

# Trace elements as tracers of environmental pollution in the canal sediments (alluvial formation of the Danube River, Serbia)

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**Abstract** The purpose of this study was to examine the levels of trace elements and to discuss the origin and mobility of these contaminants in the canal sediments (alluvial formation of the Danube River). The most significant fractions binding all of the studied elements were oxides and silicates. The high proportion of elements in the residual fraction and the generally low contents of extractable elements reflected the background geochemical conditions. The contents of trace elements (except Hg and As) were dominantly controlled by the presence of Fe and Mn oxides as well as by the grain size and the geochemical composition of the sediment. The studied alluvial sediments were not heavily contaminated; there were only few sites where an anthropogenic influence on the concentrations of some metals (Cu, Cd, Zn, and Pb) was noticed. The results from this study show that impact of Pančevo industrial zone on the quality of the Danube River and its contamination with trace element is minor.

**Keywords** Sediment · Sequential fractionation · Geochemical normalization · Trace elements · Principal component analysis · Cluster analysis

## Introduction

Contamination by potentially toxic elements in the natural environment is one of the major problems for human health and environment quality (Chen et al. 2000) because these elements are indestructible and most of them have toxic effects on living organisms when they exceed a certain concentration (Ghrefat and Yusuf 2006). Trace element may be introduced into the aquatic systems by both natural processes (e.g., weathering and erosion) and as a result of human activities, for which reason they can be useful tracers of environmental pollution (Manta et al. 2002). In recent years, investigations of these potentially toxic inorganic pollutants have increased (van Ryssen et al. 1999; Li and Thornton 2001; Relić et al. 2005; Silveira et al. 2006; Farkas et al. 2007; Daesslé et al. 2009; Ahmad et al. 2009; Morillo et al. 2008; Egiarte et al. 2009; Mil-Homens et al. 2009; Nguyen et al. 2009; Widmeyer and Bendell-Young 2008).

The mobility, transport, and partitioning of trace metallic and metalloid elements in natural aquatic and terrestrial systems is a function of the chemical form of the element which, in turn, is

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controlled by the physicochemical and biological characteristics of that system (Kersten 2002). If trace metals reach sediment, they could be bound on to hydrated oxides of iron and manganese, organic compound, clay minerals, etc. and may be associated with them in different ways. Many researchers have attempted to assess geochemical and chemical behavior of metals and to investigate their chemical fractionation in contaminated soils and sediments using metal sequential extraction methods (van Ryssen et al. 1999; Li and Thornton 2001; Silveira et al. 2006; Farkas et al. 2007; Egiarte et al. 2009). Despite the potential limitations of sequential extraction procedures, particularly relating to the potential for reagents to be nonselective and for metal ions to be re-adsorb to different sediment phases, this method remains a powerful technique in the assessment of the significance of heavy metal pollution of the environment (Farkas et al. 2007). Bacon and Davidson (2008) concluded that this method will have a healthy future in the twenty-first century.

The aim of this study was to characterize and to classify the canal sediments (alluvial formation of the Danube River) according to their degree of contamination with trace metals. To achieve these goals, there were employed: (1) determination of distribution, fractionation, contents, and possible dangerous levels of potentially toxic elements; (2) influence of the geochemical composition of the sediment on metal concentrations; (3) the method of geochemical normalization, and (4) the method of multivariate analysis. The trace elements included in this investigation were: chromium, nickel, copper, zinc, cadmium, lead, mercury, and arsenic. The major elements, such as iron, manganese, potassium, and magnesium, were also analyzed as their occurrence can control the chemical behavior of many trace metals. The chemical analyses also include Al, which is considered indicative of the grain size of sediment. This alluvial sediment was chosen for the present investigations because there is little information on the pollution with potentially toxic elements and their mobility at the investigated locality. A systematic approach to the problem of sediment quality in Serbia is just beginning (Prica et al. 2008). This study could contribute new knowledge to scientist working on the Danube investigation,

since that result will be able to show the impact of the Pančevo industrial zone on the contamination with trace element of water and sediment of the Danube River.

## Materials and methods

### Sampling location

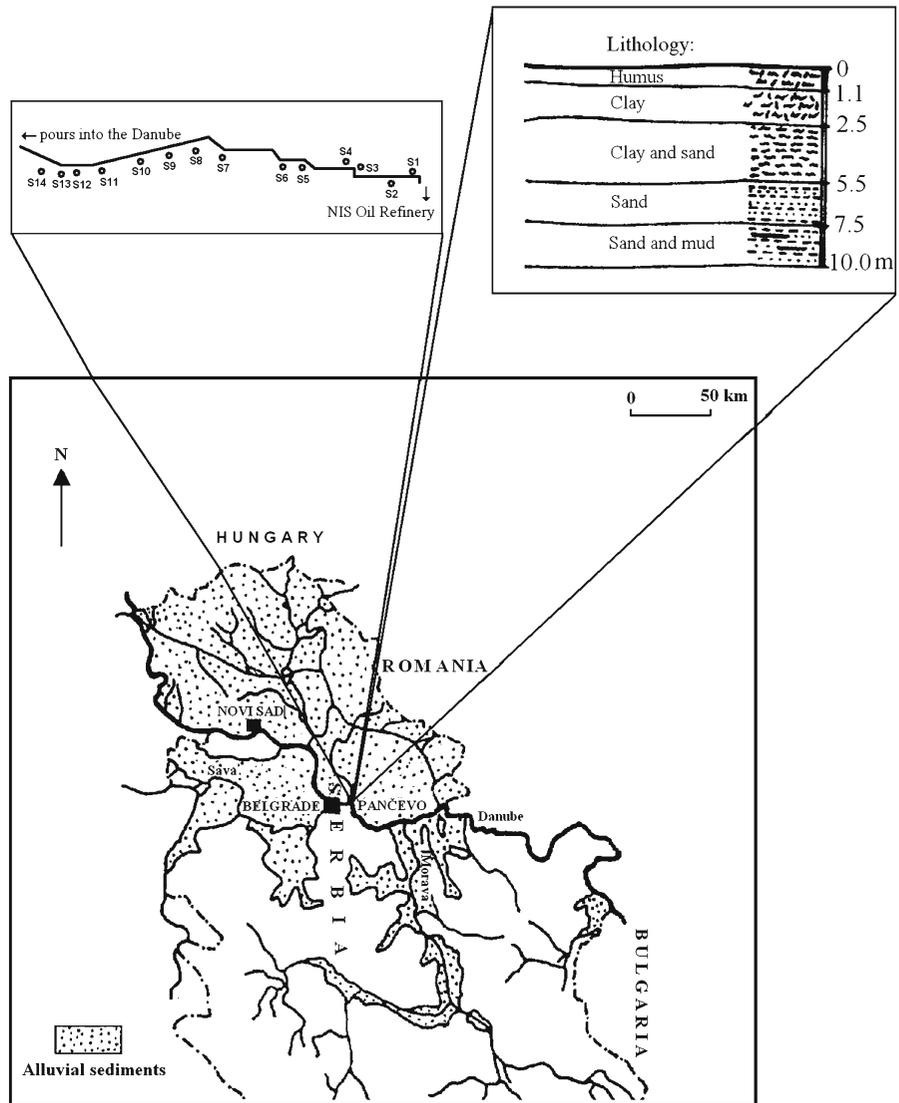
The study area represented alluvial sediments from the canal for waste water, which is located in the industrial zone southeast of the city Pančevo, about 15 km east of Belgrade (Fig. 1). Pančevo is located in the Vojvodina region of Serbia, at 44.87° north, and 20.66° east. The samples of alluvial sediments were taken in August and September of 2001 along the canal, which begins at the Oil Refinery Pančevo, passes different industrial formations, and flows into the Danube. The samples were taken from 14 drill holes (marked as S1–S14) at different depths, up to 5 m. The drill hole denoted S1 is nearest to the refinery, and S14 is nearest to the entrance of the canal into the Danube (Fig. 1). The denotations of the other holes are in accordance with principle that the number increases with increasing distance of the drill hole from the refinery (from S1 to S14). The drill holes are getting under top level of underground water because the level of underground water is reaching values up to 3 m under ground surface. Samples from the drill hole for chemical analyses were collected from the whole depth interval. At each sampling site was collected approximately 1 kg of sediment. The sediment samples were frozen after sampling and preserved in a freezer until the analyses.

### Sediment analysis

The proportions of the sand, silt, and clay fractions were determined by the S. Rutkovski method (Korunović and Stojanović 1975). The sediment types were differentiated by texture according to the US Department of Agriculture (USDA) textural triangle (Darmody and Marlin 2002).

The determination of total carbon (TC) content in the investigated sediments was performed by elemental analysis, using the Vario EL III

**Fig. 1** Map of the studied area (modified from Jovančičević and Polić 2000), location of the sampling sites (marked as S1 to S14) and sediment profile



C,H,N,S/O elemental analyzer (Elementar) and represents the sum of inorganic and organic carbon.

The sediment samples were analyzed by a modified version of the Tessier (Tessier et al. 1979) sequential extraction procedure (SE). The procedure applied in the present investigation is described elsewhere (Polić and Pfendt 1992; Relić et al. 2005; Sakan et al. 2007).

The extractants and operationally defined chemical fractions applied in this research were as follows: The first step (exchangeable fraction, F1) was: 10 g sediment sample was extracted with 1 M  $\text{CH}_3\text{COO}(\text{NH}_4)$ , extraction for 2 h at room

temperature ( $22^\circ\text{C}$ ). The second step (represents metals bound to carbonates and easily reducible phases, F2) was: extractant 0.6 M HCl and 0.1 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , extraction for 12 h at room temperature ( $22^\circ\text{C}$ ). The third step (metals bound to moderately reducible phases, F3) was: mixture of 0.2 M  $\text{H}_2\text{C}_2\text{O}_4/(\text{NH}_4)_2\text{C}_2\text{O}_4$  is used, extraction for 10 h at room temperature ( $22^\circ\text{C}$ ). The fourth step (metals bound to organic matter and sulfides, F4) was: extractant 30%  $\text{H}_2\text{O}_2$  adjusted to pH 2.0 with  $\text{HNO}_3$ , extraction for 2 h at  $85^\circ\text{C}$ . The fifth step (residual fraction, F5) was: extractant 6 M HCl, extraction for 9 h at  $85^\circ\text{C}$ . All the chemicals used in this work were of analytical reagent grade. All

**Table 1** The average values of the relative standard deviation (%)

	Cu	Cr	Zn	Pb	Fe	Mn	Ni	Cd	Mg	K	Hg	As
F <sub>1</sub>	7.4	7.6	7.2	9.2	5.1	4.7	6.5	9.3	4.8	4.1	/ <sup>a</sup>	/
F <sub>2</sub>	4.1	5.1	8.1	2.3	4.0	2.2	7.1	7.2	2.7	6.9	9.1	7.2
F <sub>3</sub>	8.2	8.4	9.0	5.7	8.7	8.1	7.8	2.5	4.2	4.9	/	8.7
F <sub>4</sub>	4.3	7.9	8.5	4.2	4.8	4.8	6.2	6.3	7.1	5.3	/	/
F <sub>5</sub>	5.2	6.5	1.9	7.0	3.5	3.8	5.5	3.4	3.5	1.9	7.2	8.9

<sup>a</sup>Elements detected near the limit of detection or equal to the limits of detection

glassware and plastic material used were previously treated for 1 week in 2 M nitric acid and rinsed with distilled water and then with ultrapure water.

For each sequential extraction series, 10.00 g of defrosted sediment was taken without drying in order to avoid chemical transformation due to chelating, oxidation processes, etc. Control samples were processed for each extraction step. The solid/liquid ratios kept as close to 1:45 as possible during extraction of the first, second, and third fractions.

The total amounts of elements in this paper are defined as the sum of the five binding fractions (Facchinelli et al. 2001; Sakan et al. 2007). This method results in concentrations normally referred to as “pseudo-total” and “total extractable amount,” as the silicates are not completely destroyed (Facchinelli et al. 2001).

Flame atomic absorption spectrometry was used to determine the levels of the metals (SpectraAA55 Varian spectrophotometer, equipped with a hydride vapor system). The wavelengths used in this analysis were: 279.5 nm for Mn, 372.0 nm for Fe, 232.0 nm for Ni, 213.9 nm for Zn, 324.7 nm for Cu, 217.0 nm for Pb, 357.9 nm for Cr, 309.3 nm for Al, 228.8 nm for Cd, and 285.2 nm for Mg. The flame emission determination of the concentration of K was applied in this investigation (766.5 nm) and the hydride system for the determination of the content of As (193.7 nm) and Hg (253.7 nm). External standard solutions were prepared from 1,000 mg L<sup>-1</sup> stock metal solutions. For minimized interferences, multi-element standard stock solution was prepared in which the ratios of the metals in the multiple element calibration standards were analogous of their ratios in the samples. These multi-element standards and blanks were prepared in

the same matrix as employed for the extraction to minimize matrix effects and for background correction (Relić et al. 2005). In order to simulate the composition of the investigated samples, the multi-element standards also contained elements which were not determined. Possible interference effects were minimized in this manner. The calibration was checked every ten to 12 samples. As a quality control, duplicate analyses were performed on all samples, and precision was controlled. The relative standard deviations of the means of duplicate measurement were less than 10% (Table 1). The values of limit of detection (DL) for each determined element, expressed in micrograms per milliliter, were: Cr (0.03), Zn (0.005), Pb (0.05), Cd (0.01), Fe (0.5), Al (0.15), Mn (0.01), Ni (0.05), As (0.002), Hg (0.001), Cu (0.02), K (0.01), and Mg (0.05). All concentration values below the detection limit were replaced by half of the DL, as suggested by Reimann and Filmozer (1999) and Relić et al. (2005). The moisture content of each sample was determined by drying a separate 1-g sample in an oven (105 ± 2°C) to constant weight. From this, a correction to dry mass was obtained, which was applied to all reported metal concentrations.

#### Geochemical normalization

Sediments are regarded as a mixture of inorganic and organic material. For some metals, the organic material may be a metal carrier, but due to its low abundance (< 5% by weight) in most sediment (Loring 1991), the concentration of a trace element is largely determined by the composition of the inorganic material. Since the finer fractions of sediments tend to adsorb more metals than the coarser material, the metal concentrations need to be normalized to compensate for this natural

variability (Liaghati et al. 2003). Geochemical normalization is superior to granulometric methods, as it compensates for both mineralogical and the natural granular variability of metal concentrations in sediments (Loring 1991). The metals used for normalization are structurally combined in one or more of the major fine-grained trace-metal carrier(s) and reflect their granular variations in the sediments (Loring 1991).

The method of geochemical normalization consists of establishing the mathematical relationship between metal concentrations and the concentrations of conservative elements (Loring 1991). Al has been the most widely employed element for normalization. The main assumption for the application of a geochemical normalization is the existence of a linear relationship between the normalizer and the other metals and also between the normalizer concentration and the percentage of fine-grained material in the samples (Aloupi and Angelidis 2001). If these prerequisites are valid, then it is possible to produce a scatter plot of the metal and normalizer concentrations (Aloupi and Angelidis 2001). All points which are found inside the 95% confidence band can be characterized as natural sediments. If a point falls above the upper prediction limit, the sediment is considered to be metal enriched (Loring 1991). The greater distance above the prediction limit indicates a greater degree of enrichment. Points lying far below the lower prediction limit should be considered suspect and examined for analytical errors (Loring 1991).

### Statistical methods

Descriptive data analyses (mean, standard deviation, maximum and minimum concentrations) were performed in this research. To assess the relationships between the metals, principal component analysis (PCA) was employed. Multivariate analysis is often employed in environmental dataset in order to understand the distribution modes of contaminants, find out similarities/dissimilarities between parameters and samples, and elucidate possible sources of contaminants. PCA is now a well-established tool for the interpretation of a multivariate dataset among several other multivariate techniques. PCA is designed

to transform the original variables into new, uncorrelated variables (axes) called principal components, which are linear combinations of the original variables. Cluster analysis (CA) was performed to determine the relations among the sampling stations. Cluster analysis classifies objects, so that each object is similar to the others in the cluster with respect to a predetermined selection criterion. Hierarchical agglomerative clustering is the most common approach and is typically illustrated by a dendrogram (tree diagram). Hierarchical CA (Q-mode) was applied to identify similarities in the sampling stations. Detailed descriptions of the PCA method and CA are given in Davis (2002). In recent years, multivariate statistical methods have been applied widely to investigate environmental phenomena (Facchinelli et al. 2001; Relić et al. 2005; Vacaro et al. 2007; Yay et al. 2008; Yidana et al. 2008).

All statistical methods were applied using SPSS v. 11.5. SPSS is the most widely used computer program for statistical analysis. In this paper is used version 11.5 of this program. The Kolmogorov–Smirnov test was employed to evaluate the normality of the data. The data for the investigated elements showed a normal distribution.

## Results and discussion

### Results of sediment analysis

The results of the determination of the granulometric composition and the sediment type, as well as the TC content, are given in Table 2. The mean value of the silt fraction content was  $20.41 \pm 16.08\%$ , the clay fraction was  $15.09 \pm 13.63\%$ , and the sand fraction  $64.50 \pm 28.22\%$ . A high content of the sand fraction was found in most samples, in some cases 99.9%. The investigated area is part of Pannonian Plain, which is rich in sand. Large differences in the granulometric composition of different sediments were found because the sediment samples were taken from different depths.

The sediment types were determined according to the USDA textural triangle, and the results are also presented in Table 2. The following sediment

**Table 2** Characterization of sediments with respect to grain size, total carbon, and carbonate content

NS	DH	Depth (m)	0.6 M HCl ( $\text{cm}^{-3}$ )	TC (%)	Fraction of sediment (%)			The sediment type
					Silt (0.002–0.02 mm)	Clay (<0.002 mm)	Sand (>0.02 mm)	
1	S1	1.00	5.50	2.09	21.3	36.3	42.4	Clay loam
2	S1	2.40	5.50	1.10	37.0	33.9	29.1	Clay loam
3	S1	3.20	6.50	2.04	43.2	35.2	21.6	Clay loam
4	S2	1.10	6.00	2.58	41.5	23.0	35.5	Loam
5	S2	2.50	5.00	2.28	11.6	8.70	79.7	Loamy sand
6	S2	5.00	5.00	2.76	10.6	6.50	82.9	Loamy sand
7	S3	1.20	2.50	1.57	1.10	0.00	98.9	Sand
8	S3	2.20	5.50	2.74	23.4	20.6	56.0	Sandy clay loam
9	S3	2.90	5.50	2.69	11.0	8.10	80.9	Loamy sand
10	S4	1.00	3.00	1.07	1.00	0.00	99.0	Sand
11	S4	1.50	6.00	2.47	25.5	19.8	54.7	Sandy loam
12	S4	2.40	5.50	2.36	4.60	3.90	91.5	Sand
13	S5	0.90	2.00	1.02	0.40	0.00	99.6	Sand
14	S6	0.90	2.00	1.76	0.70	0.30	99.0	Sand
15	S7	1.00	9.00	2.08	27.8	31.5	40.7	Clay loam
16	S7	1.50	2.00	1.48	2.90	1.10	96.0	Sand
17	S8	1.00	2.50	2.00	0.40	0.20	99.4	Sand
18	S9	0.90	2.00	0.99	0.10	0.00	99.9	Sand
19	S10	0.50	5.00	2.84	6.10	0.90	93.0	Sand
20	S10	0.80	62.5	8.96	44.9	4.00	51.1	Sandy loam
21	S10	1.30	2.00	2.35	2.60	0.70	96.7	Sand
22	S11	0.00	2.50	2.61	34.5	22.5	43.0	Loam
23	S11	1.50	11.5	2.77	43.1	26.2	30.7	Loam
24	S12	0.30	2.00	2.10	36.3	28.4	35.3	Clay loam
25	S12	1.50	12.0	3.21	21.8	10.7	67.5	Sandy loam
26	S12	2.30	7.5	1.73	36.9	39.0	24.1	Clay loam
27	S13	0.50	3.0	1.42	25.3	26.0	48.7	Sandy clay loam
28	S13	1.40	4.0	2.95	10.8	6.80	82.4	Loamy sand
29	S13	2.70	7.5	1.76	37.2	36.2	26.6	Clay loam
30	S14	0.70	14.0	2.78	27.5	16.9	55.6	Sandy loam
31	S14	2.20	13.0	2.94	41.5	20.5	38.0	Loam

NS number of sample, DH drill hole (nomenclature of drill hole)

types were found: clay loam, loam, loamy sand, sand, sandy clay loam, and sandy loam. Most of the sediment types present had a higher content of the coarser fraction. The existence of six different sediment types is the consequence of the different textural compositions of the sediments.

The carbon determined in this study represents the TC, i.e., the sum of the inorganic and organic carbon. The TC content (Table 2) was in the range from 0.99% to 8.96% (mean value is  $2.37 \pm 1.38\%$ ).

Also given in Table 2 is the volume of 0.6 M HCl employed in the II fraction (F2) of the SE.

This acid is used for dissolution of carbonates at the beginning of the fraction, step II, before extraction with 0.1 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ . The amount of acid added depends on the carbonate content, namely the content of acid was adequate to the carbonates content (inorganic C). For an assessment of the dominate nature of the TC, correlation analysis between quantity of added acid and the TC was applied (Table 3). The high significant correlation between the investigated parameters established that TC dominantly represented carbonates in the investigated sediments. The maximum values for TC was found in the sediment

**Table 3** Results of Pearson correlation analysis

	HCl	C	Silt	Clay	Sand	As	Hg
HCl		0.922**	0.444*	-0.011	-0.248	0.822**	0.617**
C			0.374*	-0.110	-0.160	0.770**	0.683**
Silt				0.804**	-0.958**	0.353	0.105
Clay					-0.941**	0.008	-0.201
Sand						-0.205	0.037
As							0.639**
Hg							

\*  $p = 0.05$ , correlation is significant; \*\*  $p = 0.01$ , correlation is significant

sample S10/0.80 (number of sample 20, Table 2) was followed by the higher content of added 0.6 M HCl, which indicates an increased carbonate content in this sample.

### Metal fractionation

Using the method of SE, a metal fractionation was performed, i.e., an assessment of the distribution of the content metals in the different fraction was carried out. The results are given in Table 4 as the mean, maximum and minimum values, as well as the standard deviation for each metal and fraction. The percentage element distribution by fractions was calculated as the average content of the extracted element in each fraction with respect to the total content of the extracted element (Fig. 2a).

Cadmium and copper have a similar distribution in the fractions, with dominant contents of the elements extracted in F3 and F5 (Fe-oxides and residual) fractions. The fractions F5, F3, and F4 (residual, Fe-oxides, and organic and sulphides) are the most significant for binding Cr and Ni. The fractions F5, F3, and F2 (residual, Fe-oxides, and carbonate and Mn-oxide) are significant for binding Zn, Pb, and Fe. The most significant for binding As, Mn, and Mg are the fractions F2, F5, and F3 (carbonate and Mn-oxide, residual, and Fe-oxides) fractions. Finally, Hg and K are dominantly bound in the F5 (residual) fraction. Thus, the most significant phases for binding the elements are oxides, i.e., partially crystalline and crystalline oxides, and silicates. The low percent of elements that are extracted in the labile fractions (F1 and F2) indicates that percent of the metal of anthropogenic origin is low. The great percent of Mn extracted in the F2 fraction should not be attributed to a possible anthropogenic source

because Mn tends to be present in less thermodynamically stable phases in the sediments. Also, it can be observed that organic-sulphide fraction is of importance for the binding of Ni, Pb and Cd, and partially of Mn and Cu. The content of the other elements extracted in this fraction is insignificant. The high proportion of metals in the residual fraction indicates that the investigated elements are generally strongly linked to the sediments. This is not case of Cd, Pb, Mn, As, and Mg that showed relatively low residual fraction. The fractional distribution indicates the importance of the oxide fractions for the binding of the elements and the dominantly geochemical origin of most of the elements in the investigated sediments.

### Total extractable amounts of the elements and geochemical normalization

Firstly, the suitability of Al as a potential element for the normalization of the metal contents was tested. A correlation analysis of the Al content (Table 5) and the percent of the clay and silt fractions (Table 2), representing the main metal accumulators in sediments, was performed. The highly significant positive correlation between the Al content and the fraction of clay, as well as between the Al content and the fraction of silt (Fig. 3), indicates that Al can be employed as the element for normalization.

Scatter plots of the metals Cu, Cr, Zn, Pb, Cd, and Ni, to Al (Table 5) for the whole study area are also shown in Fig. 3. Each diagram shows the regression line of metal against Al with the 95% confidence band for the investigated alluvial sediments.

From the scatter diagrams for Cr and Ni, it can be observed that a large number of stations are located within the 95% confidence band, which

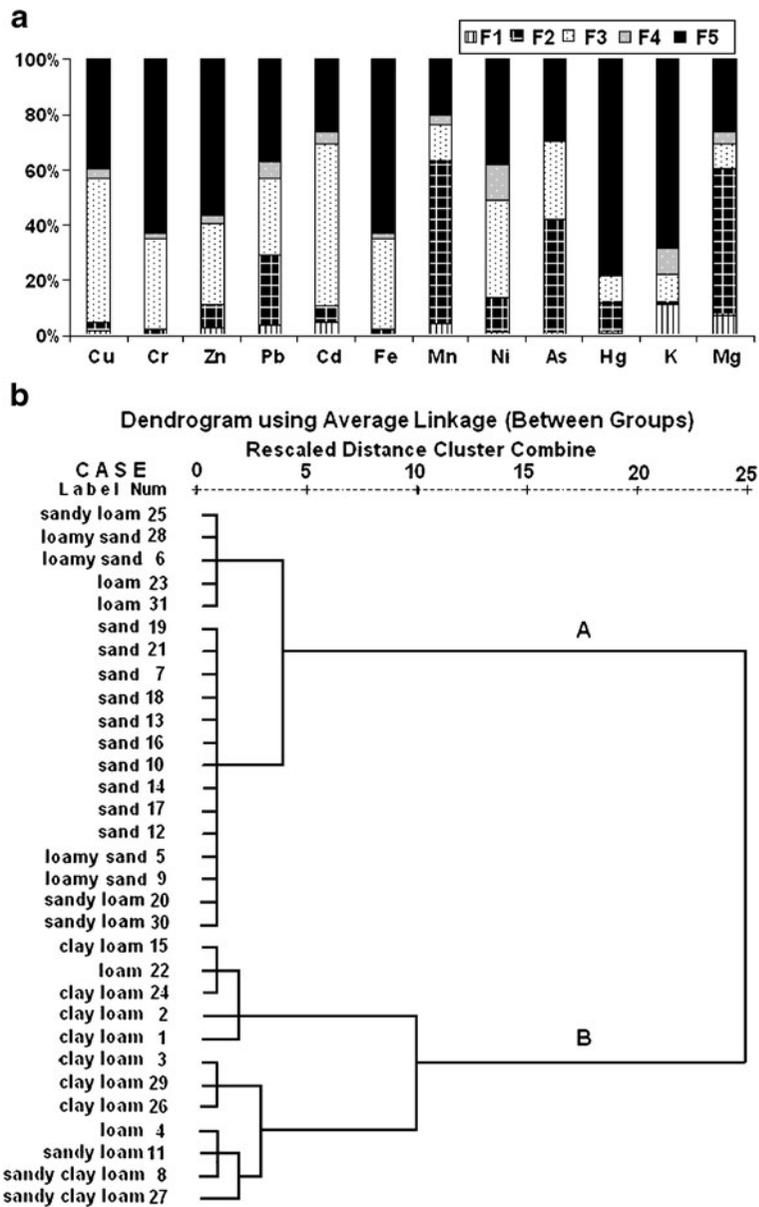
**Table 4** Summary statistics of metal concentrations in various fractions after sequential extraction ( $\text{mg kg}^{-1}$ ,  $n = 31$ )

		Binding fractions					
		F1	F2	F3	F4	F5	F1+F2+F3+F4+F5
Zn	Mean	1.52	4.86	16.2	1.76	31.4	55.8
	Max	28.4	63.8	58.2	11.1	68.5	163.6
	Min	0.03	0.03	3.97	0.03	4.53	23.5
	StDev.	5.05	11.5	11.4	2.75	20.1	30.2
Cu	Mean	0.29	0.50	8.80	0.48	6.68	16.8
	Max	1.13	5.87	21.4	2.54	65.0	87.1
	Min	0.11	0.04	1.02	0.04	0.25	1.72
	StDev.	0.19	1.09	6.83	0.58	11.5	16.5
Pb	Mean	0.43	2.90	3.25	0.80	4.27	11.6
	Max	1.36	37.1	10.6	3.10	13.7	54.4
	Min	0.25	0.13	0.84	0.26	0.57	2.99
	StDev.	0.23	8.23	2.12	0.87	4.00	11.0
Ni	Mean	0.31	2.61	7.32	2.63	8.04	20.9
	Max	0.76	7.38	20.3	9.59	20.8	39.5
	Min	0.13	0.32	2.27	0.44	0.80	6.67
	StDev.	0.14	2.08	3.78	2.32	4.81	8.33
Cr	Mean	0.26	0.31	2.88	0.74	8.32	12.5
	Max	0.69	0.93	8.36	1.49	17.5	26.1
	Min	0.03	0.01	0.72	0.14	0.72	5.52
	StDev.	0.14	0.18	1.54	0.30	5.06	5.85
Cd	Mean	0.05	0.06	0.61	0.07	0.28	1.07
	Max	0.12	0.12	1.07	0.12	0.54	1.88
	Min	0.01	0.01	0.13	0.03	0.06	0.60
	StDev.	0.03	0.03	0.16	0.01	0.11	0.26
Fe	Mean	2.73	429	5,584	374	10,765	17,155
	Max	11.4	2,878	13,027	5,273	24,447	39,181
	Min	0.30	10.4	1,575	0.28	1,330	3,194
	StDev.	3.20	726	2,687	1,171	6,316	9,152
Mn	Mean	16.7	233	51.8	14.0	79.3	395
	Max	86.4	601	172	105	216	908
	Min	0.21	9.22	17.0	1.60	14.2	68.6
	StDev.	17.2	148	33.1	20.7	43.1	208
Hg	Mean	0.001	0.004	0.006	<DL	0.06	0.07
	Max	<DL <sup>a</sup>	0.01	0.01	<DL	0.29	0.30
	Min	<DL	<DL	0.01	<DL	<DL	0.01
	StDev.	<DL	0.003	0.001	<DL	0.06	0.06
As	Mean	<DL	0.10	0.069	<DL	0.07	0.24
	Max	<DL	1.34	0.45	<DL	0.40	1.80
	Min	<DL	<DL	0.01	<DL	<DL	0.01
	StDev.	<DL	0.25	0.107	<DL	0.103	0.32
K	Mean	131	11.0	114	113	799	1,168.1
	Max	925	53.1	465	837	2,285	4,171.1
	Min	0.61	0.57	0.51	0.51	62.3	71.0
	StDev.	206	13.7	150	209	669	1,152
Mg	Mean	902	6,222	1,111	484	4,290	13,009
	Max	2,957	20,048	3,602	962	8,252	30,340
	Min	60.6	93.0	92.7	182	537	3,100
	StDev.	784	5,142	957	208	2,370	7,429

F1 exchangeable, F2 easily reducible, F3 stronger reducible, F4 metals bound to organic matter and sulfides, F5 residual, F1 + F2 + F3 + F4 + F5 total amount

<sup>a</sup>Below detection limit

**Fig. 2** **a** Percentage distribution of metals in five fractions of the sequential extraction. **b** Dendrogram of hierarchical cluster analysis of trace element concentrations in the sediments



represents the natural variability of the metal concentrations in the sediments. For these elements, only a small enrichment was recorded in some sediment samples. In the investigated sediments, similar trend in the distribution of Cr and Ni concentrations was found (Table 5). It can be assumed that the enrichment at these localities is due to possible unusual concentrations of natural Cr- and Ni-bearing minerals. The existence of amphiboles and chlorite in Vojvodina soil was

indicated (Kostić 2001), which may confirm this assumption concerning the origin of these metals.

Diagrams showing the normalization of the Cu, Cd, Zn, and Pb concentrations in relation to Al are also presented in Fig. 3. Some anthropogenic influence on the concentrations of these metals can be seen, since several points in the scatter plots are projected above the 95% confidence band of the metal to Al regression line. Thus, for Cd, there was a small enrichment in the sediments

**Table 5** Total extractable amount of element ( $F1 + F2 + F3 + F4 + F5$ ), values are expressed in  $\text{mg kg}^{-1}$ 

NS <sup>a</sup>	Cr	Zn	Pb	Cd	Fe	Al	Mn	Ni	As	Hg	Cu
1 (S1/1.00)	11.8	72.6	54.4	0.94	19,338	22,199	424	29.6	0.52	0.04	26.3
2 (S1/2.40)	12.8	77.5	42.6	0.62	28,193	30,362	577	35.7	0.46	0.06	33.5
3 (S1/3.20)	10.5	69.6	15.6	1.19	23,576	18,066	554	31.6	0.25	0.04	87.1
4 (S2/1.10)	14.5	65.6	18.7	1.21	23,569	21,724	633	29.4	0.49	0.04	26.0
5 (S2/2.50)	8.88	29.4	10.0	1.01	14,238	9,666	326	14.8	0.25	0.06	11.7
6 (S2/5.00)	8.62	31.4	12.0	0.95	14,477	8,268	204	12.5	0.05	0.04	10.8
7 (S3/1.20)	6.40	62.4	13.0	0.98	10,117	7,781	200	13.2	0.13	0.05	3.75
8 (S3/2.20)	11.6	56.4	17.5	1.07	18,517	15,232	474	23.1	0.24	0.03	19.7
9 (S3/2.90)	6.96	33.4	13.3	0.83	11,608	16,167	284	13.4	0.27	0.20	8.53
10 (S4/1.00)	5.52	164	13.2	0.81	7,715	3,281	222	16.2	0.10	0.03	3.72
11 (S4/1.50)	10.2	62.6	17.9	0.86	18,477	19,140	544	23.1	0.11	0.03	20.6
12 (S4/2.40)	5.96	23.5	17.9	0.86	9,436	3,987	281	12.4	0.07	0.02	6.39
13 (S5/0.90)	8.24	25.6	5.42	0.95	7,440	2,956	109	19.5	0.29	0.05	2.09
14 (S6/0.90)	7.83	39.3	6.06	1.33	9,517	4,880	240	16.7	0.13	0.04	2.83
15 (S7/1.00)	16.3	78.2	6.39	1.25	30,631	31,168	908	35.1	0.42	0.09	26.4
16 (S7/1.50)	9.87	27.3	3.25	0.89	8,877	5,646	264	16.3	0.14	0.02	3.51
17 (S8/1.00)	10.3	27.9	2.99	0.91	8,152	8,651	236	16.3	0.09	0.11	1.72
18 (S9/0.90)	7.49	25.2	3.14	0.93	6,615	10,128	225	15.6	0.19	0.01	1.74
19 (S10/0.50)	5.62	24.9	8.83	0.60	3,194	3,022	69	6.67	0.12	0.12	5.99
20 (S10/0.80)	6.71	41.7	6.23	1.47	3,694	13,252	215	8.36	1.80	0.30	23.5
21 (S10/1.30)	11.4	38.6	5.65	1.19	7,805	5,333	136	17.6	0.16	0.22	3.06
22 (S11/0.00)	18.7	84.3	8.11	1.51	29,514	24,590	621	21.7	0.50	0.09	21.6
23 (S11/1.50)	22.7	69.0	4.13	1.19	24,007	23,225	550	27.4	0.07	0.07	20.2
24 (S12/0.30)	26.7	111	8.48	1.88	39,181	36,453	734	24.9	0.10	0.08	32.8
25 (S12/1.50)	15.5	39.3	5.61	1.06	18,598	9,990	693	17.4	0.01	0.05	10.3
26 (S12/2.30)	23.1	76.8	6.08	1.18	27,720	25,250	554	39.5	0.04	0.05	28.2
27 (S13/0.50)	14.4	52.3	5.65	1.03	22,190	16,766	531	18.6	0.04	0.04	14.9
28 (S13/1.40)	10.4	29.8	4.99	1.05	14,281	7,467	353	13.9	0.13	0.03	6.16
29 (S13/2.70)	21.3	78.0	10.3	1.17	28,275	22,797	260	30.9	0.06	0.05	26.2
30 (S14/0.70)	15.6	45.6	5.35	1.12	19,841	11,822	299	19.6	0.01	0.06	12.1
31 (S14/2.20)	22.0	65.8	8.56	1.12	22,999	14,982	514	27.1	0.17	0.04	18.1

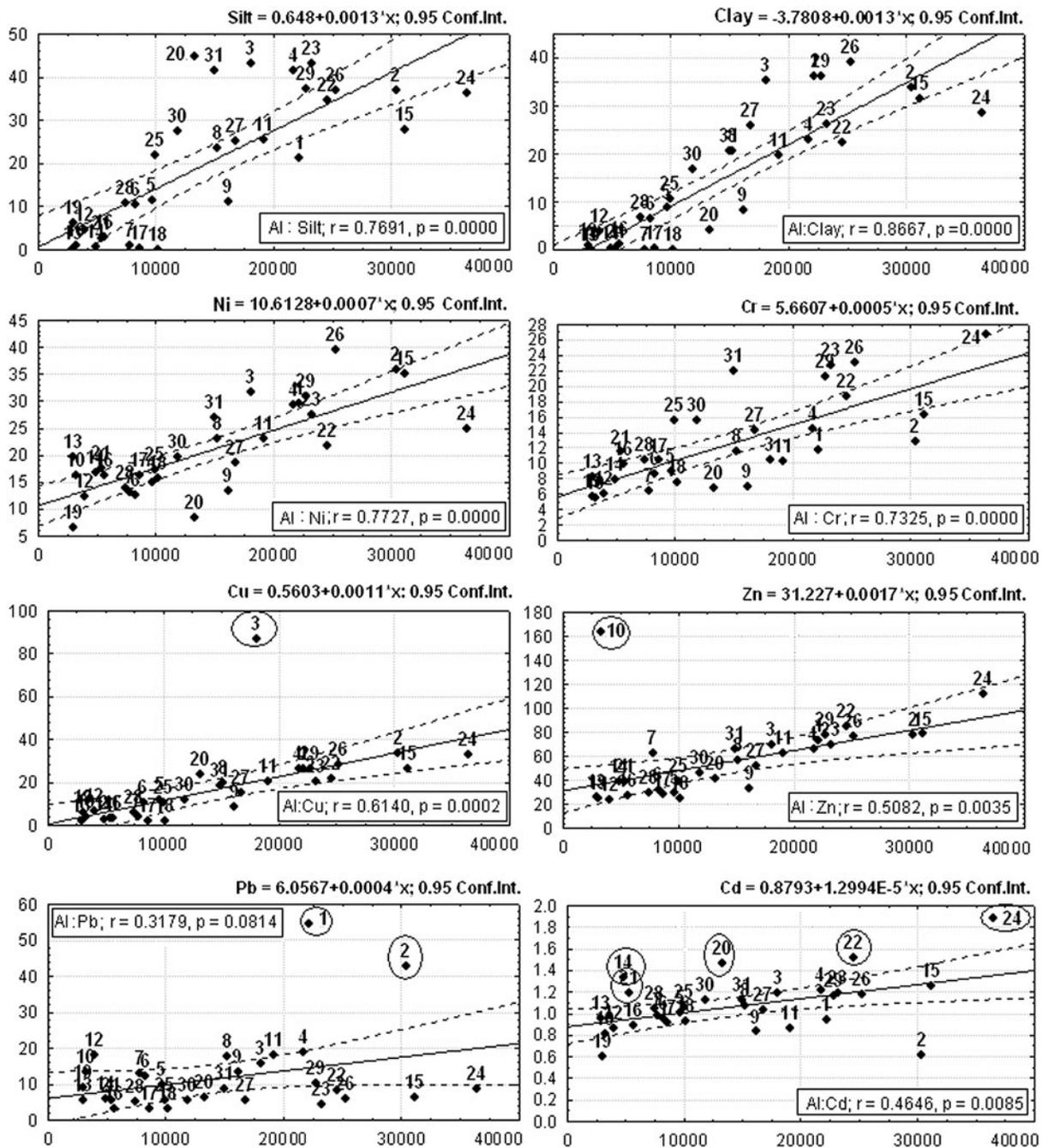
<sup>a</sup>For each, NS (number of sample, 1–31) is shown and the nomenclature of the drill hole (S)/depth (in m)

samples S6/0.90, S10/0.80, S10/1.30, S11/0.00, and S12/0.30 (14, 20, 21, 22, and 24); for Cu, in S1/3.20 (location 3); for Zn, in S4/1.00 (location 10) and for Pb, in S1/1.00 (1) and S1/2.40 (2). The enrichment with Cd was observed in sediment samples from a depth <1 m, and at some localities the concentration was close to  $2 \text{ mg kg}^{-1}$  (Table 5). These data indicate the existence of some local contamination sources of Cu, Zn, and Cd. Although the correlation between Pb and Al content was not significant ( $p = 0.08$ ), the points representing locations S1/1.00 (1) and S1/2.40 (2) fall above the 95% confidence band, indicating an influence of the refinery on Pb content in sediment. This is in agreement with results obtained for alluvial sediments at the Pančevo Oil Refinery (Relić et al.

2005), where it was stated that the anthropogenic source of lead could be result of war activities in 1999 and the burning of reservoirs of leaded gasoline within this refinery. Contamination with Pb showed a decreasing trend with increasing distance from the refinery. There was no linear relationship between Al as the normalizer and Hg and As, which may indicate other substrates, except aluminosilicates and oxides, are most significant for the binding of Hg and As in the investigated sediments.

#### Statistical analysis

In this research, correlation analysis, PCA and cluster analysis were applied to the total extracted



**Fig. 3** Scatterplot diagrams of clay, silt, and metal with respect to Al in sediments (clay, silt in %, metals in  $mg\ kg^{-1}$ )

metal content (Table 5). The normality of the distribution of each element was previously checked (Kolmogorov–Smirnov test). The data for the investigated elements show a normal distribution.

### Correlation and PCA

The results of Correlation Analysis and Principal Component Analysis (PCA) are presented in

Tables 3 and 6. The applied PCA resulted in three significant PCs (PC1, PC2, and PC3), accounting for 75.46% of the total variance of the presented data.

PC1, which explains 38.62% of the variance, is highly and positively (loadings >0.6) driven by Cu, Cr, Zn, K, Fe, Mn, and Ni. Since most of the analyzed elements are strongly associated with Fe, K, and Mn in the first component, it can be supposed that the natural element distribution associated with Fe and Mn oxides and clay minerals is reflected in the background sediment geochemistry and that the parent materials of the sediments may control the concentrations of Cu, Cr, Zn, and Ni.

PC2 (20.27% of the variance) is mainly driven by As, C, and Hg. To ascertain the dominant nature of C, a correlation analysis of the As, Hg, and C content and the quantity of added 0.6 M HCl (Table 3) in the II (F2) fraction of the SE was performed. Considering the high and significant correlation between As and Hg with the TC and the amount of added 0.6 M HCl, it can be concluded that a significant quantity of As and Hg have a carbonate origin.

The third principal component (PC3), which explains 16.57% of total variance, is related to Cr,

Mg, and Cd (positive loadings) and Pb (negative loading). It can be supposed that Cr and Cd are probably bound to Mg silicates (olivine, chlorites, etc). This assumption is in accordance with the results of the soil composition in Vojvodina, in which the existence of chlorite was confirmed (Kostić 2001). Considering that PC3 is negatively related with Pb, it can be supposed that Pb has a different behavior to Cr and Cd and a different origin with respect to the other elements. The highest concentration of Pb was observed in the sediment samples near to the refinery, indicating an anthropogenic origin and the influence of the refinery on the lead content.

The results of principal component analysis coincidentally indicate that the contents all of the trace elements (except Hg and As) are dominantly controlled by the presence of Fe and Mn oxides. There is evidence that PC1, PC2, and PC3 are related to common sources of natural processes (mainly with the dissolution of geological soil and components of the sediment).

#### Cluster analysis

The results of a cluster analysis of the investigated sediments are illustrated as a dendrogram in Fig. 2b. The samples were hierarchically clustered based on the elemental concentrations (Table 5) in the sediments. The groups defined by this procedure were identified as cluster A and cluster B. It was found that cluster A could be separated into two subclusters, and cluster B into three subclusters. Cluster A is composed of sediment samples with dominate coarse texture, i.e., with higher contents of sand (sandy loam, loamy sand, loam, and sand). Sediment samples with a dominant fine texture and a much greater surface area per unit volume are in cluster B.

The average concentrations of elements were calculated for the two groups of sediments (Table 7). One group represents sediment samples from cluster A, and the second represents sediment samples from cluster B. The mean concentrations all of the elements (except Hg) were higher in the samples of sediments with lower contents of sand (cluster B). The difference in Hg content in both of groups was very low, and the concentrations of Hg were close to the detection

**Table 6** Results of PCA

	Principal component loadings (Varimax normalized) <sup>a</sup>		
	PC1	PC2	PC3
Cu	0.746		
Cr	0.647		0.639
Zn	0.620		
Pb			-0.754
K	0.830		
Mg			0.699
As		0.897	
C		0.895	
Hg		0.838	
Fe	0.902		
Cd			0.606
Mn	0.837		
Ni	0.879		
Eigenvalue	5.021	2.635	2.154
% Total variance	38.621	20.270	16.571
Cumulative %	38.621	58.890	75.461

<sup>a</sup>Matrix of PCA loadings of geochemical elements and communality of the PCA components; loadings below 0.5 are not shown

**Table 7** Concentrations of elements in different sediment and soil samples (mg kg<sup>-1</sup>)

	Cu	Cr	Zn	Pb	Cd	Ni	As	Hg	Fe	Mn
Mean <sup>a</sup>	30.28	15.97	73.77	17.63	1.16	28.59	0.27	0.05	25,765	568
Deviation	18.67	5.38	15.26	15.41	0.32	6.40	0.20	0.02	6,053	159
Median	26.23	14.40	74.69	12.91	1.17	29.48	0.25	0.05	25,648	554
Mean <sup>b</sup>	8.22	10.30	44.40	7.90	1.00	16.0	0.20	0.10	11,716	285
Deviation	6.52	5.12	32.07	4.25	0.20	5.13	0.39	0.08	6,047	154
Median	6.20	8.6	33.4	6.10	1.00	16.2	0.10	0.10	9,517	240
Soil of Novi Sad <sup>c</sup>	30.86	nd	85.45	10.75	0.152	nd	0.20	nd	8,009	251.3
Soils of Belgrade <sup>d</sup>	28.3	32.1	118	55.5	nd	68	7.2	nd	nd	nd
Topsoils <sup>e</sup>	33.9	77.2	98.1	35.7	0.3	38.5	10.2	0.2	nd	nd
Subsoils <sup>f</sup>	32.1	80.9	79.4	26.7	0.2	33.4	12.0	0.1	nd	nd
Soil from Spain <sup>g</sup>	19.97	18.15	476.6	106.7	2.41	11.4	14.73	1.71	27,452	675.5
National regulation <sup>h</sup>	100	100	300	100	2	50	0.10	2	nd	nd

nd no data

<sup>a</sup>Samples of Pančevo alluvial sediments with lower sand content (cluster B), this study

<sup>b</sup>Samples of Pančevo alluvial sediments with higher sand content (cluster A), this study

<sup>c</sup>Škrbić and Čupić (2004); surface soil of Novi Sad and bank sediments of the Danube River

<sup>d</sup>Crnković et al. (2006); soils of urban and suburban areas of Belgrade

<sup>e</sup>Huang et al. (2007); agricultural topsoils (20 cm) in the Yangzhong district, China

<sup>f</sup>Huang et al. (2007); agricultural subsoils (150–00 cm) in the Yangzhong district, China

<sup>g</sup>Gallego et al. (2002); soil from Spain (0–25 cm)

<sup>h</sup>MAQ—Maximum allowed quantity (Official Gazette of Serbia 1990)

limit. This fact, as well as the assumption that oxides and clay minerals are not significant Hg accumulators, may be the reason for the slightly higher content of this element in the fraction with a dominantly sand content.

It can be concluded that trace metal contents at the investigated locality are significantly controlled by the geochemical composition of the sediment, namely with the content of clay and silt fractions.

#### Comparison with other results of the metal content of soils and sediments

The mean values of the total extractable amounts of elements from the investigated alluvial sediments, as well as the contents of the elements in sediments and soils from other localities in Serbia and the world, are given in Table 7, which also contains National soil quality guidelines for metals (Official Gazette of Serbia 1990).

All the values for the total content of the investigated elements were below the limits stipulated by national regulation (Official Gazette of Serbia 1990). The metal contents in the investigated sediments were similar to those in soils of Novi Sad

(Vojvodina) and sediments on the bank of the Danube River (near Novi Sad). Also, the metal contents in the investigated sediments were lower in comparison with values for other soils and sediments (Table 7) for which an anthropogenic origin of the metals was suggested. A comparison of the contents of elements in the investigated alluvial sediments with National quality guidelines and literature values indicates that, in general, there was no significant pollution with the investigated, potentially toxic, elements at this locality.

#### Conclusions

This study presents the importance of applying geochemical normalization, sequential extraction, principal components, and cluster analysis methods for the evaluation of sediment contamination with trace metallic and metalloid elements and the determination the origin and mobility of these contaminants in the sediments.

Sequential fractionation provides valuable information about the potential mobility of elements. In the investigated Danube alluvial sedi-

ments, oxides (partially crystalline and crystalline oxides) and silicates are the most significant fractions for binding elements. The low percentage of trace metals in the exchangeable fraction and high proportion of metals in the residual fraction suggests weak bioavailability and dominant geochemical origin of the investigated elements.

The geochemical normalization of metal data to Al indicated an anthropogenic origin of enrichments with Cd, Cu, Zn, and Pb at some localities and a dominant natural origin of enrichments with Cr and Ni. There was shown the influence of the refinery on the Pb content in the sediment, as well as the existence of some local contamination sources of Cu, Zn, and Cd were shown. The results of statistical analyses indicate a natural element distribution associated with Fe and Mn oxides and clay minerals, namely, background sediment geochemistry significantly controlled the contents and distribution of Cu, Cr, Zn, and Ni. Carbonates are important substrates for As and Hg, whereas Mg silicates have significance for the binding of Cr and Cd in the investigated sediments. For Pb is affirmed a complex chemical behavior, and a different origin was shown for Pb, with respect to the other elements.

All the values for total content of the investigated elements were below the limits stipulated by national regulation, which indicates that the investigated sediments from alluvial formation of the Danube River were not significantly polluted with trace metallic and metalloid elements. The metal contents were significantly controlled by the geochemical composition of the sediments, namely, with content of the clay and silt fraction. It can be concluded that the appreciable number of results can be used as the basic state for sediments uncontaminated with trace metals. The results from this study show that impact of Pančevo industrial zone on the quality of the Danube River and its contamination with trace element is minor. Also, these results are contributing new knowledge to scientist working on the Danube investigation and other researchers of the sediment contamination.

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