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# Spatial distribution of metals in urban soil of Novi Sad, Serbia: GIS based approach



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#### ABSTRACT

Metal concentrations in urban soils of Novi Sad, Serbia were measured and the pollution sources were identified using multivariate statistical methods. During July and August 2010, a total of 121 surface soil samples were collected across the central part of the city covering a surface area of 20 km<sup>2</sup> (4 km × 5 km). Concentrations of As, Co, Cr, Cu, Mn, Ni, Pb, and Zn were determined using the ICP-OES device. Pb concentration varied from 8.9 mg kg<sup>-1</sup> to 999.1 mg kg<sup>-1</sup> at the examined locations. A hierarchical cluster analysis was performed on the available data sets in order to identify associations among metals. GIS mapping technique was applied to produce geochemical maps showing the hot-spots of metal contamination. The elemental relationship in correlation matrix and the results of multivariate statistics supported a natural origin of As, Co, Cr, Mn, and Ni, while Cu, Pb, and Zn originated from anthropogenic inputs. Distribution patterns obtained using GIS mapping technique implied that traffic was the most important source of pollution.

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#### 1. Introduction

The soil is a complex heterogeneous medium comprising mineral constituents, organic matter, living organism, aqueous and gaseous components (Alloway, 1990). It is a significant component of urban ecosystems, contributing directly or indirectly to the general quality of life of city residents. As urban areas are densely populated, the environmental quality of urban soil is closely related to human health and wellbeing. Heavy metals in urban areas are of great concern, due to their nonbiodegradability, long residence time and long biological half-lives for elimination from the body. Metals can be easily transferred into the human bodies by dust ingestion, dermal contact or inhalation. Excessive exposure to metals might cause toxic effects to biological organism. Various activities such as smelting processes, disposal of urban and industrial waste (Thornton, 1991), and atmospheric pollution resulted from motor vehicles and combustion of fossil fuel (Simonson, 1995), are usually the main anthropogenic sources of heavy metals in soils.

One of the main objectives of the heavy metal's evaluation is to distinguish natural background levels from human pollution, to identify their sources, and to assess potential health risks associated with heavy metals. Geostatistics, multivariate methods and Geographic Information System (GIS) mapping are powerful analysis tools that have been used in numerous studies for determination of spatial distribution, and behavior of pollutants in urban areas (Gong et al., 2010; Guagliardi et al., 2012; Imperato et al., 2003; Lee et al., 2006; Morton-Bermea et al., 2009; Rodriguez-Salazar et al., 2011; Yuan et al., 2013). Kriging is one of the most commonly applied interpolation methods in environmental studies (Buttafuoco et al., 2010; Dayani and Mohammad, 2010; Hani and Kariminejad, 2010; Khalil et al., 2013; Lin et al., 2011; Xie et al., 2011).

There has been no detailed investigation of urban soil pollution in Serbia, due to the lack of strict application of environmental protection legislation (Crnković et al., 2006; Marjanović et al., 2009; Škrbić and Đurišić-Mladenović, 2012). The present study is focused on the investigation of urban soil pollution in the central part of the Novi Sad city. The economic mismanagement in the last decades leads to decay or demise of once large industrial combines. One of the biggest industrial combines in the city is the oil refinery, located 3 km northeast of the city center along with the thermal power plant. The refinery complex consists of production facilities and storage tanks for crude oil and oil products (mainly gasoline and diesel fuel). It is considered that the main 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 highest concentrations of pollutants are expected in the vicinity of strategic transport links and high volume traffic roads. Ecological and human health risks of heavy metal contamination in the study were assessed by comparing the results with the Dutch and Serbian soil quality guidelines with literature data for urban soils in the region and some European cities.

The aims of the study were: to determine the concentration of metals in urban soils; to perform statistical analysis of the data in order to distinguish pollution sources; and to produce geochemical maps of metals and identify possible hot spots of elevated concentrations using GIS technology.

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#### 2. Materials and methods

#### 2.1. The study area and soil sampling

Novi Sad is the second largest city in Serbia after Belgrade, with population estimated to be about 370,000. It is located in the southern part of the Pannonian Plain on the Danube River. The Investigated area of Novi Sad is completely covered by Holocene alluvial deposits. These alluvial sediments characterized by different grain size texture have been formed by The Danube River fluvial activity. The terrace consists of Holocene sand shoals, sandy clay and sand. Meandering of the Danube River created typical fluvial morphology including many point bars and related inter depressions. The whole part of Novi Sad area lies on a fluvial terrace with an elevation of 72–80 m above sea level (latitude 45° 15′ N; longitude 19° 50′ E). Autochthonous (indigenous) soil type is fluvisol according to World reference base for soil resources (ISSS, 2006).

The study includes the central part of the city covering a surface area of 20 km<sup>2</sup> (4 km × 5 km), which was divided using a square grid of 400 m × 400 m. The samples were taken in each of these squares giving a total amount of 121 samples. Sampling locations are shown on the map of Novi Sad presented in Fig. 1. Each of the composite topsoil samples (0–10 cm depth) was made by mixing sub-samples from twelve random points within about 30 m<sup>2</sup> grid in each sampling site. The initial quantity of samples were taken within the distance of 1–2 m from

#### Table 1

Statistical description of physical and chemical soil characteristics (N = 121).

oH—KCl	CaCO <sub>3</sub> (%)	OM (%)	AL P <sub>2</sub> O <sub>5</sub> (mg/100 g)	Sand (%)	Silt (%)	Clay (%)
7.53	11.6	2.86	36.3	76.3	15.3	8.4
7.54	11.4	2.92	29.8	78.0	15.2	6.8
7.19	3.8	1.47	6.0	46.8	2.3	1.6
7.89	19.4	3.86	131.5	95.9	29.7	23.5
).13	3.5	0.56	22.8	9.0	5.1	4.4
).02	0.30	0.20	0.63	0.12	0.33	0.52
	0H-KCl 7.53 7.54 7.19 7.89 0.13 0.02	H-KCI CaCO <sub>3</sub> (%) 7.53 11.6 7.54 11.4 7.19 3.8 7.89 19.4 1.13 3.5 0.02 0.30	H-KCl CaCO3 (%) OM (%)   7.53 11.6 2.86   7.54 11.4 2.92   7.19 3.8 1.47   7.89 19.4 3.86   0.13 3.5 0.56   0.02 0.30 0.20	H-KCl CaCO <sub>3</sub> OM AL P <sub>2</sub> O <sub>5</sub> (%) (%) (mg/100 g)   7.53 11.6 2.86 36.3   7.54 11.4 2.92 29.8   7.19 3.8 1.47 6.0   7.89 19.4 3.86 131.5   0.13 3.5 0.56 22.8   0.02 0.30 0.20 0.63	$\begin{array}{c ccccccc} H-KCI & CaCO_3 & OM & AL P_2O_5 & Sand \\ (\%) & (\%) & (mg/100 g) & (\%) \\ \hline \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	$\begin{array}{c ccccccc} H-KCI & CaCO_3 & OM & AL P_2O_5 & Sand & Silt \\ (\%) & (\%) & (mg/100 g) & (\%) & (\%) \\ \hline \end{tabular} \\ \hline $

OM: organic matter, AL P<sub>2</sub>O<sub>5</sub>: available phosphorus, SD: standard deviation, RSD: relative standard deviation.

the pavement. The soil samples were taken using a stainless steel hand auger and stored in polyethylene bags for transport and storage. Sampling was carried out in July and August of 2010.

#### 2.2. Chemical analysis and mechanical properties

Chemical properties were obtained following standard procedures. The soil samples were airdried at room temperature and milled to a particle size of <2 mm, in accordance with ISO, 11464 (2006). Mechanical properties of soil were determined by the internationally recognized pipette method. The size fractions were defined as sand (0.02–2 mm), silt (0.002–0.02 mm) and clay (<0.002 mm). Soil type was determined according to the ISSS soil texture classification. The pH value in 1:5 (V/V)



Fig. 1. Sampling sites denoted on the map of the city of Novi Sad.



Fig. 2. Textural classification of the collected soil samples (Moeys, 2014; Scheffer and Schachtschabel, 1989).

suspension of soil in 1 mol/L KCl using glass electrode was determined by the ISO 10390: 2010. The free CaCO<sub>3</sub> content was determined by ISO, 10693 (1995)-volumetric method. The organic matter content was measured by oxidation using the sulfochromic oxidation method (ISO, 14235, 1998). Available phosphorus  $(P_2O_5)$  was determined by ammonium lactate extraction (AL method by Egner and Riehm, 1955), followed by spectrophotometry. The samples were analyzed for "pseudo-total" contents of As, Co, Cr, Cu, Mn, Ni, Pb, and Zn after 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 °C using a Milestone Vario EL III for 55 min. The concentration of metals was

## Table 2

Metal concentrations (mg k	g-1	') in url	ban soils (	of Novi Sad	(n =	121
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Metal concentrations (mg kg	tal concentrations (mg kg <sup>-1</sup> ) in urban soils of Novi Sad ( $n = 121$ ).										
	As	Со	Cr	Cu	Mn	Ni	Pb	Zn			
Mean	6.5	7.3	28.0	38.8	368.6	28.7	82.3	100.3			
Median	6.3	7.2	28.4	27.7	363.6	27.7	48.7	100.5			
Mode	6.27	7.18	26.51	/	373.6	27.68	/	108.3			
Min	2.1	3.5	10.6	4.4	199.7	10.2	8.9	46.2			
Max	11.1	11.2	50.8	459.2	622.6	74.2	999.1	193.8			
Range	9.0	7.7	40.2	454.8	422.9	64.0	990.2	147.6			
SD	1.7	1.4	6.7	58.0	70.0	8.7	110.9	29.9			
RSD	0.26	0.19	0.24	1.49	0.19	0.30	1.35	0.30			
Kurtosis	0.17	0.34	0.82	41.79	1.22	8.77	38.66	0.11			
Skewness	0.16	0.03	0.07	6.29	0.40	2.05	5.17	0.57			
p (S–W test) <sup>a</sup>	0.388	0.829	0.497	0.00	0.062	0.00	0.00	0.011			
Backg. v. <sup>b</sup>	2.2		30.0	17.1		14.8	17.2	60.3			
World soils <sup>c</sup>	6.0	8.0	70.0	30.0		50.0	35.0	90.0			
Target values <sup>d</sup>	29	9	100	36		35	85	140			
Intervention values <sup>e</sup>	55	240	380	190		210	530	720			

а p-Values of Shapiro-Wilk test for normality of the raw data. For values higher than 0.05 distribution is normal. h

Backg. v. – Background metal concentrations for unpolluted agricultural soils of the region (Ubavić et al., 1993).

<sup>c</sup> World soils (Adriano, 2001).

<sup>d</sup> Dutch standard target values for soil (VROM, 2000).

e Dutch standard intervention values for soil: Values for soil remediation proposed by Dutch Ministry of Housing, Spatial Planning and Environment (VROM, 2000).

### determined by ICP-OES (Vista Pro-Axial, Varian) in accordance with US EPA method 200.7:2001. The limits of detection for examined metals were: 1.5 mg kg<sup>-1</sup> (As); 2.5 mg kg<sup>-1</sup> (Co); 5 mg kg<sup>-1</sup> (Cr); 5 mg kg<sup>-1</sup> (Cu); 5 mg kg<sup>-1</sup> (Mn); 1 mg kg<sup>-1</sup> (Ni); 5 mg kg<sup>-1</sup> (Pb); and 5 mg kg<sup>-1</sup> (Zn).

#### 2.3. Statistical analysis

Descriptive statistical analysis was carried out using Microsoft Office Excel 2003. The Pearson's correlation coefficients between analyzed metals were calculated using Statistica 10 software package (Statistica 10, 2012). Only the correlation coefficients significant at the 0.01 level are discussed in the paper. Multivariate statistics including cluster analysis (CA) and principal component analysis (PCA) of the raw data was

carried out using Statistica 10 software package. The data were standardized to the Z-score (with a mean of 0 and a standard variation of 1) and then classified using the Ward's method (Ward, 1963). In the



Fig. 3. Frequency histograms of metal concentrations for As, Co, Cr, Mn, Ni, Cu, Pb, and Zn.

PCA, the principal components were determined based on the correlation matrix. Varimax rotation with Kaizer's normalization was used in order to facilitate the interpretation of results (Micó et al., 2006).

#### 2.4. Geostatistical analysis based on GIS

Geostatistics is based on the theory of a regionalized variable which is distributed in space and shows spatial autocorrelation such that samples close together in space are more alike than those that are further apart (Dayani and Mohammad, 2010). Geostatistical methods are commonly used in combination with various GIS applications. Kriging is one of the most frequently used methods of geostatistical interpolation (Charlesworth et al., 2003; Guney et al., 2010; McGrath et al., 2004). Ordinary kriging is a linear spatial interpolator that estimates spatial data at unsampled locations using a linear weight function of adjacent data points (Cressie, 1990).

The GIS mapping technique was employed to produce the spatial distribution maps of total metal concentrations for eight metals observed in the urban soil of Novi Sad. The software used for the mapping and spatial analysis was ArcView 9.3 (ESRI, 2012) and Quantum GIS 1.7.0 (QGIS). The metal concentrations are interpolated with the ordinary kriging method. Grid was performed based on a size of  $25 \times 25 \text{ m}^2$  using available input points.

#### 3. Results and discussion

#### 3.1. Soil characteristics

The chemical parameters: pH (KCl), calcium carbonate (CaCO<sub>3</sub>), organic matter (OM) and available phosphorus (AL  $P_2O_5$ ) are given in Table 1. The pH values determined with KCl range in a narrow interval (7.19–7.89) for all soil samples, which suggests sub-alkaline conditions. CaCO<sub>3</sub> contents of the analyzed soils vary from 3.8 to 19.4% with an average value of 11.6%. More than 2/3 of soil samples are found to contain medium to high levels of CaCO<sub>3</sub>. The organic matter contents range from 1.47 to 3.86% with a mean value of 2.86%, which means that the soils are weakly to moderately fortified with organic matter.

The results of particle size analysis and mechanical structure of the soil samples are presented in Fig. 2. The mean values of the particle size fractions of the soil samples are 76.3% sand, 15.3% silt and 8.4% clay. The soils of the study area show a sandy texture. Most of the soil samples (70%) are classified as sandy loam, 14.9% loamy sand and sand, 12.4% as clay loam and sandy clay loam and 2.5% as loam.

#### 3.2. Metal concentrations

Concentrations of all metals investigated in urban soils of Novi Sad and basic statistical parameters of the raw data set are given in Table 2 together with the background metal concentrations for unpolluted agricultural soils of the region (Ubavić et al., 1993) and world soils. Soil quality standards have been established in many countries

Correlation matrix of the metal concentration in study area.

	Со	Cr	Cu	Mn	Ni	Pb	Zn
As	0.73	0.57	-0.10	0.57	0.73	-0.10	0.14
Со		0.70	-0.16	0.80	0.54	-0.21	-0.11
Cr			0.05	0.63	0.64	0.16	0.32
Cu				-0.10	0.04	0.18	0.40
Mn					0.34	0.01	0.02
Ni						0.03	0.29
Pb							0.50

Bolded values are significant at 0.01 level.

to evaluate the contamination and risk assessment for heavy metals in soils (Biasioli et al., 2007; Guagliardi et al., 2013; Luo et al., 2012). The results were compared with the Serbian (OG RS, 88/2010) i.e. Dutch (VROM, 2000) quality standard values. The Serbian limit and remediation values for the soil that is not used for agricultural production are the same as the Dutch target and intervention values for soil contamination.

The metals, in descending order of mean concentrations, were Mn, Zn, Pb, Cu, Ni, Cr, Co, and As. The largest mean value is obtained for Mn (368.6 mg kg<sup>-1</sup>), and it is comparable to the average upper crustal abundance of 530 mg kg<sup>-1</sup> (Wedepohl, 1995). The mean concentration of Cu (38.8 mg kg<sup>-1</sup>) slightly exceeds the limit value (36 mg kg<sup>-1</sup>), while the mean concentration of Pb (82.3 mg kg<sup>-1</sup>) is very close to the limit value (85 mg kg $^{-1}$ ). The remediation values exceeded for two metals – at three locations for Cu (with the largest concentration of 459.2 mg kg<sup>-1</sup>) and at one location for Pb, where a concentration of 999 mg kg<sup>-1</sup> is obtained. In comparison with the background values in the region represented by the unpolluted agricultural soils (Ubavić et al., 1993), minimal enrichment is found for Co and Cr. Most of the soil samples for Cu, Ni and Zn show minimal enrichment, and 20-35% moderate enrichment (2–5 times higher than the background values). The highest contamination is found for Pb, for which 20% of the samples show significance (5-20 times higher than the background value), and 10% display a very high enrichment (20–40 times higher than the background value).

The widest range of values is observed for Pb and Cu. Pb concentrations range from 8.9 to 999.1 mg kg<sup>-1</sup> and Cu concentrations from 4.4 to 459.2 mg kg<sup>-1</sup>. The medians for these two metals are significantly lower than the mean value, which is consistent with the high skewness, showing that there were some very high values (outliers). This is due to the fact that these elements do not have a normal distribution. Considering the calculated values of RSD, the metals can be classified into two groups. For Pb and Cu the values were above 100%, and below 30% for others. Smaller RSD values indicate the data to be more homogenous. As high RSDs are a reliable indicator of anthropogenic activities, wide variations seen for the Pb and Cu quantities could be directly related to anthropogenic sources (Manta et al., 2002). Existence of outliers for these metals (three for Cu and one for Pb) and wide confidence interval

# Table 3 Average metal concentration (mg $\rm kg^{-1})$ in urban soils from European cities.

Study area	As	Со	Cr	Cu	Mn	Ni	Pb	Zn	Reference
Urban area of Novi Sad	6.5	7.3	28	38.8	368.6	28.7	82.3	100.3	This study
European cities <sup>a</sup>	13	6.4	59	46		22	102	130	Luo et al. (2012)
Beograd (Serbia)		16.5		46.3	417.6		298.6	174.2	Marjanović et al. (2009)
Zagreb (Croatia)		10.9	54.6	56.1		35.2	23.2	77.9	Sollito et al. (2010)
Ljubljana (Slovenia)			34	39		26	87	148	Biasioli et al. (2007)
Sevilla (Spain)			34	55		28	123	105	Biasioli et al. (2007)
Torino (Italy)			171	90		185	169	182	Biasioli et al. (2007)
Murcia (Spain)			19.2	11.8	149.7	11.7	67.9	21.57	Acosta et al. (2010)
Berlin (Germany)	5.1		35	79.5		10.7	119	243	Birke and Rauch (2000)

<sup>a</sup> Median, the data are summarized for 34 European cities (Luo et al., 2012).



Fig. 4. Hierarchical dendrogram for eight metals obtained by Ward's method.

of the mean (Cu: 28.3–49.2 mg kg<sup>-1</sup>; Pb: 62.4–102.3 mg kg<sup>-1</sup>) also confirm the previously mentioned statement.

The histograms for the concentrations of As, Co, Cr, Mn, Ni, Cu, Pb, and Zn are shown in Fig. 3. The statistical distribution of the data was checked with the test of Shapiro–Wilk for normality with a confidence interval of mean 95%. The application of the Shapiro–Wilk test (p > 0.05) confirmed that the original data sets for As, Co, Cr, and Mn are normally distributed.

A review of representative published results for some European cities and urban areas in the region is presented in Table 3. Comparison of the mean values obtained in this study reveals that the concentrations of Cu, Pb, and Zn in soils are slightly lower, while the concentrations of Co and Ni are slightly higher than the average values for 34 European cities given in Luo et al. (2012). Taking the Western Balkan cities into consideration, it can be seen that our results are very similar to the values of metal concentrations for Ljubljana reported in Biasioli et al. (2007). In Belgrade, one of the largest capitals in the region, a considerably higher concentration of Pb (Marjanović et al., 2009) was found, due to the enhanced traffic density. Among other elements, Pb is mostly derived from traffic pollution. For a number of years unleaded petrol has been in use in many countries but in Serbia, leaded petrol was still in use at the time of sample taking. Comparing the values of metal concentrations with the background values for agricultural soils and world soils (Table 2) indicates that the urban soils of Novi Sad are significantly polluted with the so-called "urban" metals (Cu, Pb, Zn).

#### 3.3. Metal clustering and correlations

Correlation analysis is performed to estimate the extent of relationship between any pair of variables in a group of selected metals.



Fig. 5. Factor loadings for two principal components (PCs) after varimax rotation.

Inter-element relationships provide information on metals and their pathways – high correlation among the metal's concentration could indicate a common source (Romic and Romic, 2003). Table 4 presents the correlation coefficients between investigated metals. Strong positive correlation exists between As, Co, Cr, Mn, and Ni, for example: As–Co (r = 0.73), As–Ni (r = 0.73), Co–Mn (r = 0.80), Cr–Mn (r = 0.63) and Cr–Ni (r = 0.64). These results, together with relatively low concentrations and standard deviations, suggest a major natural origin from parent material (sandy alluvial deposit). On the other hand, there are statistically significant correlations between Cu, Pb, and Zn: Pb–Zn (r = 0.50) and Cu–Zn (r = 0.40), showing a possibility of a common source. Taking into account the high concentrations obtained for these metals it can be concluded that they are derived from anthropogenic sources. Similar observations are reported in Manta et al. (2002) and Massas et al. (2010).

Aiming to identify two distinct groups of metals as tracers of natural or anthropogenic sources an explorative hierarchical cluster analysis is performed on the data set of metal concentrations. The results are illustrated by a hierarchical dendrogram in Fig. 4. The lower the value on the distance cluster, the more significant association is (Lee et al., 2006). According to the degree of association between metals, two distinct clusters could be identified: the first cluster includes As, Co, Cr, Mn, and Ni and the second Cu, Pb, and Zn. Such result is consistent with the elemental relationship in correlation matrix (Table 4), supporting a natural origin of As, Co, Cr, Mn, and Ni, while Cu, Pb, and Zn predominantly derive from anthropogenic inputs. Pb, Cu, and Zn could be emitted from fuel combustion (Chen et al., 2010). Lead content is controlled by a long-

Table 5				
Total variance	explained	for heavy	metal	contents.

Component	Initial eigenvalues			Extractio	Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	
As	3.5	43.80	43.80	3.5	43.80	43.80	3.5	43.79	43.79	
Со	1.9	23.86	67.65	1.9	23.86	67.65	1.9	23.86	67.65	
Cr	0.9	10.77	78.43							
Cu	0.7	9.25	87.68							
Mn	0.4	4.62	92.30							
Ni	0.3	4.22	96.52							
Pb	0.2	2.03	98.55							
Zn	0.1	1.45	100.00							

Extraction method: principal component analysis.

term anthropic activity related to the use of Pb in gasoline (leaded gasoline was still in use in Serbia in 2010). Zn and Cu are emitted through tire/brake abrasion, some mechanical vehicle parts contain Cu, and Zn is often added to motor oil (Davis et al., 2001).

#### 3.4. Principal components analysis

The main objective of PCA is to reduce high dimensionality of the sample/variable space by projecting the data into a much smaller subset of new uncorrelated variables called principal components (PCs) (Einax et al., 1997). Original variables are transformed to principal

components using the eigenanalysis. The eigenvalues are the corresponding variances of the principal components in decreasing order of importance. The strategy of the analysis is to keep enough principal components to have a cumulative variance explained by them >50– 70%. Kaiser criterion retains only PCs with eigenvalues that exceed one. The obtained components are rotated using a varimax normalization algorithm.

The results of the PCA of the data obtained in this study (set of eight variables and 121 samples) are presented in Table 5. The plot of PC loadings is shown in Fig. 5. Two principal components with eigenvalues greater than 1.0 are extracted from the available dataset, with



Fig. 6. Spatial distribution of As, Co, Cr, Mn, Ni, Cu, Pb, and Zn in urban soils of Novi Sad.



Fig. 6 (continued).

cumulative variance of 67.6%. As seen in Table 5, after varimax rotation the corrections for percentages of variance are minimal. The first component explaining 43.8% of the cumulative variance has high PC loadings for As, Co, Cr, Mn, and Ni and suggests that the distribution of these elements is mainly influenced by natural sources. The second component explaining 23.9% of cumulative variance, exhibits elevated loadings for Cu, Pb, and Zn, indicating anthropogenic intrusion in the soil samples. The PCA is in total agreement with the cluster analysis, where two strong clusters with equal grouping of the metals are obtained.

#### 3.5. Mapping and spatial analysis

The metal concentrations are used as the input data for the gridbased contouring maps, to study the distribution of metals in the investigated urban soil of Novi Sad. Kriging was adopted for the interpolation of geographical data. The variogram is used to express the variance of property changes over the surface, based on the distance and direction separating two sampling locations.

The resulting contour maps of levels of metals investigated in urban soils and kriging standard deviation maps are illustrated in Figs. 6 and 7, respectively. As seen from the maps, the spatial distribution of As, Co, Cr, Mn, and Ni is distinctly different from the one of the trace elements such as Cu, Pb, and Zn. The former distribution and the fact that the contribution of As, Co, Cr, Mn, and Ni is very low, suggest that their distribution pattern could be influenced by natural sources, such as alluvial deposits in recent pedogenesis. Adriano (2001) suggested that the parent material present in alluvial areas, principally of calcareous nature, determines Mn, Cr, and Ni contents. Some studies have also reported high Cr and Ni levels in the alluvial soils of the region (Abollino et al., 2002; Biasioli et al., 2006; Facchinelli et al., 2001). Moreover, variations in Cu, Pb, and Zn levels demonstrated patterns very similar to those of the most heavily contaminated areas appearing in the vicinity of major roads. Samples taken near high volume roads show greater concentration levels for these metals. Pb mostly ranged from 200 to 320 mg kg<sup>-1</sup>, Zn from 100 to 190 mg kg<sup>-1</sup>, and Cu from 30 to 90 mg kg $^{-1}$ . Interestingly, there was one hot-spot of very high Pb concentration (999 mg kg<sup>-1</sup>) in the south-eastern part of the city at the site close to the low volume traffic road. It was identified that the source of pollution was a small lead accumulator plant located about 50 m from that sampling location. There were two hot-spots of high Cu concentrations, greater than 400 mg kg<sup>-1</sup>. One of the locations is in the vicinity of the high volume traffic road and the other close to the low volume traffic road, probably implying the existence of different sources of Cu origin. In agreement with Pearson's correlations, cluster analysis and PCA, the spatial analysis suggests that the increase of Cu, Pb and Zn came from a common anthropogenic source related to traffic activities.

#### 4. Conclusion

The concentration of eight metals (As, Co, Cr, Cu, Mn, Ni, Pb, and Zn) in urban soils of Novi Sad was determined using ICP-OES technique. The highest contamination is found for Pb for which 30% of samples show significant or very high enrichment. Most of the soil samples for Cu, Ni, and Zn show minimal and 20–35% moderate enrichment. The comparison of the obtained data with those previously published for

the region and some European cities, showed similar level of metal concentrations.

The results of descriptive statistics, correlation analysis, clusters, and PCA in this study agree with each other. All the results distinguish two groups of metals. The first group includes As, Co, Cr, Mn and Ni, the metals mainly influenced by natural inputs. The second group contains Cu, Pb and Zn which are related to anthropogenic activities. Spatial interpolation and GIS mapping techniques are employed to identify the spatial patterns for eight metals in the study area. Spatial distribution patterns of Cu, Pb and Zn show differences from the other investigated elements. Distribution patterns of the metals suggest that vehicle traffic represents the most important pollutant source for the studied urban environment.

Environmental quality of urban soils is of vital importance as majority of people now live in urban areas. As typical contaminants in urban environment heavy metals are useful indicators of environmental pollution. Determination of heavy metal levels and their spatial variations is essential for a better understanding of pollution sources and possible risks for the environment and human health.

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Fig. 7. Maps of kriging standard deviations of As, Co, Cr, Mn, Ni, Cu, Pb, and Zn.



Fig. 7 (continued).

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