediment certified reference material (BCR 701) for three-step sequential extraction. The recovery values found were within 84.1–107.2%, whereas the detection limits for the analysed elements in the soil samples were as follows (mg kg^{-1}): As-0.04, Cd-0.008, Cr-0.011, Cu-0.007, Fe-0.011, Mn-0.001, Ni-0.029, Pb-0.001, and Zn-0.004.

Assessment of Metal Contamination

The Pollution Index (PI) and the Nemerow Pollution Index (PI$_N$) were calculated using Eqs. 1 and 2, respectively, as proposed by Hu et al. (2013):

Table 1 The optimized BCR sequential extraction scheme

Extraction step	Reagents	Fraction	Conditions
I	40 cm^3 0.11 mol dm^{-3} CH_3COOH	Exchangeable and acid soluble	16 h (overnight), room temperature
II	40 cm^3 0.5 mol dm^{-3}, $NH_2OH{\cdot}HCl$ (pH 1.5)	Iron and manganese oxides	16 h (overnight), room temperature
III	10 cm^3 8.8 mol dm^{-3} H_2O_2	Organic matter and sulphides	1 h (water bath), 85 °C
	10 cm^3 8.8 mol dm^{-3} H_2O_2		1 h (water bath), 85 °C
	40 cm^3 1 mol dm^{-3}, CH_3COONH_4 (pH 2)		16 h (overnight), room temperature
IV	8 cm^3 aqua regia, ($HCl:HNO_3 = 3:1$)	Residual	1 h (water bath), 85 °C
	8 cm^3 aqua regia, ($HCl:HNO_3 = 3:1$)		1 h (water bath), 85 °C

$$\mathrm{PI} = \frac{C_i}{S_i} \tag{1}$$

$$\mathrm{PI_N} = \sqrt{\left[\frac{\mathrm{PI}^2_{i\,\mathrm{ave}} + \mathrm{PI}^2_{i\,\mathrm{max}}}{2}\right]} \tag{2}$$

C_i is the metal concentration in a soil sample and S_i is its reference value. The S_i values for Cr, Cu, Ni, Pb, and Zn were specified by national regulations (OGRS 2010). $PI_{i\ ave}$ and $PI_{i\ max}$ are the mean and maximum of the pollution indices for each metal.

Determination of the Mobility Factor

The mobility factor (MF) was calculated using Eq. 3, as proposed by Kabala and Singh (2001):

$$\mathrm{MF} = \frac{F1}{\sum F} \times 100 \tag{3}$$

$F1$ is the concentrations of toxic metals extracted in the acid soluble/exchangeable fractions and $\sum F$ represents the sum of all the fractions.

Determination of the Individual and Global Contamination Factor

Individual contamination factors (ICF) and the global contamination factor (GCF) were calculated using Eqs. 4 and 5, respectively, as proposed by Barona et al. (1999) and Matong et al. (2016):

$$\mathrm{ICF} = \frac{F1 + F2 + F3}{F4} \tag{4}$$

$$\mathrm{GCF} = \sum \mathrm{ICF} \tag{5}$$

$F1$, $F2$, $F3$, and $F4$ are the concentrations of toxic metals extracted in the acid soluble/exchangeable, reducible, oxidizable, and residual fractions.

Statistical Analysis

Correlation analysis and principal component analysis (PCA) were used to establish the possible sources of toxic metals, as well as the interelement relationship in soil. Statistical calculations were performed using the SPSS software package, version 20.0. The graphs were created using Microsoft Excel for Windows 7.

Results and Discussion

A range of chemicals, including metals such as Cu, Mn, Zn, Cd, and Pb, frequently pollute soils in industrial areas (Trujillo-González et al. 2016). Toxic metals are permanently present in soils, but their mobility and availability to plants are governed by soil characteristics, such as organic matter and clay content, soil pH, physical composition, moisture content, and calcium carbonate content (Ghrefat et al. 2012; Yang-Guang et al. 2016). If the concentration of toxic metals in soil is significantly above the mean values described for worldwide soils and/or above the background value, it points to potential contamination due to the natural geochemical origins of the soil or anthropogenic sources.

Soil Properties

The selected physical and chemical soil parameters are presented in Table 2. The data show that the range of pH values across the entire study area was narrow (from 8.44 to 8.61), meaning that these soils are classified as alkaline (Soil Survey Division Staff 1993). This pH range indicates that all the soils examined in this study have a similar effect on metal availability. Soil pH plays an important role in controlling the mobility of metals from soil to plants, and it is widely accepted that heavy metal mobility and potential bioavailability to plants increases at low pH (Behera and Shukla 2015; Shahid et al. 2017), whereas alkaline soil conditions immobilize metals and result in their low bioavailability (Bielicka-Giełdoń et al. 2013). In addition, other soil

Table 2 Average values for selected physical and chemical parameters of selected urban soils

City	pH (H_2O)	OC (%)	Total sand (2.0–0.02 mm) (%)	Silt (0.02-0.002 mm) (%)	Clay (< 0.002 mm) (%)
Pančevo	8.44	3.00	45.83	27.96	26.21
Smederevo	8.51	2.68	53.13	25.95	20.92
Obrenovac	8.44	2.10	36.27	34.71	29.02
Belgrade	8.47	5.56	52.23	27.43	20.34
Control site	8.61	7.60	35.57	37.29	27.14

properties and adsorption and complexation mechanisms may influence metal availability, especially in soils contaminated by anthropogenic activities (Chang et al. 2014). Alkaline reactions can be caused by alkalizing materials, e.g., calcium carbonate or calcium-magnesium carbonate in gravel, tiles, cement, concrete, mortar, etc., as well as atmospheric particulate deposition (Yang-Guang et al. 2016). The content of OC in the examined soil samples ranged from 2.10 to 7.60% with higher average values at the control site. Organic carbon is an important chemical component of organic matter, because its presence or absence can markedly influence how chemicals will react in the soil, i.e., organic matter constitutes a natural protective barrier against metals by reducing their mobility (Bielicka-Giełdoń et al. 2013; Arenas-Lago et al. 2014; Dou et al. 2013). The examined soil samples were predominantly composed of sand, followed by silt and clay. However, amounts varied among the soil samples: the lowest total sand fraction content (35.57%) was measured at the control site, whereas the highest (53.13%) was in Smederevo. The silt fraction varied from 25.95% in Smederevo up to 37.29% at the control site, and the clay fraction from 20.34% in Belgrade to 29.02% in Smederevo. Toxic metal adsorption tends to be greater in the fine-grained soil fraction than in coarse-grained soils, because it contains soil particles with large surface areas, such as clay minerals (Bradl 2004). This is supported by the results obtained in this study, particularly at the sampling points in Smederevo, where a significant proportion of Cr, Cu, and Ni was found in the reducible fraction and Mn and Zn in the oxidizable fraction.

Pseudo-total Concentrations and Partitioning of Toxic Metals in the Selected Urban Soils

To estimate the environmental status of soil, several guidelines were used: the mean values of the background concentrations of toxic metals in two soil types common worldwide from Kabata-Pendias and Pendias (2001); background values in the studied soils as proposed by Mrvić et al. (2009, 2011) and Knežević (2014); the Regulations of the Government of the Republic of Serbia (OGRS 1994, 2010). The arithmetical median method was used for the calculations of the background concentrations method MAD (median of absolute deviations from data median) (Reimann et al. 2005; Mrvić et al. 2011) for each city.

The pseudo-total concentrations of metals in the soil samples and the background values for the studied soils are presented in Tables 3 and 4, respectively, and the results of the partitioning study for the selected elements in urban soils are presented in Fig. 2. As concentrations of As and Cd were below the detection level in all the analysed samples, they were not discussed any further.

The average pseudo-total concentrations for Cr varied widely, from 21.08 to 107.15 mg kg^{-1}, with concentrations above the mean values described for global soils (47–51 mg kg^{-1}, Kabata-Pendias and Pendias 2001) measured at P-1, P-2, S-1, S-2, and S-3, and O-1 and O-2. Levels of Cr above the background values for the investigated area were measured at P-1, P-2, S-2, and S-3. The highest Cr concentrations were measured at S-2 and S-3, where levels were above the limit for standard values established by local regulations (OGRS 2010), with levels above maximum allowable concentrations (MAC) established by local regulations (> 100 mg/kg, OGRS 1994) at S-3. The elevated content of Cr in Smederevo and Pančevo could come from the proximity to industry. However, since background values described for the selected soil samples were similar to those obtained, it could also indicate the geological origin of Cr (Mrvić et al. 2011). Chromium exists in various states of oxidation, but the two most environmentally important are hexavalent chromate (Cr(VI)) and trivalent chromite (Cr(III)), which are redox and pH sensitive (Adriano 2001; Shahid et al. 2017). The oxidation/reduction processes of Cr(VI) and Cr(III) in soil are thermodynamically spontaneous and can take place simultaneously (Shahid et al. 2017). Our analysis does not distinguish between these different oxidation forms of Cr, but bearing in mind that Cr(III) is poorly water soluble and almost completely precipitates at a pH above 5.5, it can be assumed that in the studied soils with a pH > 8, the dominant form of chromium is Cr(III). The fractionation profile of Cr furthermore proved that a major portion is bound to the residual fraction (70–80%), whereas the rest is mainly distributed in organic matter, sulphides, and iron and manganese oxides. The content of Cr in the acid

Table 3 Pseudo-total toxic metal concentrations in selected urban soils (mg kg^{-1} d.w., mean and SD of three replications in parentheses)

Sampling sites and sampling points	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Pančevo 1	58.49 (1.43)	37.07 (1.40)	42,001.41 (440.95)	701.27 (13.99)	**71.24** **(2.43)**	47.21 (0.18)	47.36 (1.49)
Pančevo 2	57.79 (1.51)	28.73 (0.99)	33,361.78 (662.70)	606.19 (14.08)	**80.40** **(3.40)**	46.38 (0.81)	39.41 (1.09)
Pančevo 3	21.08 (0.49)	26.94 (0.31)	28,527.93 (555.25)	529.13 (18.41)	32.52 (0.46)	35.83 (0.92)	34.94 (0.55)
Smederevo 1	63.20 (2.00)	48.29 (0.99)	30,533.85 (317.19)	565.84 (17.00)	**91.54** **(3.18)**	51.13 (0.02)	173.23 (7.18)
Smederevo 2	93.88 (3.24)	41.78 (1.58)	32,702.62 (456.53)	517.43 (15.43)	**118.74** **(2.77)**	99.20 (2.77)	138.05 (1.25)
Smederevo 3	**107.15** **(3.88)**	46.72 (1.69)	27,246.61 (310.36)	470.19 (14.55)	**154.51** **(4.76)**	**102.27** **(4.60)**	106.21 (1.43)
Obrenovac 1	54.75 (2.45)	41.18 (0.93)	35,609.20 (391.50)	652.22 (20.91)	**91.71** **(0.29)**	59.49 (1.99)	65.51 (1.58)
Obrenovac 2	54.71 (1.39)	32.75 (0.65)	40,285.21 (485.78)	896.23 (49.11)	**85.42** **(1.45)**	51.87 (1.23)	43.12 (0.88)
Obrenovac 3	36.66 (0.98)	30.71 (2.02)	30,422.09 (1227.07)	546.47 (26.37)	**62.93** **(0.46)**	45.24 (2.00)	41.26 (0.50)
Belgrade 1	25.31 (1.13)	36.30 (1.99)	28,511.28 (1443.46)	474.21 (36.82)	47.43 (0.80)	49.18 (1.77)	67.46 (0.34)
Belgrade 2	25.87 (0.96)	46.62 (2.09)	22,066.92 (835.08)	403.03 (13.35)	43.81 (1.49)	**163.48** **(5.82)**	211.13 (6.29)
Belgrade 3	25.06 (0.89)	36.38 (1.23)	25,369.88 (266.64)	444.59 (18.31)	40.06 (0.88)	53.83 (1.29)	105.76 (4.52)
Control 1	36.19 (1.13)	28.61 (0.95)	33,240.96 (881.01)	619.26 (30.93)	**51.97** **(0.53)**	54.75 (2.18)	39.26 (1.33)
Control 2	32.80 (1.10)	32.25 (1.37)	32,199.79 (1452.32)	505.57 (25.25)	49.36 (1.51)	73.15 (0.86)	47.85 (1.50)
Control 3	30.89 (0.99)	29.29 (1.20)	35,275.07 (1989.67)	624.81 (26.45)	42.60 (0.68)	44.49 (2.10)	46.27 (1.28)
[a]Mean	47–51	13–23	–	270–525	13–26	22–27	45–60
[b]MAC	100	100	–	–	50	100	300

Values above the MAC are in bold

[a]Mean values of toxic metals (Kabata-Pendias and Pendias 2001)

[b]Maximum allowable concentration of toxic metals (OGRS 1994)

Table 4 Toxic metal background values (mg kg^{-1} d.w.) in selected urban soils (Mrvić et al. 2009, 2011; Knežević 2014)

City	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Pančevo	47.508	37.796	50,351.84	689.548	49.315	25.114	96.450
Smederevo	69.000	58.500	23,911.08	620.521	103.000	53.500	115.000
Obrenovac	79.000	28.000	41,266.52	863.701	131.000	35.123	74.000
Belgrade	61.000	30.000	24,771.00	489.288	72.000	37.000	68.000

soluble/exchangeable fraction is very low: below the detection limit. Such results prove that Cr has a strong association with the insoluble fraction and is stable under anthropogenically altered-induced conditions with lower transfer ability, which is in line with earlier reports (Ghrefat et al. 2012; Osakwe 2013; Bielicka-Giełdoń et al. 2013). Low and relatively uniform Cr concentrations (< 36 mg kg^{-1}) at all the sampling points and its release in the residual and oxidizable fractions are characteristics of soils from Belgrade and the control site. At all the sampling points in Smederevo, the highest Cr content was determined in the residual fraction (approximately 69%), followed by a significant proportion of this element associated with the reducible (approximately 16%) and oxidizable fractions (approximately 14%). Bearing in mind the fractionation profile of Cr and the fact that metals originating from anthropogenic sources are most often

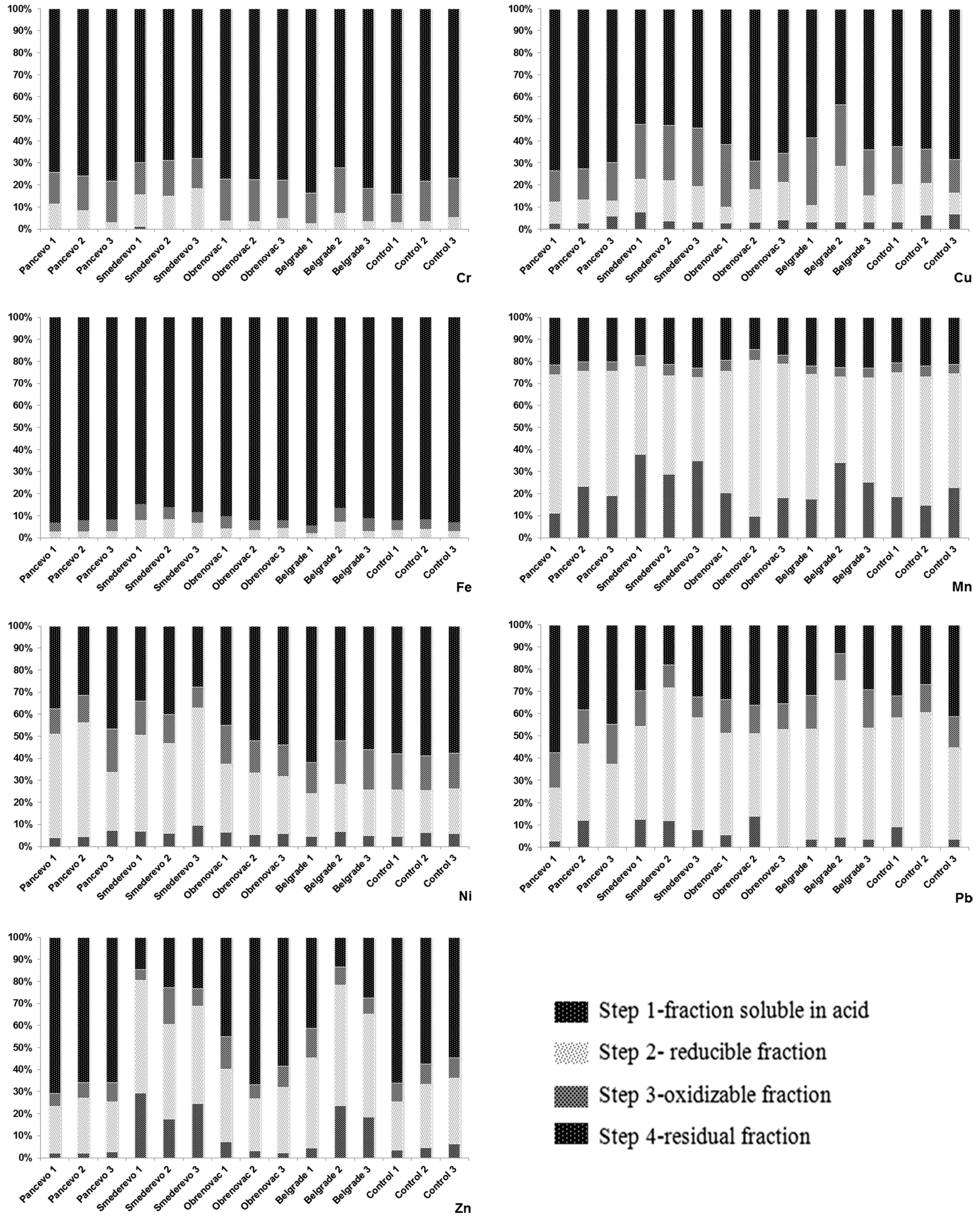

Fig. 2 Partitioning of Cr, Cu, Fe, Mn, Ni, Pb, and Zn in selected urban soils from Pančevo, Smederevo, Obrenovac, and Belgrade

released in the acid soluble/exchangeable, reducible, and oxidizable fractions, while elements of geological origin remain tightly bound to the residual phase (Ghrefat et al. 2012), it is reasonable to assume that Cr in Smederevo originates from both natural and human sources.

Copper levels varied from 26.94 to 48.29 mg kg^{-1}, with levels above the average values for worldwide soils (13–23 mg kg^{-1}, Kabata-Pendias and Pendias 2001) measured at all the sites. Cu levels above the background values for the investigated area were measured at all the sampling points in Belgrade and Obrenovac. Furthermore, Cu concentrations above the limit for standard values established by local regulations (OGRS 2010) were measured at P-1 and at all the sampling points in Smederevo, whereas concentrations of Cu above MAC established by local regulations (> 100 mg/kg, OGRS 1994) were not measured. Although copper in urban soils mostly originates from traffic and braking (Van Bohemen and Van de Laak 2003; Akan et al. 2013), the elevated content of Cu in Smederevo likely has a local character and probably originates from its industry, as shown by the findings of Dragović et al. (2014), who found increased Cu concentrations in surface soils around the steel plant in Smederevo. The fractionation profile of Cu showed similar trends as Cr: most of the Cu is bound to the residual fraction (40–70%), followed by the oxidizable fraction. The tendency of Cu to be associated with organic matter and sulphides (the oxidizable fraction) has been widely reported in other research (Imperato et al. 2003; Mahanta and Bhattacharyya 2011; Yutong et al. 2016) and can be attributed to the greater stability of organo-Cu complexes influenced by the high affinity of Cu(II) to humic organic matter (Mahanta and Bhattacharyya 2011). The reducible fraction (the Fe–Mn oxide fraction) also has considerable levels of Cu, and, at some sampling points, an equal amount to the oxidizable fraction. The Cu content is lowest in the acid soluble/exchangeable fraction, and it increases continuously through the steps of sequential extraction.

Iron levels ranged from 22.07 to 42.00 g kg^{-1} with the lowest level measured at B-2 and the highest at P-1. Levels of Fe above the background values for the investigated area were measured at all the sampling points in Smederevo and at the control site, as well as at B-1 and B-3. The Fe content above the background values in Smederevo could be explained by the fact that dust produced in the steel production process contains Fe, Zn, Ca, and Si in the form of oxides (Dragović et al. 2014), which could easily be transferred to soil. However, the highest Fe content in soil was observed in the residual fraction (approximately 90.6%), whereas the rest is distributed mainly in organic matter and sulphides (approximately 4.9%) and iron and manganese oxides (approximately 4.4%). A very small amount was associated with the acid soluble/exchangeable fraction (0.02%). These results are consistent with numerous studies (Jaradat et al. 2006; Lu et al. 2007; Tokalioğlu et al. 2010; Osakwe 2013), indicating that Fe is insoluble and relatively immobile in the selected soil samples.

Anthropogenic sources of Mn include mining, smelting, traffic, and agriculture. Manufacturing processes in the production of steel, glass, dry batteries, and chemicals also are known to increase Mn content (WHO 2004). In this study, Mn concentrations varied between 403.03 mg kg^{-1} at B-2 and 896.23 mg kg^{-1} at O-2, with concentrations above the mean values described for worldwide soils (270–525 mg kg^{-1}, Kabata-Pendias and Pendias 2001) measured at S-1, C-1, C-2, and at all sampling points in Pančevo and Obrenovac. Levels of Mn above the background values for the investigated localities were measured at P-1 and O-2. Given the nature of the industry in Pančevo (chemical manufacturing, oil refinery, etc.), Smederevo (steel manufacturing), and Obrenovac (thermoelectric power plant), concentrations above the average values for global soils are to be expected. The highest Mn content was determined in the reducible fraction (approximately 53%). A significant part of this element also was associated with the acid soluble/exchangeable (approximately 22%) and residual fractions (approximately 20%), which shows that it has a weak association with organic matter and sulphides. Manganese bound to the oxidizable fraction constitutes about 4.5% of the total Mn in the soil and this fraction has similar values at all the sites. The highest Mn content found in the reducible fraction is to be expected due to manganese oxyhydroxides being a principal target of the hydroxylammonium chloride reagent (Davidson et al. 2006). The reducible and acid soluble/exchangeable fractions may release Mn in a suitable chemical environment and therefore may present a risk to ecosystems. The results obtained from other urban soil studies also have shown that the reducible form is the most important fraction for Mn (Wilcke et al. 1998; Davidson et al. 2006; Mahanta and Bhattacharyya 2011). Similar results were obtained for agricultural soils (Tokalioğlu et al. 2010). In contrast, Lu et al. (2007) reported that Mn is uniformly distributed between the extractable, reducible and residual fractions, and that the lowest amounts are associated with the oxidizable fraction.

Nickel concentrations varied widely between 32.52 and 154.51 mg kg^{-1}, with levels above the mean values for global soils (13–26 mg kg^{-1}, Kabata-Pendias and Pendias 2001) measured at all the sites. Concentrations above the background values for the investigated localities were measured at the same sampling points as for Cr (P-1, P-2, S-2, and S-3) and above the limit for standard values established by local regulations (OGRS 2010) at all the sampling points, aside from P-3. Concentrations of Ni above MAC established by local regulations (> 50 mg/kg, OGRS 1994) were measured at P-1, P-2, at all the sampling points in Smederevo and Obrenovac, and at sampling point C-1. The Cr and Ni distribution trends were generally similar, indicating that these metals may have had the same source. Although it is known that Serbian soils are characterized by a high Ni content due to their geological origin (Kuzmanoski et al. 2014), the concentrations above the background values for the investigated area (Mrvić et al. 2011) measured in Pančevo and Smederevo are most probably the result of industrial emissions (such as the petrochemical complex in Pančevo and the steelworks in Smederevo) (Wei and Yang 2010). The fractionation profile of Ni at P-1, P-2 and at all the sampling points in Smederevo indicates that it is predominantly bound to iron and manganese oxides (40–55%), with the rest being associated with the residual (27–40%), organic (9–15%), and acid soluble/exchangeable (4–9%) fractions. It is known that a suitable environment (redox potential, salinity, and pH) can lead to the release of Ni bound to iron and manganese oxides, i.e., the reducible fraction, representing a threat to the environment (Jain et al. 2007). A higher content of extracted Ni in the reducible fraction, as well as an elevated pseudo-total content of extracted Ni, was observed at all the sampling points in Smederevo, which indicates Ni from both natural and anthropogenic sources (Ghrefat et al. 2012). At all the other sampling points, the largest portion is bound to the silicate lattice and crystallized oxide minerals (45–65%). At these sampling points, a significant part of this element was also associated with the reducible fraction (approximately 23%) and organic matter (approximately 15%). Similar results were previously reported by Lu et al. (2007) and Ghrefat et al. (2012). Irregular patterns of Ni partitioning in soils have been reported in literature. For example, other researchers (Davidson et al. 2006; Osakwe 2013) have found that Ni was mainly associated with the residual phase.

Lead is a major pollutant in urban soils. In our study, its concentrations in the soil samples varied widely, between 35.83 and 163.48 mg kg^{-1}, with levels above the mean values for global soils (22–27 mg kg^{-1}, Kabata-Pendias and Pendias 2001) measured at all the sites. Moreover, at all the sampling points, apart from S-1, levels above the background values were measured. Concentrations of Pb above the limit for standard values established by local regulations (OGRS 2010) were measured at S-1, S-2, and B-2, whereas levels above MAC established by local regulations (> 100 mg/kg, OGRS 1994) were measured at points S-3 and B-2. The most probable sources of lead at these sampling points are motor vehicle emissions, proximity to streets, and the lead particulate matter emitted from industrial activities (Imperato et al. 2003; Akan et al. 2013; Zhao et al. 2014). Furthermore, another possible reason for the higher content of Pb in the sampled soils also could be the fact that leaded petrol was used in Serbia until 2010 (Ghariani et al. 2010). In the soil from all the sampling points in Pančevo, the greatest amount of Pb is distributed between the reducible (Fe–Mn oxide) and residual fractions, whereas at all the other sites the highest proportion of Pb is bound to iron and manganese oxides (the reducible fraction). The lowest levels of Pb occurred in the acid soluble/exchangeable and oxidizable fractions (6 and 13%, respectively). The relatively high percentage of Pb in the reducible fraction may be due to its tendency to adsorb on clay minerals (Borgese et al. 2013), the levels of which in the sampled soils are enough to bind a certain amount of Pb, and/or because of the reaction of Pb with Fe and Mn oxides, which are important scavengers of metals in soils, particularly with a pH > 7 (Borgese et al. 2013; Jaradat et al. 2006), as is the case with our soil samples. The results obtained point to the low to moderate mobility of Pb in the sampled soils, indicating that Pb can be remobilized if environmental conditions allow and when it is, it can represent a potential threat to the environment (Jaradat et al. 2006). Ramos et al. (1994) found that most Pb was associated with the Fe–Mn oxide fraction in polluted soils in Spain, with very low amounts in the exchangeable fraction. These results are in broad agreement with ours and with previous studies in other urban regions (Wilcke et al. 1998; Davidson et al. 2006). In our study, the highest level of the total content of extracted Pb was detected at B-2, which indicates the presence of contamination sources of this element in the vicinity of this site (proximity to roads and traffic).

As far as Zn concentrations in the urban soil samples are concerned, they varied between 34.94 and 211.13 mg kg^{-1}, with levels above the mean values for global soils (45–60 mg kg^{-1}, Kabata-Pendias and Pendias 2001) at all the sampling points in Smederevo and Belgrade and at O-1. Concentrations above the background values for the investigated area were measured at S-1, S-2, B-2, and B-3. Concentrations of Zn above the limit for standard values established by local regulations (OGRS 2010) were measured at S-1, S-2, and B-2, whereas MAC established by local regulations (> 300 mg/kg, OGRS 1994) were not surpassed at any point. Motor vehicle emissions and other waste products from traffic could be one of the potential sources of Zn in Belgrade and in Smederevo (Akan et al. 2013; Benhaddya et al. 2016). Furthermore, the significant Zn content in Smederevo quite likely originates from suspended particles produced during the iron and steel production process, as previously established by Dragović et al. (2014) in the same area. The greatest proportion of Zn is associated with the residual fraction at all the sampling points in Pančevo, Obrenovac, and at the control site (approximately 61%). The percentage of Zn in this fraction points to its lithogenous origin and inability to mobilize. In percentage terms, this is followed by the reducible fraction at these sites with a range from 21 to 33% and an average of 26.3%. An average of 8.8% of Zn was associated with organic matter and sulphides. These results are consistent with those previously reported by Lu et al. (2007) and Yutong et al. (2016). The percentage of Zn in the acid soluble/exchangeable (3.6%) fraction is very low in the soil samples in this study. In Smederevo and Belgrade, a large proportion is bound to iron and manganese oxides (approximately 46%). The rest of the Zn is associated with the residual (approximately 23.8%) and acid soluble/exchangeable (approximately 19.6%) fractions. It was previously reported that the major fraction of Zn was associated with iron and manganese oxides (49.5%) and approximately 24% was bound to the residual fraction. Such results suggest that some Zn is potentially available for plant uptake, as well as for biota, and can present a high potential risk in soils due to its great mobility and bioavailability in the environment (Jiang et al. 2013). In this study, at all the sampling points in Pančevo, Obrenovac and the control site, the order of dominance of the Zn fractions was as follows: residual > reducible > oxidizable > acid soluble/exchangeable. Similar findings were reported by Wilcke et al. (1998) and Imperato et al. (2003). However, Li et al. (2001) reported that the reducible fraction was the predominant fraction for Zn, which is consistent with our findings for Zn at all the sampling points in Smederevo and Belgrade, indicating the heterogeneity of urban soils.

It has been reported that toxic metals with wide concentration ranges are predominantly from anthropogenic sources (Han et al. 2006; Manta et al. 2002). However, an elevated mean concentration of some elements does not necessarily reflect the impact of anthropogenic pressures but also could be explained by the specific nature of the substrate in the urban parks. It often is a mixture of different source materials, including soil materials derived from different parent materials, construction debris, and industrial waste (Mitrović 1998).

Relationships Between Toxic Metals and Source Identification

To establish interelement relationships in the soil samples, Pearson's correlation coefficients of toxic metals were calculated and are presented in Table 5. The pairs of Cr–Ni (r = 0.977**), Fe–Mn (r = 0.899**), Cu–Zn (r = 0.842**), Pb–Zn (r = 0.750**), Cu–Pb (r = 0.636**), Cu–Ni (r = 0.559**), and Cu–Cr (r = 0.520**) show high correlations, which may suggest a common origin (at 99% confidence level). In contrast, Fe and Mn are negatively correlated with Pb (− 0.508**; − 0.487**), Zn (− 0.572**; − 0.520**), and Cu (− 0.337*; − 0.347*), reflecting their different sources. Fe and Mn are predominantly of geological origin, whereas Cu, Pb, and Zn emissions are mainly related to traffic and industry.

PCA was performed to identify possible contributing factors to the metal concentrations found and to determine any common origin of the metals (Banerjee 2003). The results of the PCA for the metal content in urban soils are shown in Table 6. Three principal components were considered in the PCA, accounting for more than 90% of the total variance. The first principal component (PC1) explains approximately 50% of the total variance and loads heavily on Cu (0.811), Pb (0.817), and Zn (0.905). This factor may be attributed to anthropogenic sources. In the current study, in addition to vehicle emissions, this metal contamination may be linked to industrial pollution, especially in Smederevo, where these metals probably originate from industry. The sources of Cu emissions are mainly traffic-related, such as brake abrasion and the corrosion of metal car parts, whereas Zn is mainly a product of the wear and tear of tyres and brake pads, and Pb may be released during combustion processes (Van Bohemen and Van de Laak 2003). Han et al. (2006) reported

Table 6 Results of PCA (Varimax normalized)

Element	PC1	PC2	PC3
Cr	0.175	0.968	0.125
Cu	0.811	0.444	− 0.160
Fe	− 0.328	0.158	0.904
Mn	− 0.263	0.071	0.939
Ni	0.185	0.972	0.094
Pb	0.817	0.115	− 0.301
Zn	0.905	0.103	− 0.313
Eigenvalues	3.524	2.334	0.596
Variance %	50.342	33.345	8.519
Cumulative %	50.342	83.686	92.205

Table 5 Correlation matrix for the metal concentrations

Metal	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Cr	1.00						
Cu	0.520**	1.00					
Fe	0.219	− 0.337*	1.00				
Mn	0.133	− 0.347*	0.899**	1.00			
Ni	0.977**	0.559**	0.160	0.125	1.00		
Pb	0.241	0.636**	− 0.508**	− 0.487**	0.250	1.00	
Zn	0.226	0.842**	− 0.572**	− 0.520**	0.231	0.750**	1.00

*$p < 0.05$ level; **$p < 0.01$ level

that Cu, Pb and Zn mainly originate from industrial sources, coupled with traffic sources. PC2 explains approximately 33% of the total variance and is loaded primarily with Cr (0.968) and Ni (0.972), indicating both natural and anthropogenic sources. The dominant factor loading of Ni and Cr suggests that their origin in Smederevo and Pančevo could be associated with local emission sources, such as chemical manufacturing and the oil refinery in Pančevo and the steelworks in Smederevo. PC3 explains only 8.5% of the total variance but is strongly positively loaded with Fe (0.904) and Mn (0.939), which may be relevant to the natural origin of the soil. The relationships between the metals based on the first three principal components are illustrated in Fig. 3a.

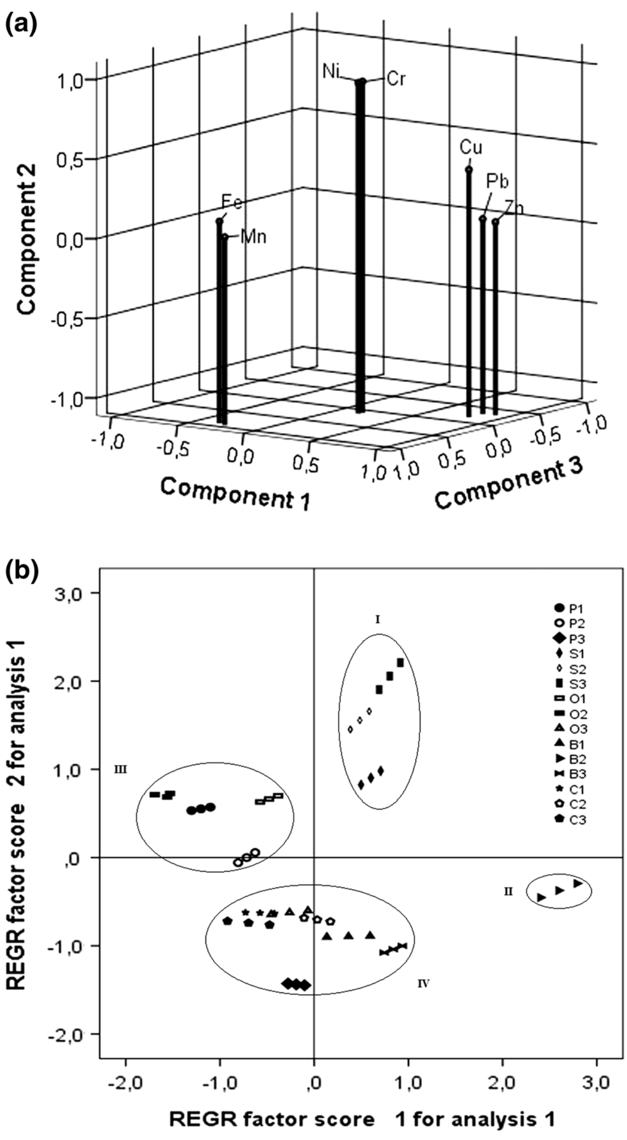

Fig. 3 PCA for selected elements in soil: **a** loading plot, **b** score plot

The loading plot (Fig. 3b) displays four isolated groups of samples. The first group contains soil samples from Smederevo, which are characterized by high Cr, Cu, Pb, Ni, and Zn content. The second group contains soil samples from Belgrade (B-2), and these samples are characterized by high Cu, Pb, and Zn content. The third group contains samples from Pančevo (sampling points P-1 and P-2) and Obrenovac (sampling points O-1 and O-2), which are characterized by high Mn and Fe content, whereas the fourth group contains the other soil samples, where the elements are mostly of natural origin.

Contamination Assessment

Pollution Index and Nemerow Pollution Index

To assess the level of metal contamination, as well as the geogenic and potential anthropogenic impact on the investigated soil samples, the pollution index (PI) and Nemerow pollution index (PI_N) were calculated. The results of the PI and PI_N and the relationships between the PI and PI_N and metal pollution levels are summarised in Table 7. The mean PI values were generally low, indicating that there was no apparent pollution of soils. However, the highest PI value for Ni (a high level of pollution) was found in Smederevo, followed by Obrenovac with a moderate level of pollution. The PI values were generally higher in Smederevo and Belgrade. These are areas exposed to high car exhaust emissions, dense population, and industrial activities. The degree of metal enrichment could be stated as follows: Ni > Cu > Pb > Zn > Cr. Conversely, the results

Table 7 Mean PI of Cr, Cu, Ni, Pb, and Zn in the selected soil samples and the corresponding PI_N

City	PI							PI_N					
	Pollution degree[a]		Cr	Cu	Ni	Pb	Zn	Pollution level[a]		Mean	Min	Median	Max
Pančevo	≤ 1	Non pollution	0.45	0.86	1.70	0.53	0.30	<0.7	Clean	0.87	0.32	0.56	1.98
Smederevo	1–2	Low	0.96	1.50	3.93	1.11	1.16	0.7–1	Warning limit	1.93	1.07	1.31	4.50
Obrenovac	2–3	Moderate	0.45	1.01	2.05	0.63	0.35	1–2	Slightly polluted	0.97	0.41	0.68	2.21
Belgrade	> 3	High	0.28	1.21	1.44	1.11	1.02	2–3	Moderately polluted	1.23	0.28	1.39	1.65
Control			0.32	0.77	1.29	0.64	0.29	> 3	Seriously polluted	0.70	0.31	0.73	1.35

[a] Classification of soil pollution by toxic metals based on the PI and PI_N (Yang et al. 2011)

for the Nemerow pollution index (PI_N) for all the samples varied from 0.28 to 4.50. Soil samples from Smederevo had slight to serious pollution levels, which could be explained by the proximity of the steelworks. Soil samples from Belgrade exhibited slight levels of pollution, while those from Pančevo and Obrenovac revealed a warning limit of pollution.

Mobility of Metals

The mobility and availability of metals depend on the chemical form in which a metal is present in the soil, as well as on the strength with which it is bound to the soil matrix (Mahanta and Bhattacharyya 2011; Osakwe 2013). Toxic metals in the acid soluble/exchangeable fraction ($F1$) are considered readily and potentially mobile, whereas the reducible and oxidizable fractions are relatively stable under normal soil conditions. Toxic metals that are present in the residual fraction are entrapped within the crystal structure of the minerals, which is why they are the least mobile (Lu et al. 2007; Mahanta and Bhattacharyya 2011). To evaluate the mobility of metals, some researchers have used the relative index or mobility factor (MF), presented as the ratio of metals present in the water/soluble, exchangeable and carbonate fractions and the amount of metals extracted in all fractions (Kabala and Singh 2001; Olajire et al. 2002; Lu et al. 2007). As in phase I, which represents the acid/soluble fraction (the fraction in which water-soluble/exchangeable, carbonate-bound metals are extracted with 0.11 mol/L HOAc), it is acceptable to use the ratio between $F1$ and the sum of all the fractions as an index that can predict the potential mobility of metals (Lu et al. 2007). A high MF value indicates relatively high mobility and the biological availability of toxic metals, whereas a low MF value reflects the high stability of toxic metals in soil (Kabala and Singh 2001; Olajire et al. 2002; Lu et al. 2007). The results of the MF Cr, Cu, Fe, Mn, Ni, Pb, and Zn in the soil samples are presented in Table 8.

The results of this study showed that the MF for Cr, Cu, Mn, Fe, Ni, Pb, and Zn was generally below 10%, indicating their low mobility and high stability in these soil samples. The exception was Zn in Smederevo and at B-2 and B-3. The MF for Fe (0.02%) suggests that Fe is immobile in the studied soils. The MF for Pb was moderate (12–14%) at P-2, S-1, S-2, and O-2. The highest MF for Mn (> 30%) was found at S-1, S-3 and B-2. In our study, Mn was identified as the most mobile element, having the highest extractability in the first step (exchangeable and acid soluble), which is in line with the findings of Mahanta and Bhattacharyya (2011).

Table 8 The mobility, individual, and global contamination factors of Cr, Cu, Fe, Mn, Ni, Pb, and Zn

Sampling sites and sampling points	MF (%)							ICF							GCF
	Cr	Cu	Fe	Mn	Ni	Pb	Zn	Cr	Cu	Fe	Mn	Ni	Pb	Zn	GCF
Pančevo 1	0.00	2.74	0.02	11.02	3.94	3.04	1.87	0.35	0.36	0.07	3.59	1.66	0.74	0.41	7.19
Pančevo 2	0.00	2.89	0.02	23.26	4.26	12.18	1.95	0.31	0.38	0.09	3.96	2.18	1.61	0.52	9.05
Pančevo 3	0.00	5.88	0.01	19.10	7.15	0.00	2.67	0.28	0.43	0.09	3.92	1.14	1.24	0.52	7.62
Mean	0.00	3.84	0.02	17.79	5.12	5.07	2.16	0.31	0.39	0.08	3.82	1.66	1.20	0.48	7.95
Smederevo 1	1.02	7.92	0.06	37.92	6.83	12.69	29.45	0.43	0.91	0.18	4.71	1.94	2.37	5.81	16.36
Smederevo 2	0.00	3.81	0.02	28.63	5.85	12.05	17.39	0.45	0.89	0.16	3.65	1.49	4.54	3.36	14.55
Smederevo 3	0.00	3.40	0.03	34.76	9.36	8.14	24.45	0.47	0.86	0.13	3.34	2.61	2.09	3.28	12.78
Mean	0.34	5.04	0.04	33.77	7.35	10.96	23.76	0.45	0.89	0.16	3.90	2.01	3.00	4.15	14.56
Obrenovac 1	0.00	2.83	0.03	20.15	6.50	5.83	7.12	0.29	0.62	0.11	4.13	1.22	1.99	1.22	9.58
Obrenovac 2	0.00	3.08	0.01	9.69	5.31	14.02	3.09	0.29	0.45	0.08	5.89	0.92	1.78	0.50	9.90
Obrenovac 3	0.00	4.32	0.01	18.16	5.69	0.71	2.14	0.28	0.53	0.09	4.82	0.85	1.83	0.71	9.11
Mean	0.00	3.41	0.02	16.00	5.83	6.85	4.12	0.29	0.53	0.09	4.95	1.00	1.87	0.81	9.53
Belgrade 1	0.00	3.43	0.02	17.35	4.47	3.66	4.32	0.19	0.71	0.06	3.50	0.61	2.17	1.24	8.48
Belgrade 2	0.00	3.44	0.01	34.16	6.76	4.60	23.62	0.38	1.30	0.16	3.38	0.92	6.81	5.99	18.94
Belgrade 3	0.00	3.49	0.01	25.12	4.69	3.54	18.36	0.23	0.57	0.10	3.35	0.78	2.45	2.51	9.97
Mean	0.00	3.45	0.01	25.54	5.31	3.93	15.43	0.27	0.86	0.10	3.41	0.77	3.81	3.24	12.47
Control 1	0.00	3.48	0.01	18.55	4.55	9.29	3.27	0.19	0.60	0.09	3.84	0.72	2.13	0.53	8.11
Control 2	0.00	6.50	0.05	14.70	6.21	0.00	4.56	0.28	0.57	0.09	3.54	0.70	2.74	0.72	8.65
Control 3	0.00	6.94	0.03	22.50	5.79	3.72	6.08	0.30	0.46	0.08	3.68	0.73	1.43	0.82	7.49
Mean	0.00	5.64	0.03	18.58	5.52	4.34	4.64	0.25	0.55	0.08	3.69	0.72	2.10	0.69	8.08

Individual and Global Contamination Factor

The global contamination factor (GCF) reflects the overall potential risks posed by toxic elements to the environment (Nemati et al. 2009), whereas the individual contamination factor (ICF) reflects the risk of soil contamination by a certain pollutant (Barona et al. 1999). The ICF and GCF were calculated to estimate the degree of toxicity or the risk toxic metals pose to the environment relative to their retention time. The number of toxic elements determined in a soil sample and their respective calculated ICF influences the GCF. When the ICF is low, the relative metal retention time is high and the risk to the environment is low, whereas a high ICF reflects the opposite (Barona et al. 1999). These methods of assessment based on the contamination factor have been used by numerous authors (Barona et al. 1999; Mashal et al. 2015, Matong et al. 2016). The results of the ICF and GCF for Cr, Cu, Fe, Mn, Ni, Pb, and Zn in the soil samples are presented in Table 8.

In the studied soil samples, the highest ICF average values for Cr, Cu, Fe, Ni, and Zn were found in Smederevo, indicating the highest risk of contamination, whereas the highest mean values for Mn and Pb were found in Obrenovac and Belgrade, respectively. However, this is not unexpected bearing in mind the fact that iron smelters can lead to the extensive contamination of surrounding soils with toxic metals depending on the types of scrap metals processed (Dragović et al. 2014). The highest ICF values for Cu, Pb, and Zn were found in Belgrade at B-2, indicating that B-2 is at a higher risk of contamination than the other investigated points. Because B-2 is the closest to a road, it implies that Cu, Pb, and Zn mainly originate from anthropogenic sources, such as vehicular traffic. The average ICF values for the examined elements exhibited the following sequence: Mn > Zn > Pb > Ni > Cu > Cr > Fe. The GCF showed high contamination by the tested metals at all the sites. The highest level of the GCF was found at B-2, whereas the lowest value was at P-1. A high GCF in top soil can be explained by the tendency of toxic metals to accumulate near the surface of the soil (Hu et al. 2013). According to the results obtained, sampling points located near a road had higher contamination and were at greater environmental risk.

Conclusions

This study investigated the fractionation, mobility, and contamination of potentially toxic metals in soils taken from urban parks in Serbian cities exposed to different sources of pollution. It revealed that concentrations of some metals (Cr, Cu, Fe, Mn, Ni, Pb, and Zn) exceed the limits established by local regulations, as well as the background values, which may represent an environmental threat at certain localities. Based on the obtained indices and the pseudo-total content of toxic metals, it can be concluded that the overall soil status at the selected sampling sites ranges from the warning limit to slightly polluted. However, BCR sequential extraction showed that any change in the environment can produce conditions that can lead to the accessibility of the selected elements, making them available and mobile, thus posing a risk to organisms. This is the case with Mn, which is probably of geochemical origin and is not present in quantities that could be harmful to the environment, but the results revealed its high mobility, which can potentially represent an environmental threat. According to the ICF and GCF, the most polluted sampling point was B-2, but the city with the highest level of overall pollution was Smederevo.

The results of correlation analysis and PCA supported each other. The examined metals were classified into three main groups according to their sources: natural, anthropogenic, and both natural and anthropogenic.

Heavy metals may remain in urban soils for a long time, which might lead to a further potential threat to ecosystems and human health. The data on the chemistry and mobility of metals in urban soils obtained in this study has enabled an estimation of potential hazards to the environment and human health, which can provide more reliable information for the risk management of metals in the urban environment.

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Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflicts of interest.

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