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Seasonal variation in element concentrations in surface sediments of three rivers with different pollution input in Serbia

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Abstract
Purpose The main objective of this study was to evaluate the concentrations and seasonal variations of trace elements in surface sediments of three major rivers in Serbia—the Danube, the Zapadna Morava (ZM), and the Južna Morava (JM)—according to sediment quality guidelines. The ZM and the JM create the Velika Morava River, one of the most important tributaries of the Danube, which has been characterized as a source of heavy metal pollution.
Materials and methods The total concentrations of 15 elements (Al, As, B, Ba, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sr, and Zn) were determined in surface sediments (0–15 cm depth) collected during three seasons using inductively coupled plasma spectroscopy (ICP-OES). Principle component analysis (PCA) was used to identify the main variations in metal concentrations and grain size distribution. Scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDS) was used for grain analysis.
Results and discussion PCA and three-way MANOVA results showed significant differences in element concentrations and grain size distribution between the rivers, and significant seasonal differences for each river. The concentrations of Cu and Ni exceeded sediment quality guideline levels in the ZM and the Danube, respectively, while excess Hg was detected in all three rivers. Concentrations of Al, Ba, Cu, Fe, Sr, and Zn significantly varied between seasons in the Danube and the ZM, being the highest in the summer. In the JM, concentrations of Al, As, Fe, Mn, and Zn varied with season, with the lowest values in the summer. The ZM had the highest percentage of silt and clay, and SEM-EDS analysis of ZM sediments showed associations of Cu with carbonate hydroxides and/or iron oxides in particles <100 μm. The results suggested that mining and industrial activities could be the sources of increased levels of metals in the ZM.
Conclusions The sediments collected from the ZM were considerably more polluted with heavy metals in comparison to the JM. Cu was identified as a heavy metal of greatest risk in the ZM. The ZM was indicated as the main source of heavy metal delivery in the Velika Morava and Danube rivers. It is suggested that the main factors influencing pollution levels could be anthropogenic sources and industrial and mining activities, while seasonal changes might be related to dynamics of water flow and morphological characteristics of the two tributary rivers.

Keywords Heavy metals · Particle size · River sediments · Danube · Zapadna Morava · Južna Morava

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Abbreviations

ICP-OES	Inductively coupled plasma optical emission spectroscopy
SEM-EDS	Scanning electron microscopy/energy dispersive X-ray spectroscopy

1 Introduction

Environmental pollution is one of the biggest challenges of modern society. High contamination of aquatic systems with heavy metals requires additional efforts to understand and minimize its effects, since these elements are not biodegradable and their elevated uptake by various organisms may affect all species in an ecosystem (Fernandes et al. 2007; Abdel-Baki et al. 2011). Therefore, metals are often defined as "chemical time bombs" (Stigliani 1993). Bioassimilation, bioaccumulation, and biomagnification of metals in aquatic organisms results in potential long-term effects on human health and on the ecosystem itself (Snodgrass et al. 2008; Besser et al. 2009; Suthar et al. 2009).

There are two major routes for metals to enter aquatic environments: natural, via rock weathering and erosion, and from anthropogenic sources. Anthropogenic sources include a complex combination of urban, industrial, and agricultural activities; terrestrial and storm water runoff; and sewage disposal (Schueler 2000; Çevik et al. 2009). In most circumstances, the main input of metals into sediments comes from mining and industrial plants along the rivers (Ridgway et al. 2003; Sundaray et al. 2011). Some of the established hotspots of metal contamination are in the proximity of industrial plants (Buccolieri et al. 2006). In the last few decades, emissions of metals have declined in developed countries (Voet et al. 2000; Hjortenkrans et al. 2006); however, in developing countries, metal emissions are growing due to increased industrialization and urbanization (Govil et al. 2008; Wu et al. 2011). Developing countries, as diverse as Egypt, Algeria, China, and Colombia, have invested substantial sums in wastewater treatment without achieving a significant impact in terms of environmental improvement (Abdel-Dayem et al. 2007; GWI 2010). Various studies have demonstrated that concentrations of metals in sediments can be sensitive indicators of overall contamination of aquatic systems (Bellucci et al. 2002). Once metals reach aquatic sediments, they can be immobilized by processes such as flocculation, adsorption, and coprecipitation (Caccia et al. 2003). Aquatic sediments can either retain metals or release them into the water column through various processes of remobilization (Pekey 2006).

The speciation of metals in sediment depends on geological background levels, concentration of chelating/complexing agents, pH, and ion-exchange properties of the sediment (Luoma 1983). The determination of metal concentrations in sediments can be a sensitive indicator of the overall contamination in aquatic systems (Bellucci et al. 2002) and represents a useful tool for identification of anthropogenic contamination sources (Bidhendi et al. 2007).

The aim of this study was to determine concentrations of heavy metals in surface sediment cores of three rivers in Serbia—the Danube, the Zapadna Morava (ZM), and the Južna Morava (JM)—in different seasons. The Danube was chosen as a major European river that runs through highly populated and industrialized countries. Both ZM and JM are tributaries of the Velika Morava that flows into the Danube; the first one receives excessive pollution from industry and agriculture, while the second one runs through a less densely populated and industrialized region. To our knowledge, there are no existing reports considering the metal accumulation in sediments of the ZM and JM.

2 Material and methods

2.1 Study area

A topographic map of all three rivers is shown in Fig. 1. Of approximately 2800 km of the total length of the Danube River, 599 km (approximately 20 %) flows through Serbia. The Danube River basin covers 87 % of the Serbian territory. It also represents the most developed and the most densely populated part of Serbia and comprises the Tisza River sub-basin, the Sava River sub-basin, and the Velika Morava sub-basin. The average width of the Danube in Serbia is 1 km, thus forming a total water surface of 520 km^2 with an average flow rate of 2500 $m^3\ s^{-1}$, (Gavrilović and Dukić 2014). Nowadays, the alluvial area of the Danube is ~1000 km^2, while the reservoir of the hydroelectric power plant Iron Gate I has a surface area of ~253 km^2 and that of Iron Gate II is ~80 km^2. The Serbian section of the Danube mainly covers the region of the Middle and, partly, the Lower Danube, with a relatively low overall river slope value (Gavrilović and Dukić 2014).

The ZM River is 308 km long. Its average flow rate is 120 $m^3\ s^{-1}$ (Gavrilović and Dukić 2014) and it has a large number of meanders. All rivers in its basin have a snow–rain regime, with substantial amounts of water during the spring season and minimal water flow during the summer season. The ZM basin is exposed to heavy anthropogenic influences from the highly populated area through which it flows (Gavrilović and Dukić 2014).

The JM River is 295 km long. Its average flow rate is 100 $m^3\ s^{-1}$. It runs through a complex valley that is composed of a number of crags and ravines. The JM connects the Aegean and the Pannonian basin. Due to a large amount of erosion in its basin, this river is rich in sediments (Gavrilović and Dukić 2014).

2.2 Sample collection

The three chosen sampling sites were in the region of Belgrade (the Danube River-D), the region of Southern and Eastearn Serbia (the JM River), and the region of Šumadija and Western Serbia (the ZM River). The

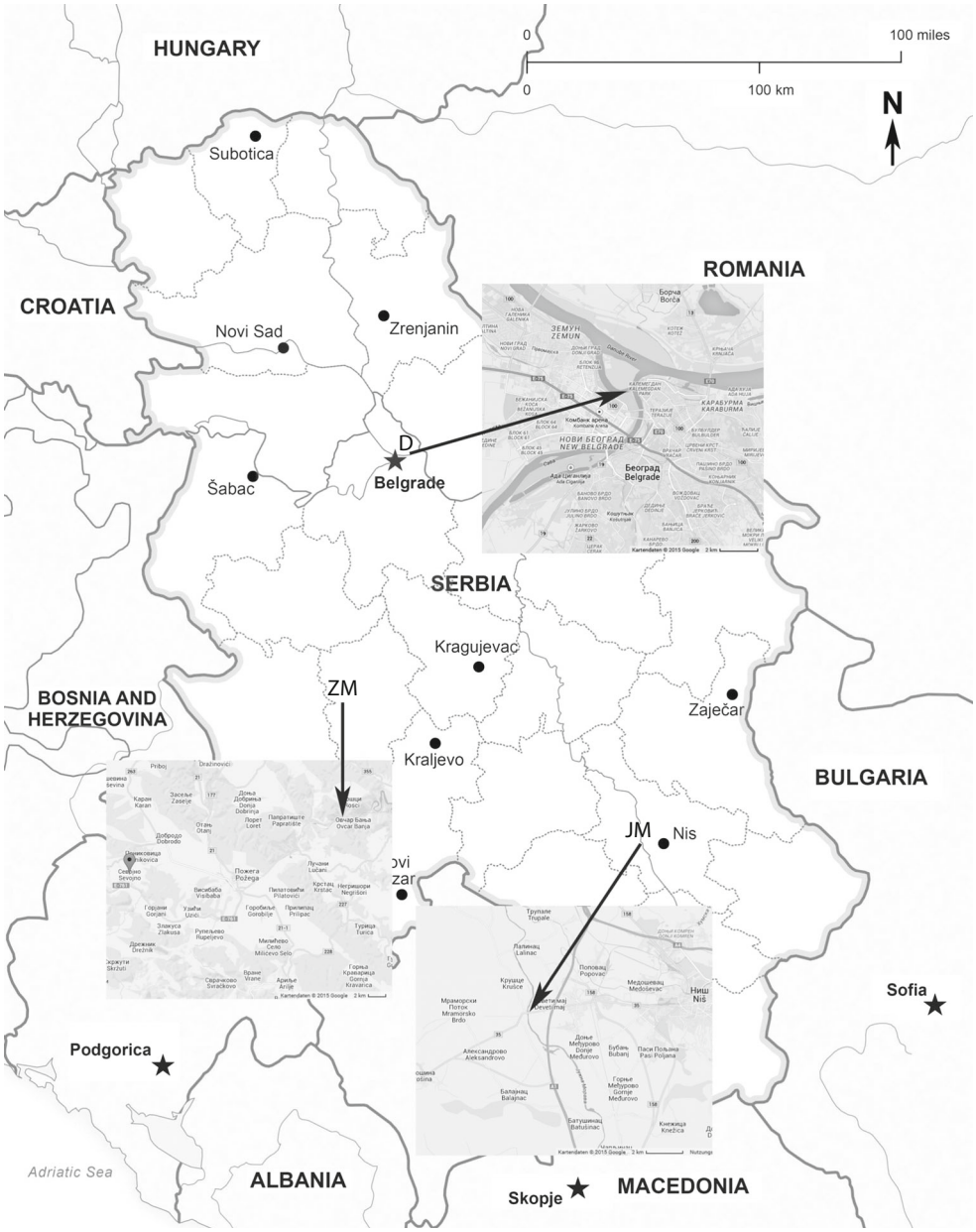

Fig. 1 Map of the sampling area in Serbia. Positions of sampling sites on the rivers of Danube (D), Zapadna Morava (ZM), and Južna Morava (JM) are indicated by arrows. Sediments samples were collected from 0–15 cm depth in April, July, and November 2012

sampling was done in three seasons, April, July, and November 2012. One spot was selected on each river and a 10-m long transect line starting from the river bank was positioned at the river bottom (the Danube 44° 49′ 22.04″ N, 20° 26′ 17.60″ E, 77 m above the sea level (asl); the ZM 43° 53′ 56.97″ N, 20° 10′ 47.18″ E, 308 m asl; the JM 43° 18′ 47.84″ N, 21° 47′ 9.31″ E, 178 m asl; Fig. 1). On each river, three samples were taken along the 10-m long transect starting from the river bank using 20-cm long plastic tube corers for every season. Tube corers were carefully pushed in the sediment to minimize compaction and rotated during insertion. Afterwards, the tube was withdrawn and the sample collected. In total, 27 sediment cores were collected. Sediments were transferred to the laboratory and, in order to preserve the sediment profile, cores were frozen at 0 °C. Afterwards, all cores were cut into 5-cm long increments (0–5, 5–10, and 10–15 cm) and dried to a constant weight. Sediments from the Danube were collected by SCUBA diving using the same method, while the other two rivers were shallower and sampling did not require diving.

2.3 Size fractionation

Dried sediment samples were fractionated into eight sizes using a nest of sieves: <63 μm, 63–125 μm, 125–250 μm, 250–500 μm, 500 μm–1 mm, 1–2 mm, and >2 mm

(Laboratory Test Sieve BS 410–1, Endecotts Ltd., UK) according to the method of Blott and Pye (2001).

2.4 Determination of total element concentrations

Sediment samples were dried at 70 °C to a constant weight and then homogenized with a pestle and mortar. Samples were used for determination of total element content (all fractions with different mobility and availability). For the total element content, 0.4 g of the sediment sample was digested in 10 ml 69 % HNO_3 (Merck Suprapure, Darmstadt, Germany) in a microwave oven (Speedwave MWS-3+; Berghof Products + Instruments GmbH, Germany) and diluted to 25 ml using deionized water. All samples were filtered before analysis. For quality assurance, one duplicate sample was collected at every site in every season to test variability. Metal concentrations were measured using inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectro-Genesis EOP II; Spectro Analytical Instruments GmbH, Kleve, Germany). Calibration curves were obtained after proper dilution of ICP multi-element standard solution (1000 mg l^{-1}; Merck, Germany).

2.5 SEM-EDS analysis

Sediment samples from ZM, which contained the highest concentration of Cu, were chosen for scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis. Dry samples were passed through a 1-mm sieve and small amounts were fixed on a supporting plate with double-faced tape and coated with gold. Analysis was performed with JEOL JSM-6610LV SEM instrument (Tokyo, Japan) equipped with X-Max Large Area Analytical Silicon Drift connected with INCA Energy 350 Microanalysis System at 25 kV accelerating voltage.

2.6 Statistical analysis

Principal component analysis (PCA) was applied to analyze the data. PCA was used as an unsupervised statistical method to identify the main variations in a data set. The untreated data for elemental concentrations in each river and season, as well as granulation of sediments, were used as input variables. PCA was used for visualization and exploration of variations in a data set. Calculations were performed using the Solo version 7.0 (Eigenvector Inc., Chelan, WA, USA) software package. Exploratory and descriptive data analysis was performed using the SPSS 13.0 software. A three-way MANOVA was used to test the differences between levels of 15 elements (Al, As, B, Ba, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sr, and Zn) in sediments of the three rivers (Danube, ZM, and JM) in three seasons (April, July, and November) at depths of 5, 10, and 15 cm (in total nine sediments per river, three per season). Tests of homogeneity of variances based on Levene statistics were used. As ANOVA is robust to the violation of the null hypothesis—that the group variances are equal when the groups are of approximately equal size—it was used in the analyses, and post-hoc intergroup comparisons of elemental levels (between pairs within the rivers) were performed by Duncan's (equal variances assumed) and Tamhane's tests (equal variances not assumed). One-way MANOVA was used to test the differences between grain size of the sediment cores of the three rivers (Danube, ZM, and JM) and post hoc intergroup comparisons were performed by Duncan's test.

3 Results

3.1 Concentrations of elements in river sediments

Average metal concentrations over three seasons significantly differed between the rivers (Table 1). The Danube sediments had the highest concentrations of Pb and Ba, while both the Danube and the ZM had higher concentrations of Fe, Co, and B than the JM. All three rivers differed from each other in concentrations of Al, Cr, Cu, Ni, Zn, Mn, and Sr in the following order: Danube > ZM > JM, except for Cu, which was the highest in the ZM. Average concentrations of Hg and Mo were similar for all three rivers (Table 1). The concentration of Ni in the Danube and the ZM in all three sampling periods was higher than the maximum allowed concentrations (MAC) based on the National Standards of the Republic of Serbia issued in the National regulation for borderline values of metals in river sediments in the Republic of Serbia (2014). In addition, the level of Hg was above the maximum allowed concentrations in all three rivers, and the level of Cu in the ZM was above the maximum allowed concentration in all three sampling periods. Concentrations of As, Cr, Pb, and Zn were below MAC. There is no regulation in Serbia regarding maximum levels for other heavy metals and trace elements.

The Danube and the ZM had higher concentrations of Al, Cr, Fe, Ni, and Zn than in the JM in all three seasons (Table 2). In addition, the Danube had the highest concentrations of Pb, B, and Sr, while the ZM had the highest concentrations of Cu. Concentrations of Al, Ba, Cr, Cu, Fe, Sr, and Zn significantly differed between the seasons in the Danube with the highest concentrations in July. Differences between seasons in Al, As, B, Ba, Cu, Fe, Hg, Mn, Ni, Sr, and Zn concentrations were also observed in the sediments of the ZM with the highest concentrations also in July. In the JM, only the concentrations of

Table 1 Total heavy metal concentrations (mg kg^{-1}) in the sediments of the Danube, the Zapadna Morava (ZM), and the Južna Morava (JM) (mean± standard deviation)

River	Danube	Zapadna Morava	Južna Morava	MAC (mg kg^{-1})
Element	Mean±standard deviation (mg kg^{-1})			
Al	10591.31±3521.31[a]	8328.17±3344.92[b]	3851.72±1529.14[c]	n.a.
As	21.58±16.65[a]	16.33±5.84[a,b]	11.08±11.70[b]	42
B	118.92±39.85[a]	113.82±43.78[a]	75.58±46.28[b]	n.a.
Ba	128.09±34.95[a]	66.57±40.37[b]	61.09±46.62[b]	n.a.
Co	15.61±7.23[a]	14.40±11.62[a]	8.83±8.43[b]	n.a.
Cr	101.57±40.78[a]	80.34±31.40[b]	22.99±10.48[c]	240
Cu	65.04±39.28[a]	188.57±98.22[b]	10.53±5.35[c]	110
Fe	23064.12±6128.92[a]	23237.56±6557.87[a]	9400.78±3365.68[b]	n.a.
Hg	16.67±10.00	14.48±8.64	18.76±15.95	1.6
Mn	626.07±210.84[a]	418.42±153.00[b]	272.96±119.70[c]	n.a.
Mo	19.48±20.02	32.18±77.00	20.10±32.84	n.a.
Ni	108.52±22.01[a]	92.67±20.96[b]	27.75±20.97[c]	44
Pb	90.09±44.38[a]	50.14±67.04[b]	38.98±53.47[b]	310
Sr	95.13±32.27[a]	36.95±13.43[b]	22.53±12.61[c]	n.a.
Zn	250.86±80.82[a]	143.33±56.36[b]	47.36±17.98[c]	430

The values with different letters (a, b, c) in the same row are significantly different (Duncan's or Tamhane's test, $p<0.05$). MAC-Maximal acceptable concentrations provided by national regulation for borderline values of metals in river sediments in the Republic of Serbia

n.a. not available

Al, As, Fe, Mn, and Zn showed statistically significant seasonal differences, with higher values in samples collected during April and November.

Figure 2a displays the PCA score plot for the first and second components of all samples and they explain 61.14 % of the variance. It exposes the best separation of sediments in the three rivers based on element concentrations. The Danube sediments were mostly differentiated by high levels of Pb, Zn, Ba, Mn, Cr, Ni, Al, and Sr. The ZM sediments were rich in Cu, while the JM sediments were less polluted. Differentiation of sediments from the ZM with higher concentrations of Cu is in accordance with anthropogenic input of this element into ZM (Fig. 2a).

MANOVA showed that depth was not a significant factor (depth, $F=1.555$, $p=0.058$; river*depth, $F=0.855$, $p=0.777$; season*depth, $F=1.163$, $p=0.222$; Table S1—Electronic Supplementary Material) and hence it was removed from further analyses.

PCA biplots of seasonal variations in element concentrations in sediment samples are presented on Fig. 2b–d. The first and second components explain 63.75, 82.9, and 72.3 % of variance in elemental concentrations of sediments collected in the Danube, the ZM, and the JM, respectively. Higher concentrations of elements were measured in the samples collected during July in the Danube (Fig. 2b) and the ZM (Fig. 2c), while samples collected during April and November had lower concentrations of investigated elements. In the JM, lower metal concentrations were observed in July compared to that in April and November (Fig. 2d).

3.2 Analysis of the sediment grain size

Grain size distribution was similar at all three depths (0–5, 5–10, and 10–15 cm) in all three rivers (Table 3). Analysis indicated that most sediments collected from the JM consisted generally of medium sand (65 %) and fine sand (22 %), and no grains >1 mm were found. In the Danube, grains from silt to gravel were found, mostly as coarse sand (17 %) and very coarse sand (22 %). One-way MANOVA showed significant differences in grain size among the three rivers ($F=26.022$, $p<0.001$). The ZM had the highest percentage of silt and very fine sand (about 13 % each). The ZM had significantly higher content of silt than the Danube and the JM. On the contrary, the JM had significantly higher contents of fine and medium sand than the other two rivers, but the lowest content of both silt and very fine sand (Table 3).

Figure 3 displays the PCA for the first and the second component which explain 78.17 % of variance among three rivers sediments based on sediment granulation. It clearly differentiated the JM sediments with particle sizes of 125–250 and 250–500 μm from the grain size of sediments in the Danube and the ZM.

Table 2 Total heavy metal concentrations in the sediments of the Danube, the Zapadna Morava (ZM), and the Južna Morava (JM) in three seasons (mean±standard deviation)

Element	River								
	Danube			Zapadna Morava			Južna Morava		
	April	July	November	April	July	November	April	July	November
Al (g kg^{-1})	11.7±4.7^{a,b}	11.7±2.7^{a}	8.2±1.9^{b}	8.4±3.1^{a,b}	10.2±1.9^{b}	6.1±3.5^{a}	4.4±1.1^{a}	2.7±8.1^{b}	4.7±1.9^{a}
As (mg kg^{-1})	32.3±25.4	17.9±3.9	14.5±6.6	17.7±5.0^{a}	19.0±5.3^{a}	11.9±4.3^{b}	16.2±12.1^{a}	3.2±2.1^{b}	14.0±13.8^{a,b}
B (mg kg^{-1})	106.7±63.1	133.0±24.4	117.1±13.7	89.1±59.0^{a,b}	142.3±15.9^{a}	103.2±31.0^{b}	66.3±57.0	72.5±51.1	89.3±24.6
Ba (mg kg^{-1})	135.3±42.2^{a,b}	147.4±22.0^{a}	101.6±21.0^{b}	54.0±30.3^{a}	94.5±93.0^{b}	46.0±23.9^{a}	71.6±57.0	32.6±9.4	81.2±47.9
Co (mg kg^{-1})	18.4±11.5	14.6±2.1	13.8±4.5	11.0±3.7	20.4±16.9	10.4±2.9	10.7±9.8	4.5±1.3	11.5±10.2
Cr (mg kg^{-1})	82.0±30.9^{a}	126.7±30.1^{b}	96.1±48.6^{a,b}	61.9±32.7	91.4±20.6	84.0±34.4	19.3±10.1	25.3±7.5	24.3±13.4
Cu (mg kg^{-1})	41.0±12.0 ^{a}	104.2±43.9 ^{b}	49.9±17.7 ^{a}	178.4±75.6^{a,b}	259.3±39.1^{a}	124.0±112.7^{b}	11.1±5.5	7.3±2.3	13.4±6.1
Fe (g kg^{-1})	23.5±7.4^{a,b}	26.1±3.8^{b}	19.5±5.2^{a}	23.7±6.3^{a,b}	26.5±3.9^{a}	19.1±7.0^{b}	10.8±2.5^{a}	6.8±1.7^{b}	10.5±4.1^{a,b}
Hg (mg kg^{-1})	16.3±14.6	14.5±6.0	19.3±8.0	9.7±9.1^{a}	20.0±7.6^{b}	12.3±6.0^{a,b}	18.3±18.3	17.6±16.2	20.5±14.6
Mn (mg kg^{-1})	625.4±256.7	739.9±152.5	513.00±162.4	416.7±148.7^{a,b}	515.1±81.7^{a}	311.1±148.6^{b}	283.3±62.0^{a}	186.5±47.2^{b}	358.6±161.5^{a,b}
Mo (mg kg^{-1})	30.2±31.3	14.6±8.4	13.7±7.8	86.2±130.2	11.8±6.7	7.8±5.3	34.9±52.3	11.1±11.5	13.3±12.4
Ni (mg kg^{-1})	108.5±19.6	117.7±24.9	99.4±19.5	79.7±25.4^{a}	102.9±12.4^{b}	92.3±18.5^{a,b}	29.0±24.6	21.1±8.2	33.7±26.4
Pb (mg kg^{-1})	104.6±75.2	86.4±14.1	79.3±13.0	30.3±18.1	84.9±98.6	28.2±14.7	45.9±64.1	18.3±7.8	54.3±67.5
Sr (mg kg^{-1})	65.6±20.6^{a}	121.8±14.8^{b}	97.9±30.9^{c}	35.2±14.0^{a,b}	45.3±5.3^{a}	28.9±13.7^{b}	20.5±6.9	16.6±5.5	31.3±18.4
Zn (mg kg^{-1})	229.9±74.7^{a}	325.7±49.8^{b}	197.0±55.8^{c}	142.6±43.0^{a,b}	177.9±33.2^{a}	104.9±63.0^{b}	55.2±14.7^{a}	32.2±9.0^{b}	55.4±19.0^{a}

The values with different letters (a, b, c) in the same row for one river are significantly different (Duncan's or Tamhane's test, $p<0.05$). Bold letters indicate Tamhane's test

Sediment particles in the ZM were differentiated with the particle size of <63 and 63–125 μm, while particles in the Danube had variable sizes.

3.3 SEM-EDS analysis of sediment particles

The content of mineral species along the ZM sediment core at 0–15 cm depth was similar, and quartz, alkaline feldspar, mica, gypsum, pyrite, and calcite were commonly observed. Iron oxides and hydroxides were also observed as well as different Cu phases. SEM-EDS analyses of the ZM sediment samples showed that Cu was present in the form of carbonate hydroxides, most likely malachite ($Cu_2(CO_3)(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$) (Fig. 4, Spectrums 1–4, Table 4).

4 Discussion

The Danube Delta is the best preserved and the second largest delta in Europe and represents a habitat for over 300 bird species and 45 freshwater fish species (Gâștescu 2009). Therefore, it is important to determine the factors which may affect overall heavy metal concentrations in the Danube Delta sediments, such as the levels and dynamics of heavy metals in the sediments of the Danube tributaries. The Velika Morava represents one of the main tributaries of the Danube in Serbia, and it enters the Danube 1103 km before entering the Black Sea, delivering a large amount of sediment. This 185-km long river is created from the ZM and JM rivers (Gavrilović and Dukić 2014).

We observed higher average concentrations of Al, B, Co, Cr, Cu, Fe, Mn, and Ni and different seasonal dynamics in the ZM than in the JM sediments (Tables 1 and 2, Fig. 2a, c, d). On the other hand, the Danube had the highest average concentrations of Zn, Pb, Ni, Mn, Cr, Al, and Sr of all the three rivers (Table 1, Fig. 2a, b). Concentrations of Pb, Zn, Ni, Cr, and As measured in the sediments of the three rivers in this study are within the range of concentrations reported for another Danube tributary in Serbia, the River Sava, while Cu concentrations measured in the ZM exceed the values reported for the River Sava (Milačić et al. 2010). However, in comparison with the earlier reports on metal concentrations in the Danube at several locations in Serbia (Milenković et al. 2005), we measured higher contents of Pb, As, and Cu in its sediments. Milenković et al. (2005) measured the concentrations of heavy metals before and after the confluence of the Velika Morava River and the Danube River and the reported Cu, Cr, Ni, Pb, and Zn values were much higher after

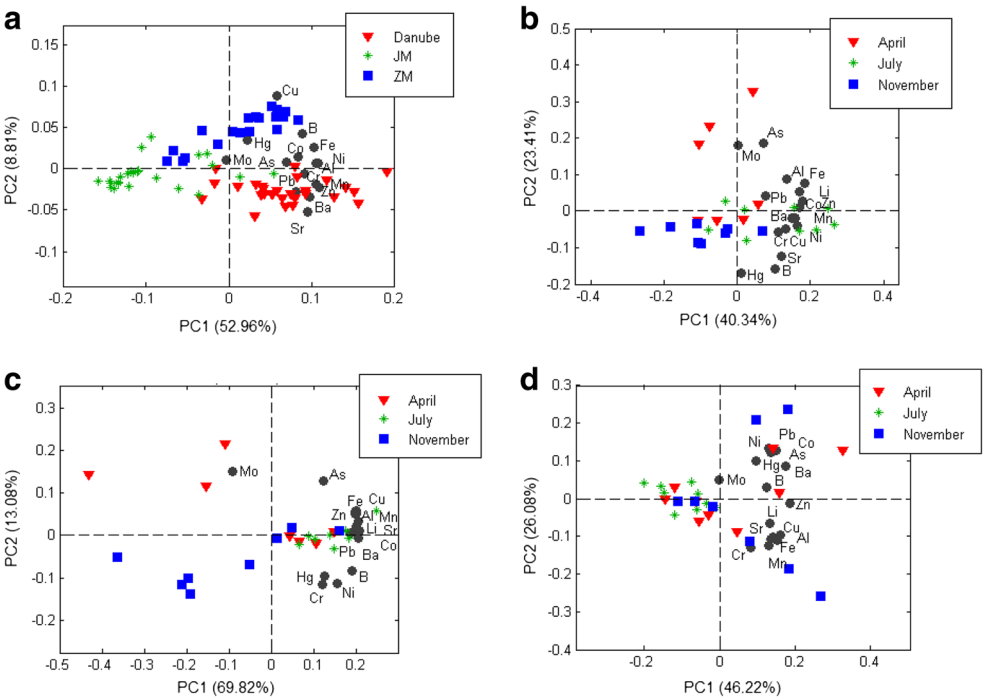

Fig. 2 The PCA plots of elemental concentrations in sediments of the Danube, the Zapadna Morava (ZM), and the Južna Morava (JM) rivers. Average element concentrations for all three rivers (**a**), seasonal changes in element concentrations in the Danube (**b**), the Zapadna Morava (**c**), and the Južna Morava (**d**)

the confluence (Milenković et al. 2005). Thus, we can assume that heavy metal pollution is delivered by the ZM into the Danube, since the concentrations of these metals in the JM sediments were significantly lower compared to the ZM sediments (Table 1). Extensive study within the Joint Danube Survey (Woitke at al. 2003) identified zones with increased heavy metal concentrations from 1300 to 1000 km from the Danube Delta. The area includes the Velika Morava tributary catchment, and this river was identified as one of the specific point sources of heavy metal pollution (Woitke et al. 2003). Our results support these findings, while higher contents of Pb, Ni, Cr, and Zn in the Danube than reported by Woitke et al. (2003) may indicate that, with time, the accumulation of metals in the sediments has increased. Sediment material is susceptible to downstream transportation by water flow from the source area towards the outlet of the river basin. At the end of the river, much of the sediment is deposited in the estuary and on the seabed of the coastal zone, which may result in increased metal accumulation (Rovira et al. 2014).

The ZM river basin is much more economically developed than the JM River basin. Common for all settlements along its banks are very old sewage networks, without filtering plants for the treatment of the industrial sewage coming from wood, textile, and metal industries. Moreover, intensive agriculture is yet another diffuse source that affects the pollution level in the ZM (Urošev 2006). Upstream from the sampling site, Cu

Table 3 Grain size composition of the sediments of the Danube, the Zapadna Morava (ZM), and the Južna Morava (JM) (mean± standard deviation)

River Grain size	Danube	Zapadna Morava Mean±standard deviation (%)	Južna Morava
<63 μm (silt and clay)	9.39±7.00^{a}	13.23±3.06^{b}	2.21±1.75^{c}
63–125 μm (very fine sand)	9.25±3.42^{a}	12.55±5.44^{a}	4.15±2.64^{b}
125–250 μm (fine sand)	9.99±7.79^{a}	8.82±4.02^{a}	22.39±9.62^{b}
250–500 μm (medim sand)	9.79±2.41^{a}	11.19±2.90^{a}	64.32±13.66^{b}
0.5–1 mm (coarse sand)	16.62±5.23^{a}	19.76±9.01^{a}	6.94±3.99^{b}
1–2 mm (very coarse sand)	21.54±5.06^{a}	15.84±6.07^{b}	n.d.
>2 mm (gravel)	23.43±9.63^{a}	18.61±11.65^{a}	n.d.

The values with different letters (a, b, c) in the same row are significantly different (Duncan's test, $p<0.05$)
n.d. not detected

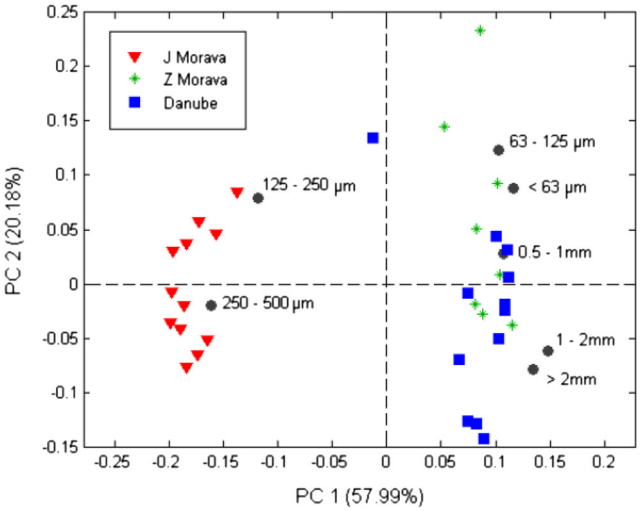

Fig. 3 The PCA plot of particle sizes in sediments of the Danube, the Zapadna Morava (ZM), and the Južna Morava (JM) rivers

and Al rolling mills are located in the town of Sevojno (Fig. 1) and their industrial waste is discharged directly in the river without pre-treating. The ZM river basin is also very rich in chromium ore and coal. Some of the most used transportation routes, accompanied by railway tracks, are positioned along the ZM flow path that runs through Central Serbia. Roads and parking lots are major sources of Ni, Cu, Zn, Cd, and Pb (Wei and Yang 2010; Duong and Lee 2011) and can also contribute to river pollution. The ZM is known as a river that often floods. During flooding, fertile agricultural land can be contaminated by metals from the river sediments (Krüger et al. 2005; Adamo et al. 2006) which can enter food webs.

Copper concentrations measured in the ZM (Table 1) exceeded the maximal allowed concentrations according to the national regulation for borderline values of metals in river sediments in the Republic of Serbia. Copper is associated with organic matter, oxides of iron and manganese, silicate, clays, and other minerals (Koshy 2002). It has been shown that Cu binding to organic matter is associated with fine sediments (Duong and Lee 2011). In this study, ZM had the highest values of silt and very coarse sand (Table 3, Fig. 3) compared to the Danube and JM, although the distribution of coarse particles in the Danube and ZM was similar. Positive correlation coefficients for Cu have been observed for silt and clay, but not sand, in river sediments by Rangel et al. (2011).

SEM analysis of the ZM sediments showed associations of Cu with high proportions of C and O, as well as a small proportion of Fe. These results indicate that Cu might be associated with carbonate hydroxides, most likely malachite and azurite or iron oxides and/or iron hydroxides (Fig. 4). Copper may bind to organic matter and iron oxides in river sediments (Yu et al. 2001). High Cu concentrations were reported in river sediments close to industrial and municipal waste sources (Chen et al. 2012) and mining activities (Sracek et al. 2012). Therefore, high Cu concentrations in the ZM sediments probably partly originate from a copper industry situated upstream of the sampling site.

Highest heavy metal concentrations were found in silt and clay sediment fractions in the Estrela River (Rangel et al. 2011) which corresponds to higher heavy metal concentration in the ZM sediment compared to the Danube and the JM. In the trace elements study of sediments in Odra River (Rybicka et al. 2005), metals were predominately bound to sediment particles <100 μm, and there was no significant difference in metal concentration at 0–15 cm depth. This can be correlated to observed differences in particle size between the rivers in this study (Table 3, Fig. 3).

During the summer, concentrations of metals increased compared to spring in both the Danube and the ZM, while an opposite trend was observed in the JM (Table 2, Fig. 2b–d). However, metal concentrations measured in autumn in both the ZM and JM were similar to the values measured in spring. The ZM and JM have different flow rates during the sampling periods. Average water flows of the ZM at the closest sampling point, Kratovska Stena (time period 1954–2005), were 55.0 $m^3 s^{-1}$ in April, 22.1 $m^3 s^{-1}$ in July, and 25.6 $m^3 s^{-1}$ in November. During the same time, at the sampling point Aleksinac, the JM had average flow rates of 174.1 $m^3 s^{-1}$ in April, 48.6 $m^3 s^{-1}$ in July, and 33.0 $m^3 s^{-1}$ in November. The highest values of Ba, Ni, Hg, and Cu were observed during the summer period in the ZM (Table 2), which corresponds to the minimal water flow rate and lowest mobility of the sediment, while metal concentrations decreased in autumn probably due to increased water flow originating from storm waters and the movement of small sediment grains downstream. Similarly, seasonal changes in the JM may be explained by variations in water flow and the influence of storm waters. Temporal changes in metal distribution were observed by Bednarova et al. (2013) in the Morava and Drevnice river basins. They indicated Cu as a major environmental risk, which is also suggested by our results on Cu levels in the ZM. Higher rainfall amounts, snow melting, and underground water levels in spring could all contribute to an increased metal runoff. In addition, the river morphology of the ZM (sandbars, meanders) may also determine the fate and mobility of pollutants compared to the JM. The smallest variations in seasonal changes were observed in the Danube, which is expected for a large water body.

Fig. 4 Images obtained by SEM-EDS analysis of sediment samples from the Zapadna Morava (ZM) River showing that Cu was observed as carbonate hydroxides. EDS spectra are shown below. The samples were coated with gold ▶

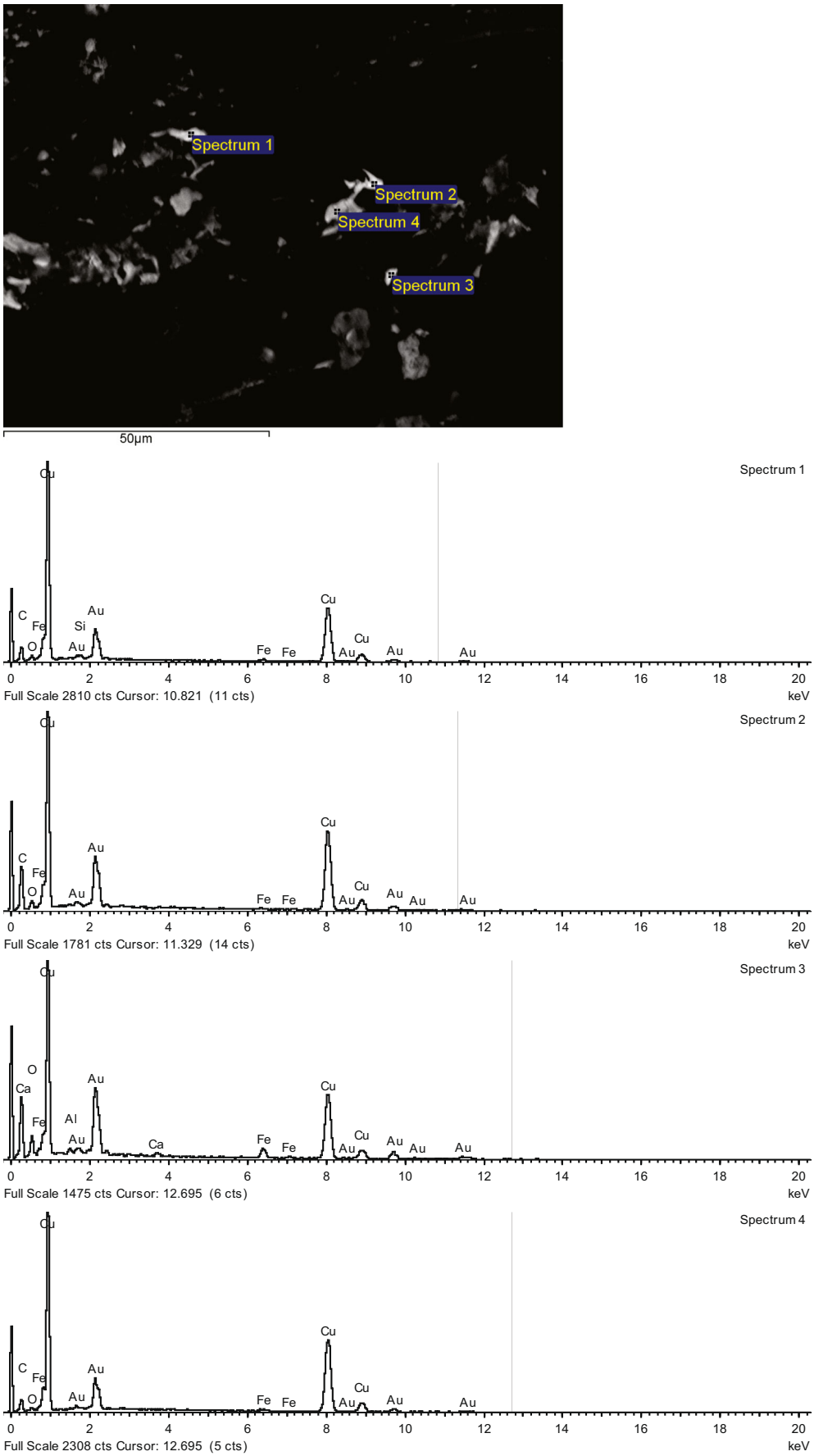
Spectrum 1
Spectrum 2
Spectrum 4
Spectrum 3
50µm
Spectrum 1
Cu
C
Fe
O
Si
Au
Au
Cu
Fe
Fe
Cu
Au
Cu
Au
Au
0 2 4 6 8 10 12 14 16 18 20
Full Scale 2810 cts Cursor: 10.821 (11 cts)
keV
Spectrum 2
Cu
C
Fe
O
Au
Au
Cu
Fe
Fe
Cu
Au
Cu
Au
Au
Au
0 2 4 6 8 10 12 14 16 18 20
Full Scale 1781 cts Cursor: 11.329 (14 cts)
keV
Spectrum 3
Cu
O
Ca
Fe
Al
Au
Au
Ca
Cu
Fe
Fe
Cu
Au
Au
Au
Au
0 2 4 6 8 10 12 14 16 18 20
Full Scale 1475 cts Cursor: 12.695 (6 cts)
keV
Spectrum 4
Cu
C
Fe
O
Au
Au
Cu
Fe
Fe
Cu
Au
Cu
Au
Au
0 2 4 6 8 10 12 14 16 18 20
Full Scale 2308 cts Cursor: 12.695 (5 cts)
keV

Table 4 Representative values of elemental composition (wt.%) of C, O, Al, Si, Ca, Fe, and Cu in surface sediment cores of the Zapadna Morava (ZM) containing Cu (Spectrums 1–4, Fig. 4), obtained by SEM-EDS analysis

Weight %	C	O	Al	Si	Ca	Fe	Cu	Total
Spectrum 1	33.2	5.1		0.5		0.9	60.3	100
Spectrum 2	47.6	4.8				0.3	47.3	100
Spectrum 3		13.7	1.7		0.7	5	78.9	100
Spectrum 4	26.4	2.5				0.6	70.5	100

Future research will focus on further sediment analysis of the Danube and identification of point contamination sources, especially in relation to its tributaries in the zone of increased sediment metal concentrations. This study indicated that the ZM was the main source of heavy metal delivery in the Velika Morava River and in the Danube River. Therefore, hot spots for remediation of contaminated sediments in the ZM should be located near the output of industrial sewage, dams, on meanders, and on sandbanks along its flow path, since they represent locations with decreased sediment mobility. On the other hand, continuous monitoring of the metal levels in the JM is recommended in the future. The final task would be a responsible control of diffuse sources of pollution over a large area, implementing appropriate land use and land management measures.

5 Conclusions

In order to decrease environmental pressure related to heavy metal concentration in sediment and their uptake by various organisms in the Danube Delta, monitoring and regulating heavy metal levels in the Danube tributaries are very important. This study gives new insights into sediment metal concentrations in three major rivers in Serbia: the Danube, the ZM, and the JM. The ZM was the most polluted by heavy metals which may be a consequence of industrial, agricultural, and mining activities. We showed here that concentrations of Cu and Ni in the ZM exceeded the sediment quality guideline levels. According to SEM-EDS analysis, showing Cu associations with carbonate hydroxides and/or Fe-oxides, we suggest that mining and industrial activities are possible sources of pollution in the ZM. The observed seasonal changes in metal concentrations in the ZM and the JM rivers could be related to changes in the water flow of the rivers combined with storm water input. The ZM River basin needs much more investigation due to the large number of tributaries with unknown heavy metal concentrations in their sediments. Therefore, an approach including identification of diffuse pollution sources is required, including a meaningful full risk assessment and evaluation, as well as implementation of remediation and mitigation measures.

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