

# Risk assessment of trace element contamination in river sediments in Serbia using pollution indices and statistical methods: a pilot study

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**Abstract** To effectively manage potential environmental and human health impacts of contaminated river sediments, it is important that information about the source (anthropogenic vs geogenic), variability and environmental risks associated with the contamination are well understood. The present study was carried out to assess the source and severity of contamination and to undertake a risk assessment for selected elements (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn) in river sediments in Serbia. The estimate of the anthropogenic component of contamination was derived by determining the total element content and the background values for elements in sediments, and the severity of pollution was assessed by calculating a number of pollution indices including the contamination factor, the enrichment factor, the index of geoaccumulation, the ecological risk factor, the potential ecological risk index, the pollution load index, the combined pollution index, the modified degree of

contamination and the toxic unit factor. This analysis indicates that river sediments in Serbia are primarily polluted with Zn, Cu and Cd. The most contaminated river systems are the Ibar, Pek, West Morava and Great Morava rivers. Mining activities were found to have a significant influence on sediment. Multivariate analyses suggested anthropogenic origins for Pb, Zn, Cd, As, Ni and Cu, whilst Fe, V, Mn, Co and Cr appear to have a mixed origin (both lithogenic and anthropogenic sources). A geochemical approach, with a calculation of pollution indices and statistical methods, is recognised as useful for the risk management of trace elements in sediments around the world.

**Keywords** Trace elements · River sediments · Enrichment factor · Modified degree of contamination · Multivariate analysis

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## Introduction

Heavy metals are widely distributed in nature, in places such as water, soil, sediments, air and various forms of organisms (Zhang et al. 2009). Metals are non-biodegradable and accumulative in nature. Contamination of the aquatic environment by heavy metals occurs as the result of various human activities (Behra et al. 2002). Elevated emissions and their deposition over time can lead to anomalous enrichment, causing metal contamination of the surface environment (Wong et al. 2006). Metal contamination in these sediments could directly affect the river water quality, resulting in potential consequences to the sensitive lowest levels of the food chain and ultimately to human health (Kabir et al. 2011).

The sediments consist of inorganic and organic particles with complex physical, chemical and biological

characteristics. They can scavenge some elements, thus acting as an adsorptive sink with metal concentrations in sediments often being many times greater than in the water column (Kalantzi et al. 2013). These metals may present both natural and anthropogenic origin. Main natural sources of heavy metals are weathering of soils and rocks and atmospheric deposition. Discharge of agricultural, municipal and industrial wastewaters into water bodies is dominant contribution from anthropogenic sources (Lin et al. 2011). To identify pollution problems, the anthropogenic contributions should be distinguished from the natural sources. Geochemical approaches, such as the enrichment factor (EF) and geochemical index methods, have been successfully used to estimate the impact of the human activities on sediments (Chabukdhara and Nema 2012) and many scientists have studied metal contamination in sediments using these approaches (Gao et al. 2013; Hui-na et al. 2012; Hu et al. 2011; Kabir et al. 2011; Harikumar et al. 2009; Abraham and Parker 2008). Calculating pollution indices of heavy metal is a powerful tool for ecological geochemistry assessment. These indexes evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed to assist sediment assessors and managers responsible for the interpretation of sediment quality (Caeiro et al. 2005).

Multivariate chemometric techniques, such as principal component analysis (PCA) and cluster analysis (CA), are often used as additional methods of monitoring heavy metals (Wang et al. 2014; Jamshidi-Zanjani and Saeedi et al. 2013; Chabukdhara and Nema 2012; Iqbal et al. 2013; Relić et al. 2010, 2011; Varol 2011; Li and Zhang 2010; Yang et al. 2009). These statistical techniques appeared to be very useful in solving many environmental compartments and the identification of existing pollution pattern.

In this study, the evaluation of the metal pollution level and possible sources compared to background pollution was performed for river sediments in Serbia. The main objectives were (1) to determine the total content of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn; (2) to carry out calculations of the contamination factor (CF), EF, index of geoaccumulation (I<sub>geo</sub>), ecological risk factor (Er), potential ecological risk index (RI), pollution load index (PLI), combined pollution index (CPI), modified degree of contamination (mC<sub>d</sub>) and toxic units to estimate the anthropogenic input of the elements and to assess the pollution status of the area; and (3) to identify the main sources of toxic elements. The authors consider that the combination of a wide range of indices as well as the use of multivariate statistical methods is a novel approach for assessing the distribution of metals in sediments which can be extended to other similar contaminated aquatic systems.

## Materials and methods

### Study area

European rivers are affected by a wide variety of pollution problems. European catchments are under pressure from ever-increasing water stresses and land-use change, especially those with a high conservation value in the Mediterranean area. In Western European rivers, very high levels of cadmium, mercury, lead and zinc have been recorded. Record levels of contaminations are observed in river basins that receive considerable discharges from industrial and mining activities and from large cities (Tockner et al. 2009). This is the case for many mining sites in the Western Balkans, where copper, lead, zinc and other elements are frequently found (Stuhlberger 2014). In Serbia, the primary extracted minerals include copper, coal, lead–zinc with associated gold, silver, bismuth and cadmium, red bauxite and modest quantities of oil and gas.

The largest and most important rivers that flow through Serbia are the Danube, Sava, Great Morava, West Morava, South Morava, Tisa, Ibar, Drina, Timok, Nišava, Tamiš and Begej Rivers. The Danube is the largest river in the country, flowing for 588 km inside Serbia, whilst forming the border with Romania, and is the second largest river in Europe. The basin drains parts of 19 countries. Some major tributaries of the Danube are still heavily polluted. Water quality in the Middle and Lower Danube remained relatively high (class II) between 1950 and the 1970s, but deteriorated afterwards due to rapid industrial development, poor pollution control and inputs from heavily polluted tributaries (Tockner et al. 2009).

The 945-km-long Sava River is the largest tributary of the Danube by volume (average discharge: 1,572 m<sup>3</sup>/s) and the second largest, after the Tisza, by catchment area (95,793 km<sup>2</sup>). In Serbia, it remains a typical lowland river. Until the 1990s, the Sava was affected by heavy pollution from the metallurgical, chemical, leather, textile, food, cellulose and paper industries, as well as from agricultural activities. The Sava is the main recipient of wastewater from many cities and is impacted by the polluted water of the tributaries (Tockner et al. 2009).

The River Tisza (966 km; 157,220 km<sup>2</sup>) is the largest Danube tributary in its length and catchment area. A small part of the Tisza watershed area lies within Serbian territory and covers only 6 % or 8,994 km<sup>2</sup>. This area belongs to the Autonomous Province of Vojvodina. It is predominantly lowland and part of the Pannonian basin, which is the largest of the sediment-filled, postorogenic basins of the Alpine region (Adriano et al. 2003). Ecological accidents that took place in 2000 in the superior watershed and their effects on the rivers upstream with resulting transboundary influences proved the necessity of a regional approach to

environmental protection and the active involvement of riverside countries in establishing common strategies and programs for preventing and reducing the risk of accidental pollution (Adriano et al. 2003).

The 308-km-long West Morava drains south-western Serbia (catchment area: 15,567 km<sup>2</sup>). The largest tributary is the Ibar.

Description of the sampling site and sampling

As riverine pollution can cross national borders, it is important that levels of pollutants in water and sediment are assessed in all the countries through which the river flows. Due to this factor, sediment samples in this study were collected from all of the main rivers in Serbia. A total of 35 samples of river sediment from 15 rivers in Serbia were collected during the year 2008 (Table 1). For the larger rivers, sampling was conducted at several locations (Fig. 1; Table 1). The sediment samples were stored at 4 °C to prevent changes in the chemical composition of the sediments. The contents of the micro- and macro-elements were determined in the granulometric fraction <63 μm of the bottom sediment samples (“grab”—the samples) after air drying for 8 days (Sakan et al. 2011). Detailed information about natural variability and sediment and soil properties in studied region is shown in paper Sakan et al. (2014).

Analytical procedures and element analysis

The total content of elements in the sediments was determined by digestion with very strong acids: HNO<sub>3</sub> + HCl + HF. A 0.5-g sediment sample was placed in a

Teflon vessel and then 9 ml HCl (37 %), 3 ml HNO<sub>3</sub> (70 %) and 3 ml HF (48 %) were added to the vessel. One Teflon vessel only contains the acid mixture for a blank. A microwave digestion system brings the sample to 165 °C in 10 min (holding time 0 s), then 175 °C in 3 min, where it was kept for 10 min (max power was 1200 W) (Rönkkömäki et al. 2008). Microwave digestion was performed in a pressurised microwave oven (Ethos 1, Advanced Microwave Digestion System, Milestone, Italy) equipped with a rotor holding 10 microwave vessels (PTFE).

After cooling the digestion system, 10 ml H<sub>3</sub>BO<sub>3</sub> (5 g/100 ml water) is added. Again, the microwave digestion system brings the sample to 175 °C in 10 min at 1420 W and holds the temperature at 170 °C for 3 min. The digestate is then diluted to a final volume of 100 ml (Nam et al. 2001).

In this research, the following elements were determined in each sample: As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn. The results are expressed in mg kg<sup>-1</sup> dry sediment. The analytical determination of the studied elements was realised with an atomic emission spectrometer with an inductively coupled plasma iCAP-6500 Duo (Thermo Scientific, UK). The detector was a RACID86 charge injector device (CID). Analytical grade chemicals were used throughout the study without any further purification. The metal standards were prepared from a stock solution of 1,000 mg L<sup>-1</sup> by successive dilutions. The concentrations obtained for all the elements in the blanks were close to the detection limit of the method, indicating that contamination was not a problem in the digestion.

Assessment of sediment contamination

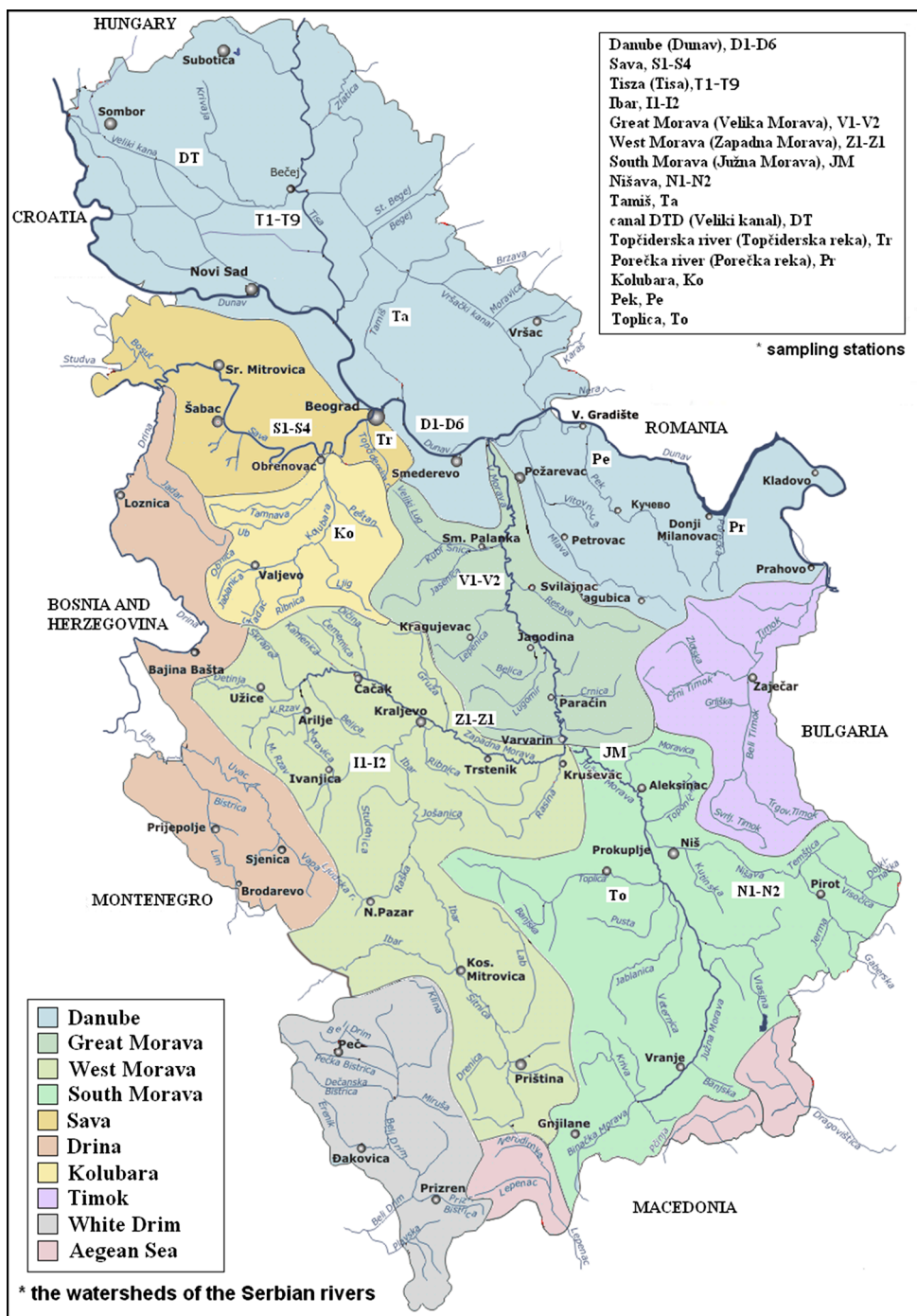
The degree of metal enrichment in sediments was carried out using following formulas:

CF was calculated as the ratio between the metal content in the sediment at a given station and the normal concentration levels (background concentration), reflecting the degree of metal enrichment in the sediment:  $CF = C_s/C_b$ . CF was classified into four groups in Hakanson (1980) and Pekey et al. (2004). EF was calculated as:  $EF = (M/Y)_{sample}/(M/Y)_{background}$ , where *M* is the concentration of the potentially enriched element and *Y* is the concentration of the proxy element. I<sub>geo</sub> was calculated as  $I_{geo} = \log_2 [C_{metal}/1.5 C_{metal (control)}]$ , where *C<sub>metal</sub>* is the concentration of the heavy metal in sample and *C<sub>metal (control)</sub>* is the concentration of the metal in the unpolluted sample or control. The factor 1.5 is attributed to lithogenic variations in the sediment (Mendiola et al. 2008). Ecological risk factor (*Er<sup>i</sup>*):  $Er^i = Tr^i C^i_f$ , where *Tr<sup>i</sup>* is the toxic–response factor for a given substance [for Hg, Cd, As, Cr and Zn, they are 40, 30, 10, 2 and 1, respectively; and 5 for Pb, Cu and Ni (Yang et al. 2009)], and *C<sup>i</sup><sub>f</sub>* is the contamination

**Table 1** Sampling locations

River	Watershed	Sampling sites
Danube	Black Sea	D1–D6
Sava	Danube	S1–S4
Tisa	Danube	T1–T9
Ibar	West Morava	I1, I2
Great Morava	Danube	V1, V2
West Morava	Great Morava	Z1, Z2
South Morava	Great Morava	JM
Nišava	South Morava	N1, N2
Tamiš	Danube	Ta
DTD canal	Danube	DT
Topčiderska River	Sava	Tr
Porečka River	Danube	Pr
Kolubara	Sava	Ko
Pek	Danube	Pe
Toplica	South Morava	To

**Fig. 1** Location map of the study area



factor (Hakanson, 1980). Ecological risk index (RI):  $RI = \sum (T_i \times C_i/C_o)$ , where  $n$  is the number of heavy metals,  $T_i$  is the toxic–response factor for a given substance,  $C_i$  represents the metal content in the sediment and  $C_o$  is the regional background value of heavy metals (Hakanson, 1980; Yang et al. 2009). PLI: the PLI for a single site is the  $n$ th root of the number ( $n$ ) of multiple CF multiplied together (Tomlinson et al. 1980; Mohiuddin et al. 2012):  $PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$ .

CPI: there are two steps in this assessment process. The first step is to determine the contamination coefficient of each heavy metal which is obtained by:  $C_f^i = C^i/C_n^i$ . In the second step: the CPI is obtained by  $CPI = \sum C_f^i/m$ , where  $C_f^i$  is the contamination coefficient of heavy metal,  $C^i$  is the concentration of each heavy metal in the sediment,  $C_n^i$  is the background values, and  $m$  is number of heavy metals and CPI.  $mC_d$ : this factor is similar to CPI according to the method of calculation:  $mC_d = \sum C_f^i (i = 1, i = n)/n$ , where

$n$  = the number of analysed elements,  $i$  = the  $i$ th element (or pollutant) and  $C_f$  = contamination factor, but differs in the gradation degree of contamination (Abraham and Parker 2008). TU is defined as the ratio of the determined content to the probable effect level (PEL) (Gao et al. 2013; Harikumar et al. 2009; Pedersen et al. 1998). The PEL is defined as the lower limit of the range of chemical concentrations that is usually or always associated with adverse biological effects (Gao et al. 2013). Sediments with measured chemical concentrations equal to or greater than the PEL are considered to represent significant and immediate hazards to exposed organisms. The PEL represents the lower limit of the range of chemical concentrations that is usually or always associated with adverse biological effects (CCME 1995). It was derived using a weight of evidence approach in which matching biological and chemical data from numerous modelling, laboratory, and field studies performed on freshwater sediments were compiled and analysed, i.e. the geometric mean of the 50th percentile of the effect data set and the 85th percentile of the no effect data set (Smith et al. 1996; CCME 1995). In this manuscript, for TU calculation used PEL values are published in Smith et al. (1996) and MacDonald et al. (2000).

#### Statistical analysis

Multivariate analysis was performed using PCA and CA. The statistical analyses were conducted using SPSS 11.0 using the log-transform normalised data set. The element used for sediment normalisation is aluminium. This element was chosen because Al is a conservative element and a major constituent of clay minerals, and has been successfully used in previous investigations (Rubio et al. 2000).

## Results and discussion

#### Performance of the analytical procedure

The accuracy and precision of the obtained results were checked by analysing sediment reference material (BCR standards, 143 and 146R). The percentage recovery of each element was obtained as: [(measured concentration in  $\text{mg kg}^{-1}$ )/mean certified value for CRM in  $\text{mg kg}^{-1}$ ]  $\times$  100]. The results indicate a good agreement between the certified and analytical values (Table 2). The recovery of elements being practically complete for most of them and the values were in the acceptable range (recovery 80–120 %) (Chang et al. 2009).

The precision is expressed as relative standard deviations. The relative standard deviations of the means of

duplicate measurement were less than 4 % (0.03–3.80 %) for all the measured elements.

#### Descriptive statistics of elements contents in sediments

The total contents and basic statistics (minimum and maximum, as well as the means and standard deviations) for the total contents of all the measured elements in the investigated river sediments are shown in Table 3. The distribution of heavy metals in studied sediments showed large spatial variations amongst the different rivers suggesting large natural variability of metal concentrations in sediments and different origins of these elements. The order of the total element content was  $\text{Zn} > \text{Cu} > \text{Pb} > \text{Ni} > \text{Cr} > \text{V} > \text{Co} > \text{Cd} > \text{As}$  (not taking into account Fe and Mn). The contents of all elements were higher than the background values for the investigated elements (Table 4). Also, the contents of Cd, Cr, Cu, Ni, Pb and Zn were above the PEL, which indicates that the investigated river systems are polluted with toxic elements and that the content of these elements in sediments poses a potential risk to aquatic life. Because of that, additional calculations were performed the severity of contamination by these elements in sediments.

#### Calculating the grade of contamination and risk category

Contamination of the investigated river sediments with the studied trace elements was assessed using: CF, EF, Igeo, Er, RI, PLI, CPI, mCd and TU. Tables 5 and 6 show the predicted severity of contamination determined by these indices and ecological risk based on the calculated factors.

Table 4 shows the background values for the elements in sediments given by other authors (Rubio et al. 2000; Sakan et al. 2009) and calculated for the investigated river sediment, as well as values for the element content in continental crust (Wedepohl 1995) and the PEL values (Smith et al. 1996; MacDonald et al. 2000). The element contents in the DTD canal (station in Vrbas) were chosen as the background values for elements in this research because there are no significant anthropogenic sources of toxic elements at this locality and the sediment samples are similar to the other investigated river sediments in geochemical characteristics and composition. Many researchers recommend that it is better to use the regional background values (Rubio et al. 2000) than the element content in continental crust or the average values of the element contents in world soils, etc. In this research, the same background values (quoted in Table 4) are used for calculating all the pollution indices. For the background value of As, the content in the continental crust is used since the content of As extracted from the DTD canal (station in Vrbas) was below the detection limit.

**Table 2** The result of accuracy and precision of applied method

Element	Certified 146R (mg kg <sup>-1</sup> )	Measured (mg kg <sup>-1</sup> )	Accuracy (%)	Certified 143R (mg kg <sup>-1</sup> )	Measured (mg kg <sup>-1</sup> )	Accuracy (%)
Cd	18.8	18.3	97.3	71.8	70.5	98.2
Co	7.39	7.62	103	12.3	12.0	101.6
Cu	838	678	80.9	130.6	111.4	85.3
Pb	609	532	87.4	179.7	212.9	118.5
Mn	323	347	107.5	904	834	92.2
Ni	70	60	85.4	299	248	82.9
Zn	3,060	2,749	89.8	1,055	1,116	106
Cr	196	167	85.2			

### Contamination factor (CF)

Values of the CF (CF, Table 6) were classified into four groups using the classification scheme given by Pekey et al. (2004) and Hakanson (1980). The results of the CF groupings are presented in Table 7 and Supplementary Table 1. The highest CF value, for Cu (very high contamination), was found at site 33 (the river Pek). CF values >6, which indicate “very high contamination”, were observed for Zn, Cu, Ni, Cd and As. For other elements, the CF values indicated: no metal enrichment to considerable contamination (Cr), no metal enrichment to very high contamination (As, Ni), moderate contamination to very high contamination (Cd, Cu, Zn); moderate contamination to considerable contamination (Fe, Mn, Co, Pb), and moderate contamination for V. From the CF values, contamination with the investigated elements can be observed, especially with Zn, Cu, Ni and Cd.

### Enrichment factor (EF)

The EF values were interpreted as suggested by Acevedo-Figueroa et al. (2006) (Table 5) and were calculated separately for all the sampling sites (Table 5, Supplementary Table 1). River sediments in Serbia showed a wide range of trace element enrichment. In general, the order of the average EF values was Cu > Zn > Cd > Co > Pb > Ni > Mn > Cr > As. According to the categories (Table 5), these findings indicate that Cu, Zn and Cd enrichment was high. From the pollution point of view, the EF of Cu in the river Pek (35.03) was the highest amongst the elements in the investigated sediments, suggesting significant contamination at this locality.

### Index of geoaccumulation (Igeo)

Müller (1979) proposed seven grades or classes based on the increasing numerical value of the Igeo index (Table 5). The greatest number of samples and elements belong to Class 1 (Fig. 2; Table 7, Supplementary Table 3), i.e.

unpolluted to moderately polluted sediment (with As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and V), Class 2 (Cd, Cu, Zn, and Pb in some samples), Class 3 (Cu in the river Pek and the West Morava 1, and Zn in the Ibar 1 and Ibar 2 and Pek) and the largest Igeo value −3.92 had the sediment from the Pek for Cu (Class 4, heavy pollution). These findings indicate that the primary contaminants in the rivers are Cu and Zn, like Cd. These results are consistent with EF values.

### Ecological risk factor (Er)

The ecological risk assessment results are summarised in Table 7 and the Supplementary Table 4. The potential Er indices of Cr, Ni, Pb, Zn and As were lower than 40 (except for arsenic at two locations in the river Ibar), which indicates a slight potential ecological risk of these elements in the main Serbian river. Amongst the studied elements, Cd and Cu present a higher ecological risk than any other elements because of their higher toxicity coefficient.

### Ecological risk index (RI)

The RI was calculated as the sum of all the calculated risk factors (Table 8 and Supplementary Table 4). The potential RI values were generally lower than 300, which suggest that sediment samples from the river catchments exhibited low and moderate ecological risk for the investigated elements. However, three (two sediment samples from the Ibar and one from the Pek Rivers) of the 34 samples of sediments had large RI values (300–600), which indicates a high ecological risk of these elements.

The contribution percent of the individual element to the overall potential ecological risk revealed that the most toxic element, Cd, is the main contributor to the total potentially ecological risk. Because Cd pollution, in general, was the result of a long history of accumulation, there is a strong potential risk to the ecosystem and the health of the residents in this region (Gao et al. 2013).

**Table 3** Total contents and descriptive statistics of elements in different river sediments, this study (mg kg<sup>-1</sup>)

	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	Al
T1	3.26	5.05	10.0	59.8	47.8	33105	1276	39.2	95.7	87.2	330	54345
T2	0.46	4.23	20.5	103	64.5	49098	1234	46.2	118	131	335	63956
T3	1.39	4.97	21.2	95.8	74.1	46711	1324	45.0	124	122	391	72870
T4	0.79	4.41	19.1	90.2	63.8	42246	1399	39.2	124	109	338	75717
T5	0.41	6.37	22.6	106	88.3	46480	1722	47.7	112	122	360	39331
T6	0.91	6.89	21.3	99.8	90.5	50118	2108	42.4	142	131	420	67904
T7	0.51	6.23	19.8	92.8	74.0	43445	1870	42.8	90.3	115	346	26311
T8	0.83	6.09	19.3	89.5	71.1	43281	1683	41.5	119	114	337	71782
T9	1.49	7.00	21.5	96.3	87.1	46932	1816	46.3	140	123	411	83795
D1	0.53	2.25	16.2	73.4	28.0	40134	1387	33.2	90.0	95.5	168	44340
D2	3.70	2.12	16.3	75.0	23.8	39637	1036	36.0	114	106	157	89119
D3	0.52	2.49	16.8	79.9	31.4	40922	979	35.8	104	107	208	54910
D4	0.41	2.35	15.4	76.1	28.9	37534	896	35.0	132	95.5	220	62215
D5	0.29	2.78	19.0	78.4	40.7	40389	1352	37.9	80.3	97.7	221	23482
D6	0.75	5.31	21.5	123	41.9	44697	1185	70.8	136	113	228	54034
S1	0.48	3.46	21.7	112	32.0	36506	1025	93.6	89.0	87.5	270	44354
S2	0.58	3.02	28.5	154	36.4	46480	1759	126	115	108	213	57957
S3	0.50	3.74	26.4	140	36.4	43872	1660	119	113	104	272	57781
S4	0.65	4.69	27.3	145	31.3	45780	1819	119	110	113	213	54741
I1	8.89	10.5	13.6	102	29.0	36863	904	142	318	72.1	947	36516
I2	6.56	8.32	36.2	230	39.4	47630	1352	274	263	101	1095	59195
V1	0.80	7.91	32.3	170	65.6	55319	1734	42.6	182	129	499	29759
V2	1.60	6.82	27.7	152	53.0	46593	1226	156	182	110	449	61204
Z1	2.15	3.60	12.2	85.6	155	33860	808	84.2	77.2	94.5	250	47320
Z2	2.06	7.50	31.8	222	52.6	46461	1032	236	213	110	660	57360
JM	1.11	3.88	23.4	106	47.9	50105	3688	55.1	150	124	238	74056
N1	0.48	2.65	16.3	86.3	85.0	38745	731	35.9	138	111	411	59353
N2	0.34	5.53	16.2	70.7	22.1	34881	770	34.6	84.1	101	114	42827
Ta	1.17	3.12	26.5	112	51.9	62800	1413	50.4	137	149	191	95849
DT	1.10	1.28	8.2	62.1	11.5	24556	648	34.7	57.8	60.4	66.7	36323
Tr	0.78	3.91	27.9	161	40.9	50739	1226	133	144	128	338	52416
Pr	0.98	3.13	23.8	118	137	51266	868	59.0	119	138	155	72811
Ko	1.13	5.45	28.7	146	39.4	47245	1352	132	126	114	417	61971
Pe	1.47	6.26	30.5	88.7	870	50977	1997	41.6	157	127	922	78474
To	0.64	5.23	29.5	148	55.6	50808	1685	115	135	137	167	34488
Min	0.29	1.28	8.22	59.8	11.5	24556	648	33.2	57.8	60.4	66.6	23482
Max	8.89	10.5	36.2	230	870	62800	3688	274	318	149	1095	95848
Mean	1.42	4.82	21.97	113	78.5	44177	1399	77.8	132	111	353	57110
SD	1.44	2.08	6.63	41.0	141	7200	556	58.5	51.0	18.4	232	17544
Median	0.80	4.69	21.5	102	47.9	45780	1352	46.3	124	111	330	57781

*Pollution load index (PLI)*

Supplementary Table 1 presents the PLI values of the studied elements. When the PLI > 1, it means that pollution exists; otherwise, if the PLI < 1, there is no metal

pollution (Varol 2011). The PLI values varied from 1.4 to 4.27 for the investigated sediments, suggesting that pollution exists. The highest PLI values were observed in the following sediments: Ibar, Pek, West Morava and Great Morava and these river systems are significantly polluted.

**Table 4** Comparison between background values for elements given by other authors and calculated for the investigated river sediment ( $\text{mg kg}^{-1}$ )

Element	Barreiro <sup>a</sup>	Continental crust <sup>b</sup>	Ría de Vigo <sup>c</sup>	Tisa River (Serbia) <sup>d</sup>	River sediment <sup>e</sup>	PEL
Cd	nd <sup>f</sup>	0.1	nd	nd	1.28	3.53
Co	16	24	11.66	nd	8.22	nd
Cr	43	126	34.04	11.37	62.13	90.0
Cu	25	25	29.41	41.97	11.50	197.0
Fe	2.69	43,200	3.51	nd	24,555.8	nd
Mn	225	716	244.33	nd	647.8	nd
Pb	25	14.8	51.29	19.3	57.79	91.3
Ni	30	56	30.32	42.27	34.69	36
Zn	100	65	105.35	127.3	66.65	315
V	nd	98	nd	nd	60.43	nd
Al	nd	79,600	nd	nd	36,323.4	nd
As	nd	1.7	nd	nd	nd	17

PEL—Probable effect level-above which harmful effects are likely to be observed (Smith et al. 1996; MacDonald et al. 2000)

<sup>a</sup> Background values of trace elements for Ría de Vigo (Barreiro) (Rubio et al. 2000)

<sup>b</sup> Element content in Continental crust (Wedepohl 1995)

<sup>c</sup> Background values for Ría de Vigo (Rubio et al. 2000)

<sup>d</sup> Background values for the Tisa river (Sakan et al. 2009)

<sup>e</sup> Background values in the studied sediments

<sup>f</sup> No data

**Table 5** Grades of enrichment factor, index of geoaccumulation, and modified degree of contamination

Enrichment factor (EF)		Index of geoaccumulation ( $I_{\text{geo}}$ )		Modified degree of contamination ( $mC_d$ )	
Value	Pollution category	Value	Pollution category	Value	Pollution category
$EF < 1$	No enrichment	$I_{\text{geo}} < 0$	uncontaminated/unpolluted ( <i>class 0</i> )	$mC_d < 1.5$	Nil/very low
$1 \leq EF \leq 3$	Minor	$0 \leq I_{\text{geo}} < 1$	unpolluted/moderately ( <i>class 1</i> )	$1.5 \leq mC_d < 2$	Low
$3 \leq EF \leq 5$	Moderate	$1 \leq I_{\text{geo}} < 2$	moderately ( <i>class 2</i> )	$2 \leq mC_d < 4$	Moderate
$5 \leq EF \leq 10$	Moderately severe	$2 \leq I_{\text{geo}} < 3$	moderately/ heavily ( <i>class 3</i> )	$4 \leq mC_d < 8$	High
$10 \leq EF \leq 25$	Severe	$3 \leq I_{\text{geo}} < 4$	heavily ( <i>class 4</i> )	$8 \leq mC_d < 16$	Very high
$25 \leq EF \leq 50$	Very severe	$4 \leq I_{\text{geo}} < 5$	heavily/extremely ( <i>class 5</i> )	$16 \leq mC_d < 32$	Extremely high
$EF > 50$	Extremely severe	$I_{\text{geo}} \geq 5$	extremely ( <i>class 6</i> )	$mC_d \geq 32$	Ultra high

### Combined pollution index (CPI)

The CPI values are shown in Supplementary Table 4. When the  $CPI < 1$ , the sediment is unpolluted; when the  $CPI \geq 1$ , the sediment is contaminated by heavy metals (Hui-na et al. 2012; Jian-Min et al. 2007). The CPI values range from 1.65 to 10.19, which indicates that the investigated sediments are contaminated with the studied trace elements. A more detailed discussion will be presented through a discussion of the  $mC_d$ , considering that these two factors are calculated in the same manner.

### Modified degree of contamination ( $mC_d$ )

The  $mC_d$  is based on integrating and averaging all the available analytical data for a set of sediment samples. Based on the values of the  $mC_d$  factors (Supplementary Table 4), it is possible to distinguish differing levels of metal contamination (Table 5). The  $mC_d$  values for the investigated sediments generally lie in the range 1.65–10.19. Using the classification system proposed for this parameter, the overall range of  $mC_d$  values indicates a low to very high degree of contamination. The  $mC_d$  data



**Table 6** Grades of ecological risk factor, contamination factor, and ecological risk index

Ecological risk factor (Er)		Contamination factor (CF)		Ecological risk index (RI)	
Value	Risk category	Value	Pollution category	Value	Risk category
Er < 40	Low	CF < 1	No metal enrichment	RI < 150	Low risk
40 ≤ Er < 80	Moderate	1 ≤ CF ≤ 3	Moderately contamination	150 ≤ RI < 300	Moderate
80 ≤ Er < 160	Considerable	3 ≤ CF ≤ 6	Considerable contamination	300 ≤ RI < 600	Considerable
160 ≤ Er < 320	High	CF > 6	Very high contamination	RI ≥ 600	Very high
Er ≥ 320	Very high	– <sup>a</sup>	–	–	–

<sup>a</sup> No data

**Table 7** CF, EF, Igeo, Er and TU values of elements in sediment samples

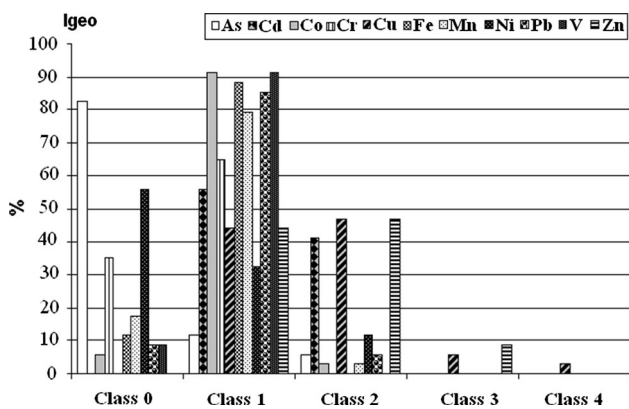
	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
CF											
Min	0.26	1.66	1.22	0.96	1.92	1.35	1.13	0.96	1.34	1.19	1.71
Max	8.08	8.23	4.40	3.71	75.67	2.56	5.69	7.89	5.51	2.47	16.43
Mean	1.30	3.84	2.72	1.84	7.00	1.82	2.19	2.28	2.33	1.86	5.42
SD	1.63	1.57	0.76	0.65	12.4	0.26	0.85	1.70	0.86	0.27	3.45
EF											
Min	0.22	0.68	0.81	0.49	0.84	0.66	0.65	0.42	0.80	0.72	0.96
Max	8.04	8.18	4.79	3.35	35.03	2.75	3.99	4.84	5.48	2.63	14.13
Mean	0.90	2.77	1.90	1.29	4.37	1.27	1.53	1.58	1.62	1.29	3.78
SD	1.42	1.78	0.90	0.65	5.84	0.50	0.81	1.20	0.93	0.50	2.82
Igeo											
Min	<0	0.10	<0	<0	0.25	<0	<0	<0	<0	<0	0.13
Max	1.68	1.70	1.08	0.20	3.92	0.53	1.33	1.66	1.30	0.50	2.39
Mean	0.84	0.86	0.60	0.18	1.15	0.22	0.42	0.80	0.43	0.24	1.14
SD	0.60	0.42	0.25	0.03	0.68	0.12	0.28	0.45	0.29	0.12	0.53
Er											
Min	2.60	49.80	–	1.92	9.60	–	–	4.80	6.70	–	1.71
Max	80.80	247	–	7.42	378	–	–	39.45	27.55	–	16.43
Mean	12.99	115	–	3.68	34.99	–	–	11.39	11.64	–	5.42
SD	16.35	47.19	–	1.31	62.01	–	–	8.49	4.33	–	3.45
TU											
Min	0.02	0.60	–	0.66	0.11	–	–	0.92	0.85	–	0.36
Max	0.52	2.98	–	2.56	4.42	–	–	7.60	3.49	–	3.48
Mean	0.085	1.394	–	1.272	0.408	–	–	2.196	1.473	–	1.145
SD	0.106	0.569	–	0.452	0.725	–	–	1.636	0.548	–	0.731

indicate a significant anthropogenic impact in sediment from the Pek, Ibar and West Morava Rivers. The mC<sub>d</sub> values in the Danube sediments indicate a low degree of contamination, whilst in other mC<sub>d</sub> sediment values indicate a moderate degree of contamination.

*Ecological toxicity (TU)*

Figure 3 shows the TU value for each metal and the sum of the TU values of all the trace elements in the

investigated sediments. The PEL values used for calculating the TU in this paper are shown in Table 4. The average trace element TU at the investigated localities followed the order: Ni > Pb > Cd > Cr > Zn > Cu > As. Based on the mean value of ΣTU, it can be concluded that potential toxicity existed for the quoted elements. All the values were higher than 4. From the toxic unit values, stations I1 and I2 (Ibar), Z2 (West Morava), V2 (Great Morava 2) and Pe (Pek) are more polluted compared to the others (ΣTU > 10).



**Fig. 2** Index of geoaccumulation (*Igeo*) of analysed elements in the sediments

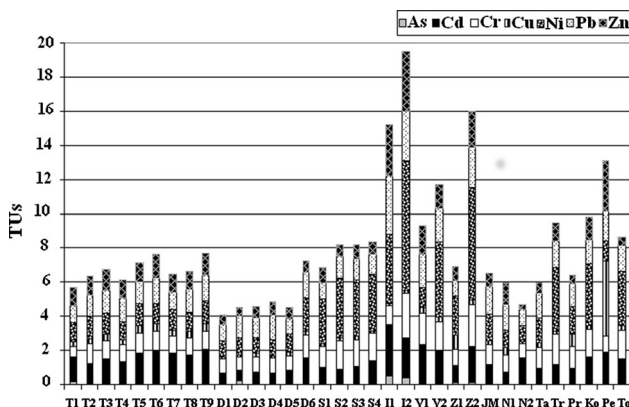
**Table 8** The average values of RI, PLI, CPI, mCd and TU in sediment samples

	RI	PLI	CPI	mCd	TU
Min	87.29	1.40	1.65	1.65	4.07
Max	575	4.27	10.19	10.19	19.46
Mean	195	2.37	2.96	2.96	7.974
SD	97.03	0.64	1.50	1.50	3.486

Trace elements and sample site grouping using principal component analysis (PCA) and hierarchical cluster analysis (HCA)

**PCA**

A PCA with Varimax normalised rotation was performed in this research. The scores and loadings of the principal components are presented in Table 9 and Fig. 4. PC1, explaining 60.86 % of the total variance, has strong positive loadings for Fe, Mn, Co, Cr, V, Pb, Cd, and Ni. PC2, explaining 15.67 % of the total variance, has strong



**Fig. 3** The TU of each element and the sum of TUs of elements in the investigated sediments

loadings for As, Pb, Zn, Cd and Ni. PC3, explaining 10.58 % of the total variance, has a strong positive loading on Cu.

Figure 5 displays isolated three groups of samples: 20 (I1), 21 (I2), 23 (V2) and 25 (Z2)—first group, 33 (Pe)—second group, and the other sediment samples constitute the third group. With regard to PCA (Q mode), sampling site 33 (Pek river) has the most polluted river sediments at the investigated localities. The contribution of Cu to the overall pollution is the most significant compared to other elements in this sediment. In the group with samples 20, 21, 23 and 25, the sediment with significant pollution is compared to other moderately polluted studied sediments.

**HCA**

Hierarchical cluster analysis (HCA) was performed on the dataset on both variables (R mode) and samples (Q mode), to identify clusters of elements and sites. The hierarchical methods are used because they are not limited to pre-determined numbers of clusters and can display the similarity of samples across a wide range of scales.

The results of the CA (R mode) are shown in a dendrogram (Fig. 6) where all the elements were grouped into four significant clusters: cluster 1 includes Fe, V, Co, Cr and Mn; cluster 2 contains Pb, Zn, Cd, and Ni, cluster 3 contains Cu, and cluster 4 contains As.

The results of the spatial cluster analysis (Q mode) are shown in a dendrogram (Fig. 7), where all 34 river sediment sampling sites were grouped into four significant clusters: Cluster 1 (T2–T9, V1, D1, D3–D6, Ta, JM, N1, and N2, CPI mean is 2.50, TU mean is 6.26), Cluster 2 (V2, Ko, Z2, S1–S4, Tr, To, Z1, Pr, T1, and D2, CPI mean is

**Table 9** Loadings of experimental variables on significant principal components for the river sediments in Serbia

	PC1	PC2	PC3
As		0.906	
Fe	0.933		
Mn	0.778		
Co	0.933		
Cr	0.862		
Pb	0.590	0.720	
Zn		0.774	
Cd	0.596	0.624	
Ni	0.579	0.630	
Cu			0.893
V	0.911		
Eigenvalue	6.694	1.724	1.164
% Total variance	60.855	15.669	10.578
Cumulative % variance	60.855	76.525	87.103

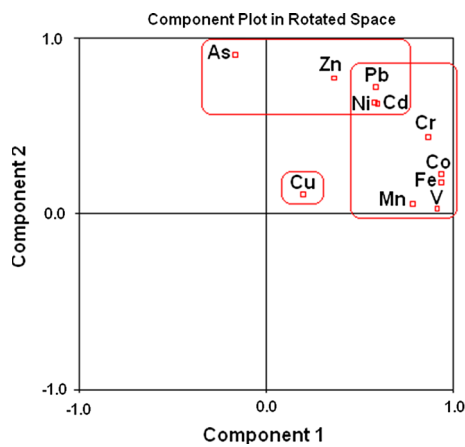


Fig. 4 PCA of selected elements (R mode)

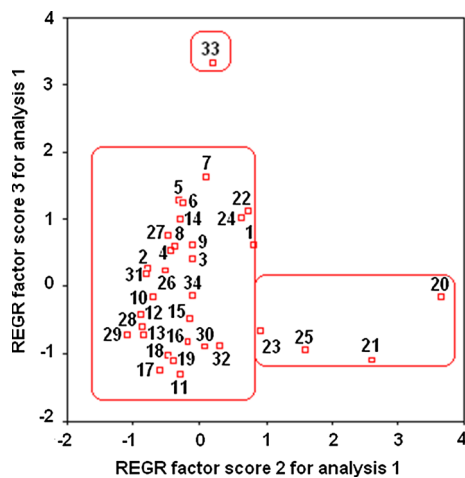


Fig. 5 PCA of selected elements (Q mode). Explanation: 1–9 (Tisa), 10–15 (Danube), 16–19 (Sava), 20, 21 (Ibar), 22, 23 (Great Morava), 24, 25 (West Morava), 26 (Južna Morava), 27, 28 (Nišava), 29 (Tamiš), 30 (Topčiderska River), 31 (Porečka River), 32 (Kolubara), 33 (Pek), 34 (Toplica)

2.75, TU mean is 8.52), Cluster 3 (I1 and I2, CPI is 4.94 and TU mean is 17.35) and Cluster 4 (Pe, CPI is 10.18 and TU mean is 13.06). The sampling sites in Clusters 1, 2 and 3 represented sediments from relatively to moderate polluted regions. Cluster 4 site (river Pek) was located in high-pollution region.

The HCA results were similar to those obtained with PCA. Elements with similar origins are (1) Fe, V, Mn, Co and Cr; (2) Pb, Zn, Cd, As and Ni; and (3) Cu. It is observed that the sources of Cu are different from the other elements.

Fe, V, Mn, Co and Cr have a combined source and these elements are derived from both lithogenic and anthropogenic sources. Iron is abundant in the Earth’s crust, though the pollution indices suggest the existence of anthropogenic sources of this element at some localities. Also, enrichment is observed for Mn in some of sediments. Cr is

Dendrogram using Average Linkage (Between Groups)

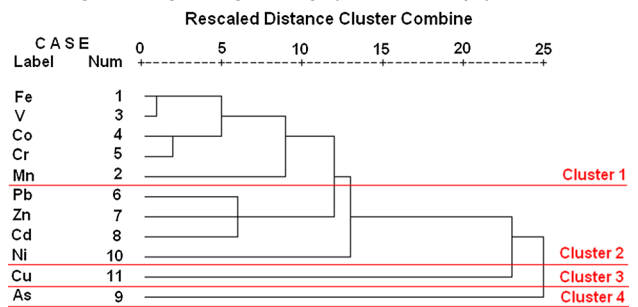


Fig. 6 Dendrogram showing clustering of the analysed elements

Dendrogram using Average Linkage (Between Groups)

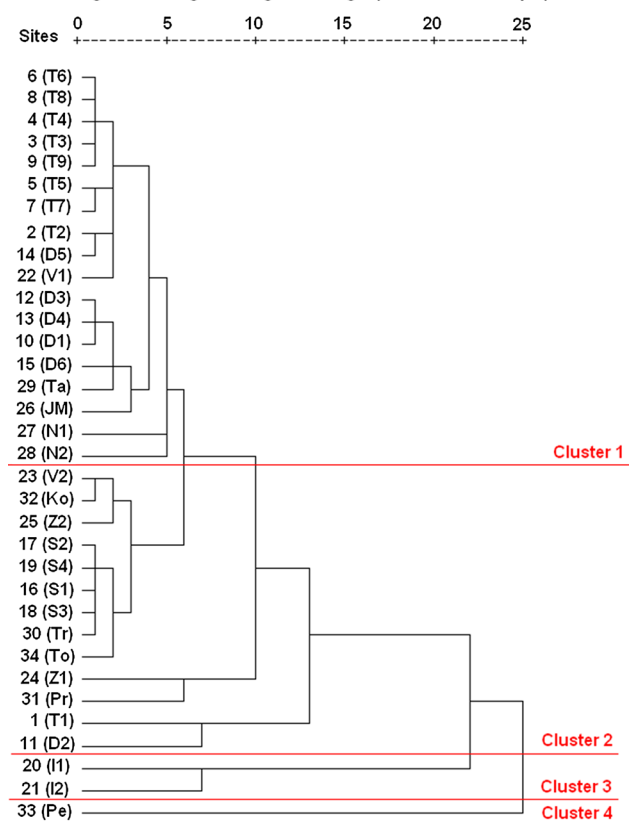


Fig. 7 Dendrogram showing clustering of sampling sites (HCA, Q mode)

generally a marker of the paint and metal industries, V is greatly impacted by anthropogenic activities such as mining and agricultural processes, and Co is mainly from anthropogenic signatures, i.e., paint, fertiliser or agrochemical industries (Li and Zhang, 2010). The low content of V, Co and Cr in the investigated sediments and the values of the calculated pollution indices, which indicate insignificant pollution, confirmed the mixed sources of Fe, V, Mn, Co and Cr at the studied locality.

Pb, Zn, Cd, As and Ni are likely to be mainly derived from anthropogenic sources. The significant anthropogenic

source of these elements is mining and smelting complexes in Serbia. These results are in accordance with Bird et al. (2010) that throughout the River Danube drainage basin, the mining and processing of metal ores lead to point-source releases of contaminant metals (Cd, Cu, Pb, Zn) and As to the local surface drainage network. The Trepca mining complex is the dominant source of lead and zinc. In addition to mining, anthropogenic sources of these elements may be direct discharges from local point sources, such as industrial and urban discharges carrying metal and metalloid contaminants. Contaminants mainly come from metallurgy and coal burning. Fertiliser and pesticides containing As can also lead to an increase in As. Ni is also mainly derived from anthropogenic activities, especially industrial sources (Gao et al. 2013).

Cu is derived from anthropogenic sources, most significantly from metallic wastewater discharges. The significant anthropogenic source of Cu is the open-pit mine in Majdanpek. Another source of Cu may be discharges from industries, as well as agricultural activities.

The obtained results indicate that the most polluted sediments at the studied localities are sediments from the Ibar and the Pek Rivers. Additionally, calculated indices suggest that the Great Morava and West Morava are also significantly polluted river systems. Pollution of these rivers is mainly caused by permanent and accidental pollution from industrial plants and mines that are located in the basins of these rivers.

One of the main sources of industrial pollution of the River Ibar is likely to be the Trepca mining complex. This huge industrial mining site had been in operation and engaged in large-scale exploitation since 1925. Since then, and until the year 2000, lead and zinc have been mined and smelted and the tailings still threaten the environment and keep polluting the Ibar (Pedersen and Klitgaard 2004). Results of Rexhepi et al. (2010) are shown that high zinc, lead and copper content in the sediment of Ibar River suggests that the lead and zinc smelter in Mitrovica still discharges strongly polluted effluents into this stream and that the high metal content could also reflect the accumulation of fine, strongly polluted particles in the river bed for a fairly long time.

The significant pollution with Cu of sediments from the Pek River is probably due to discharge from the Cu mining complex in Majdanpek. Bird et al. (2010) have shown that metal mining in Serbia is focused on the Bor and Majdanpek Cu deposits. The copper ore treatment process produced large amounts of ore waste and flotation tailing heaps, located in the vicinity of the towns of Bor and Majdanpek. In addition to permanent pollution, accidental pollution significantly affects the pollution of the Pek. The most serious incidents listed are the breaches of tailing dams at Majdanpek and Veliki Majdan causing direct,

serious contamination of the river Pek by heavy metals (Stuhlberger 2014).

In general, the results obtained using multivariate statistical analysis are consistent with that obtained using the calculation of pollution indices. Sediments in rivers in the same statistical grouping appear to indicate the same source of pollution and a similar degree of contamination. The applied methods can classify sediments in the whole investigated region according to the degree of pollution and to identify the main sources of toxic elements. The combined application of PCA and pollution indices can effectively identify the comprehensive and single pollution levels of elements in sediments, thus important to the extent determination of heavy metals pollution around the world.

## Conclusion

The impact of trace element pollution on the quality of the river sediments in Serbia was evaluated using CF, EF, Igeo, Er, RI, PLI, CPI,  $mC_d$ , and TU. The source identification carried out using multivariate analyses (PCA and CA) shows that (1) Fe, V, Mn, Co and Cr are derived from lithogenic and anthropogenic sources, (2) Pb, Zn, Cd, As and Ni are mainly derived from anthropogenic sources, and (3) Cu is derived from anthropogenic sources, most significantly from metallic wastewater discharges.

Contamination was observed in the studied elements, most of all with Zn, Cu and Cd. Cd and Cu present a higher ecological risk than any other element because of their higher toxicity coefficient. The potential Er varied amongst the studied elements in the sediments as well as in the different areas. The values of the PLI and  $mC_d$  suggest that the degree of contamination ranges from low to very high. The highest values of the pollution indices suggest a significant contribution of elements from anthropogenic sources in the river sediments from the Ibar, Pek, West Morava and Great Morava. Significant pollution indexes are also observed in the Tisa and Sava rivers. Pollution of these rivers is mainly caused by permanent and accidental pollution from industrial plants and mines that are located in the basins of these rivers. Significant influences are evident from mining complexes (mainly in Trepca and Majdanpek) on river contamination with toxic trace elements.

The above results confirmed the existence of pollution with trace elements in the studied river sediments. The calculated pollution indices and the appliance of statistical methods are recognised as useful for improving ecological risk assessment and the management of trace elements in sediments. A future fractionation sediment study is recommended to determine the proportion of the total metal pool that might be bioavailable.

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