



## Evaluation of potentially toxic element contamination in the riparian zone of the River Sava

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### ABSTRACT

Contaminated sediments transported onto the river terrace during high water events can contribute significant quantities of potentially toxic elements to riparian soils. Seven trace elements (As, Cd, Cr, Cu, Ni, Pb and Zn) were analysed in the river sediment and riparian soil of the River Sava and their spatial distribution, potential toxicity and ecological risk levels were evaluated. The results showed that levels of all the trace metals were enriched to varying extents in both the sediment (As, Cr, Ni, and Pb) and soil (Ni) when compared to reference levels for sediments and European soils. Mean concentrations of trace metals in sediment and soil, apart from Pb, increased downstream in the River Sava. The similar increasing trend of these elements in sediment and soil may be explained by their increased load due to anthropogenic pressures (As, Cr, Ni, Pb and Zn in sediment and the significant accumulation of Ni in soil) and frequent periodic flooding (As, Cd, Cr, Cu, Ni and Zn in sediment and Cd in soil are influenced by both high water events and natural factors such as the geological substrate), particularly in lowland regions. In this study, soluble As, Cd, Cr, Cu and Ni fractions in sediment and soil < 10% indicated their low mobility. The exceptions were readily soluble Pb and Zn in the sediment and soil at some sampling sites. In the lower reaches, levels of Pb in sediment was indicative of a medium environmental hazard, while there was a high environmental hazard in the upper reaches with the average Pb content in sediment higher than the PEL. Pollution factors for Pb in soil indicated a medium environmental hazard in the upper and middle reaches and a high environmental hazard at some sites in the lower stretches of the Sava River, although total Pb content in soil was within the range proposed for European soils.

### 1. Introduction

Anthropogenic activities across the world create pressure at the river catchment scale and these pressures may affect the chemical and ecological status of water bodies and influence the soil–sediment–water resource cycle (Négrel et al., 2014; Chiogna et al., 2016). Trace metal concentrations in rivers increased markedly in Europe during the 19th and 20th centuries, mainly due to mining and industrial activities, but also from sewage discharge, runoff, and atmospheric deposition (Schulz-Zunkel et al., 2013). Coastal and estuarine areas are often polluted with heavy metals originating from industrial and agricultural activities (Xie et al., 2014). Thus, riverine floodplains can adopt water quality functions from rivers, especially during periods of flooding.

Riparian sediment can be enriched with trace metals from upstream anthropogenic sources, by chemical adsorption from dissolved fractions during sediment mobilisation, and after prolonged periods of flooding (Tang et al., 2014). Trace metals are mainly bound to sediment; thus, overbank flooding is the major route for diffuse trace metal pollution into floodplain soils (Zerling et al., 2006; Ciesielczuk et al., 2014; Li et al., 2014) and the enrichment rate of heavy metals in floodplains is often a preferred indicator of a river's contamination status (Xiao et al., 2013). Due to the fact that floodplains display strong spatial as well as seasonal heterogeneity, they can be both sinks and sources for trace metals (Punshon et al., 2003; Du Laing et al., 2009). Therefore, reducing the effects of anthropogenic pressures on aquatic ecosystems is one of the major challenges facing society that needs to be addressed in the

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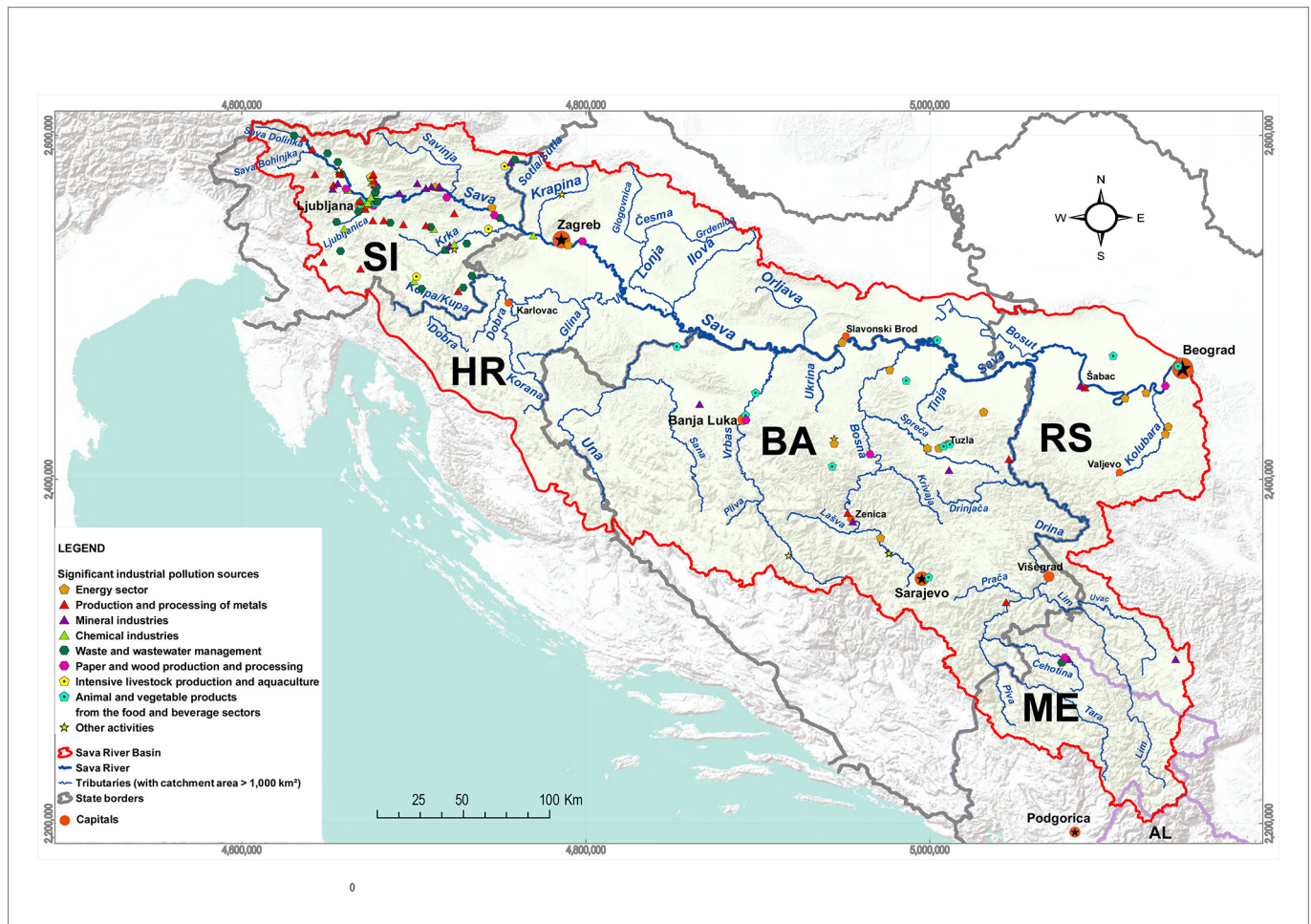


Fig. 1. Point industrial sources of pollution (based on maps ISRBC, 2009).

near future (Navarro-Ortega et al., 2015; Vörösmarty et al., 2010).

Trace metal pollution has become a critical issue because heavy metals can be retained and accumulated in riparian soils and sediments for a long time. Once the content of metals in riparian wetland sediments exceeds environmental quality standards, they pose potential ecotoxic risks for the organisms in those riparian wetlands (Leuven et al., 2005; Bai et al., 2016; Frémion et al., 2016; Tessier and Campbell, 1987; Wang et al., 2015).

Surface water flooding is also recognised as one of the most common natural disasters and is listed as a major risk for aquatic ecosystems. During flood events, sediments may be flushed into hydro-power accumulation reservoirs and down the course of a river; therefore, floods are effective agents of contaminant dispersal, leading to sedimentation on coastal soils (Dragun et al., 2009; Navrátil et al., 2008; Gozzard et al., 2011). Hence, floods play a crucial role in the remobilization of potentially toxic elements (PTE) from historically polluted deposits, whereas present-day pollutants are primarily transported during moderate and low flows (Foulds et al., 2014). Moreover, floods, which normally represent only a small percentage of annual discharge, are a phenomenon that creates and reshapes the floodplain and is responsible for the transfer of metal pollutants from temporary sinks in the river channel (Ciszewski and Grygar, 2016). Contaminated sediments transported during high water events onto the river terrace contribute significant quantities of trace metals to riparian soils. However, pollutants are not always only deposited downstream of pollution sources; their distribution also depends on fluvial erosion/deposition patterns, as well as other factors (Ciszewski and Grygar, 2016). Heavy metals are absorbed by the soil of the flood zone and

further infiltrate the soil profile (Ciesielczuk et al., 2014; Li et al., 2014). In order to prevent river pollution and improve watershed ecosystem health, it is important to understand clearly the contamination characteristics of potentially toxic elements in sediments, as well as in riparian soils and vegetation, and to target their potential sources (Saint-Laurent et al., 2010; Pavlović et al., 2016). Therefore, understanding the processes whereby metals are held in soils and the conditions under which they can be released is crucial, especially in view of impending climate change. In the future, the frequency of flood flows and droughts is expected to increase in European watersheds, including the Sava River Basin as a major drainage basin in South-eastern Europe and one of the most significant sub-basins of the Danube River Basin (Brilly et al., 2015).

To evaluate the behaviour of pollutants during the high water events, we investigated the River Sava as the biggest tributary of the River Danube with a large catchment of 97,713 km<sup>2</sup> contributing significantly to other European river catchments. Riparian and floodplain systems of the Sava River are seriously degraded by various human activities. Pollution sources are mainly related to the release of industrial waste, untreated effluents from municipalities, and contaminants arising from agricultural activities (Ščančar et al., 2015). The spatial gradient shows that the upper reaches are largely regulated by rates of high carbonate mineral weathering, the middle reaches by agricultural activity and biological processes related to eutrophication, and the lower reaches are influenced mainly by stressors related to high pollution from industrial processing, including untreated municipal wastewater discharge (Markovics et al., 2010).

In this context, the main objective of the present work was to

evaluate contamination by potentially toxic elements in the sediment and soil of the riparian zone along the River Sava during a high flow event in autumn 2014. The contamination of the riparian zone with potentially toxic elements was estimated by determining the total content of As, Cd, Cr, Cu, Ni, Pb and Zn in sediment and soil because they are listed as priority substances in the EU Water Framework Directive (WFD Directive, 2000, 2013); by identifying the most hazardous, highly mobile element fractions in river sediment and riparian soil; and by identifying the sources of these elements in soil. The ecological risk that these elements may pose to riparian soils was also assessed.

## 2. Materials and methods

### 2.1. Study area

This study was conducted along the River Sava, at selected localities in Slovenia, Croatia, and Serbia. The Sava River Basin (SRB) is a major drainage basin in South-eastern Europe and one of the most significant sub-basins of the Danube River Basin (12% of the total Danube Basin area), extending across Slovenia, Croatia, Bosnia and Herzegovina, and Serbia. Thus, land use along the River Sava is diverse and complex, reflecting differences in relief, climate, and stream flow. The greatest population densities, of over nine million people, are located in large cities, while agriculture is the dominant activity in the Croatian and Serbian parts of the watershed. Thermo- and hydroelectric power plants, oil and gas refineries with pipelines, the metallurgical, chemical and textile industries, and mining have an anthropogenic impact on the watershed (Ogrinc et al., 2015; Vidmar et al., 2017), Fig. 1.

The SRB is characterised by a diverse landscape. The northern middle part is hilly and mountainous, while the southern middle and lower parts are characterised by low mountains and flat plains. One very important geological characteristic of the SRB, influencing the regime of water and sediment, is the presence of karst phenomena. The terrain consists mostly of very thick layers of limestone, while in the rest of the basin sandstone, marls, claystones, intrusive and extrusive igneous rocks, and metamorphic rocks prevail (ISRBC, 2016).

The watershed of the Sava has a heterogeneous geological composition. Along its flow from the source to the confluence with the Danube, it accumulates alluvial sediments of Holocene age. The watershed is composed of Permo-Carbonian shales, Jurassic and Cretaceous rocks, and Paleogene, Neogene and Holocene sediments composed of clastic rocks (e.g. conglomerates, siltstones, mudstones, and sandstones), (Ogrinc et al., 2015). In terms of soil type, it is dominated by Fluvisol, apart from in its upper section. Namely, Leptosol and Calcaric Leptosol are characteristic of the upper reaches of this section, while in its lower reaches Cambisol on limestone and Cambisol on dolomite is found, as well as Humic Fluvisol. In the middle section, Fluvisols and Gleysols, abutting Stagnosols, are characteristic of the riparian zone, while in the lower section, Fluvisols abut Stagnosol, Eutric Cambisol, Chernozem and to a lesser extent, Gleysol (Panagos et al., 2011; WRB, 2006; Pavlović et al., 2017).

There are two general types of climate conditions within the Basin: an alpine or mountainous climate, prevailing in the upper Sava Basin within Slovenia and also in the Dinaric Alps at higher elevations, and a moderate continental or mid-European climate, dominating at lower elevations of the catchment, including the Pannonian lowland. The average annual air temperature of the whole basin is 9.5 °C (the temperature range is from 1.5 °C in January to 20 °C in July). The amount and annual distribution of precipitation varies within the basin (600–2300 mm), with the average being about 1100 mm/year. The mountainous parts of the basin have considerably more precipitation (2200–2300 mm) than other regions (600–700 mm). Most rain falls in late summer or during autumn. Floods usually occur in spring and autumn - in the spring as a result of snow melting and in the autumn caused by heavy rainfall. These types of floods exhibit different features

depending on the cause. High water events in spring are longer, while in autumn they have a shorter duration and very high extreme flows. A specific atmospheric depression in 2014 caused a large portion of the SRB within Croatia, Bosnia and Herzegovina, and Serbia to be hit by continuous, heavy rainfall followed by unusually rainy weather, leading to the saturation of soils across large areas of the Basin. In the future, flood flows and droughts are expected to become more frequent within the Sava River Basin. It has been established that climate change will increase peak discharges, mainly in the head part of the Sava River Basin watershed (Brilly et al., 2015).

### 2.2. Field sampling

To identify the state of soil pollution in the riparian zone, field sampling was conducted between 1 and 9 September 2014 during a sampling expedition as part of the GLOBAQUA project (Navarro-Ortega et al., 2015). In accordance with sampling protocols for the collection and preparation of samples for analyses, in the 2014 sampling campaign research was undertaken at ten sampling sites along the River Sava, having taken into consideration sample accessibility and representativeness in terms of different anthropogenic sources of pollution (e.g. industry, traffic, agricultural, and urban activities), (Fig. 1). Each sampling site comprised two sampling points – an upstream and downstream point that were located between 10 and 15 km apart. A site close to the Sava Bohinjka spring (one of the headwaters of the Sava River) was chosen as a reference location. Sampling sites including sampling codes and geographical information are presented in Fig. 2.

Soil samples were taken at each sampling location at a distance of 10–15 m from the river bank because this area usually floods during high-water events and is thus prone to the effects of pollutants from water and sediments. Composite samples for each sampling site were composed from six subsamples for each sampling point collected along the river bank, at depths of 0–10 cm, and transferred to PVC buckets and thoroughly homogenized before further treatment. Samples were kept in the dark at 4° before being analysed for trace element content.

At each sampling location, composite samples of sediment were collected using a benthic hand net, depending on the depth of the target area, in line with the recommendations for the chemical monitoring of sediment (European Communities Technical Report 2010-041, 2010). The depth of the collected sediment layer depended on the available substrate and in most cases was up to 10 cm. Wet sieving was conducted through a coarse 2 mm sieve and afterwards through a 63 µm sieve by using ambient water. Samples were transferred into plastic bottles and kept in the dark at 4° before being analysed for trace element content. The sediment fraction < 63 µm was analysed for comparison with data from other river basins (European Communities Technical Report 2010-041, 2010). During the course of sampling, water levels were extremely high, particularly in the lower reaches of the Sava - at Jasenovac (JAS), Slavonski Brod (SLB) and Županja (ZUP); consequently, it was not possible to take sediments from these sampling sites.

### 2.3. Sediment and soil analyses

In the laboratory, sediment and soil samples were dried at 40 °C for 3 days to a constant weight. The soil samples were also passed through a 2.00 mm stainless steel sieve prior to physico-chemical analysis. The pH values (pH<sub>H2O</sub>) of the soil samples were measured in a water suspension (soil:solution ratio of 1:5 w/v), with a WTW (Germany), inoLab 7110 pH meter. The total carbon content (C %) and soil organic matter content in the soil was determined by means of a titration method, using (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub> × 6H<sub>2</sub>O after digestion of samples with a dichromate-sulphuric acid solution, based on Simakov's modification of the Turin method (Simakov, 1957). Soil texture was determined by combined pipette and sieve techniques with 0.4 N solution of sodium pyrophosphate, while fractionation was carried out according to Atterberg (1911).

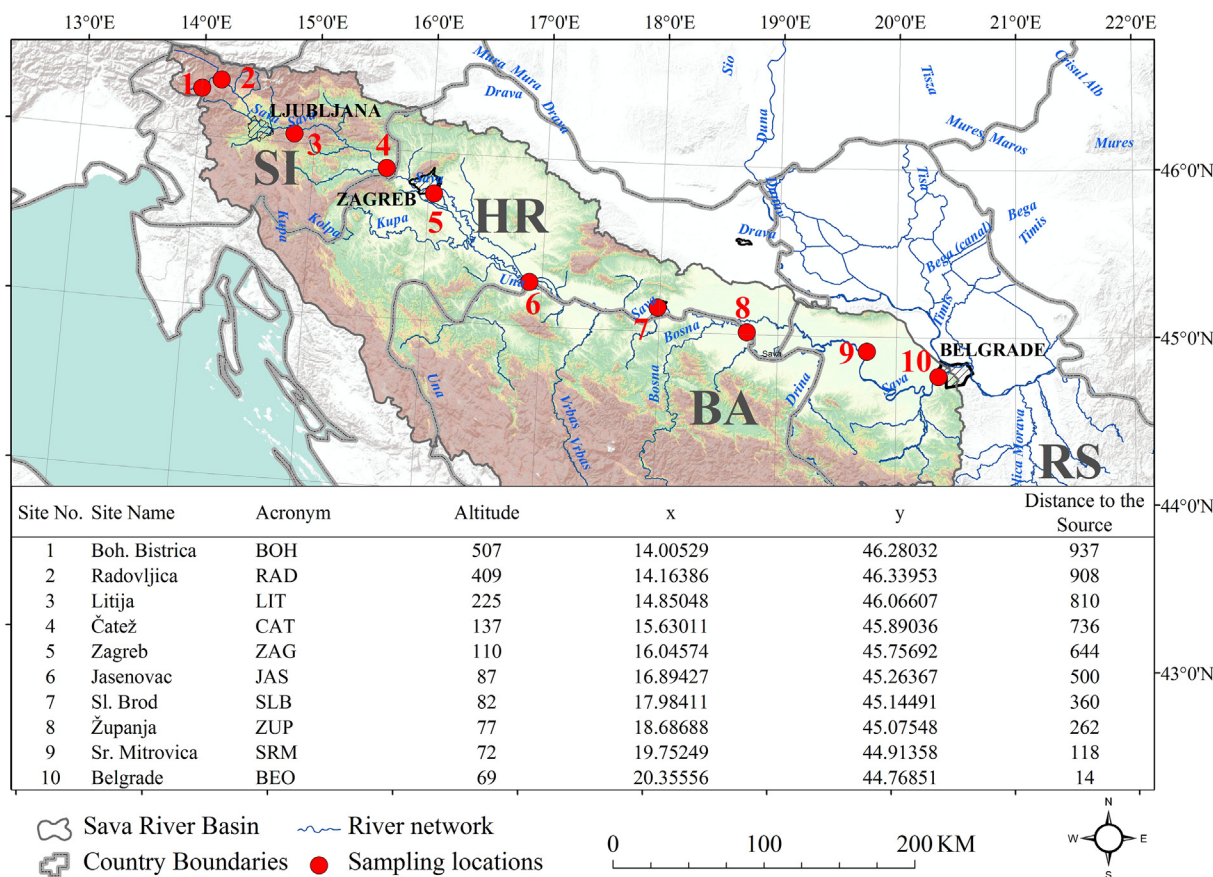


Fig. 2. Sampling sites along the River Sava.

Sequential extraction of sediment and soil samples was performed using the optimised BCR procedure, which operationally divided the heavy metals into acid soluble/exchangeable (F1), reducible - Fe and Mn oxide bound (F2), oxidisable - organic matter bound (F3), and residual - lattice bound (F4) fractions (de Andrade Passos et al., 2010; Sutherland, 2010; Sakan et al., 2016). These fractions may be considered to decrease in lability from the exchangeable to the residual (Jain et al., 2010).

The concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in each of the BCR leachates were determined through inductively coupled plasma spectrometry (ICP-OES, Spectro Genesis). For the analysis of trace metal concentrations, the complete procedures, including the duplicate analyses required to validate the laboratory tests, were used (analytical results of the quality control - uncertainties between 5% and 15% depending on the element analysed). The accuracy of the obtained results was checked by analysing the standard reference sediment (BCR 701), obtained from the Community Bureau of Reference (BCR, Geel, Belgium), for three-step sequential extraction. Measurements were performed in 5 replicates. Total concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in sediment and soil samples were estimated by adding up the concentrations in all four BCR fractions. The data is presented as mean values, with standard deviation (SD).

2.4. Quantification of soil and sediment contamination

In order to assess the level of contamination and the possible anthropogenic impact of the analysed heavy metals in the sediment and soil samples, the risk assessment code (RAC), individual (ICF) and global contamination factor (GCF), enrichment factors (EF) and geoaccumulation index (Igeo) were used.

To determine the extent of the contribution of anthropogenic sources to the toxic microelement contamination of sediments and soils

in the investigated area, the enrichment factor (EF) was calculated according to the equation modified from Hu et al. (2013):

$$EF_M = ([M]/[Mn]_{aff}) / ([M]/[Mn]_{bg})$$

where [M] is the content of any element, [Mn] is the content of manganese, and the subscripts 'aff' and 'bg' indicate content in the affected area and the background for the River Sava catchment, respectively. Manganese was used as the reference background element due to a lack of Al data, with its feasibility confirmed by Loska et al. (1997), as Mn is mainly of lithogenic origin and its anthropogenic sources are minimal. Principal Component Analysis (PCA) can assist when selecting the reference background element (Birch, 2017), as can a high correlation with the elements studied (N'guessan et al., 2009). In our study, using Mn as the reference metal was justified due to it being of lithogenic origin and correlating significantly with most of the studied elements, in particular with Cr and Ni, which are also of lithogenic origin (see Supplementary information, Tables S1 and S2). Seven contamination categories are recognised on the basis of the enrichment factor: EF ≤ 1 denotes deficiency to no enrichment, EF = 1–3 - minor enrichment, EF = 3–5 - moderate enrichment, EF = 5–10 - moderately severe enrichment, EF = 10–25 - severe enrichment, EF = 25–50 - very severe enrichment, and EF > 50 - extremely severe enrichment (Guo et al., 2014).

The geoaccumulation index (Igeo) was used to evaluate the degree of elemental pollution in soils from the study area. It was calculated according to (Müller, 1969):

$$I_{geo} = \log_2([M_{aff}]/k[M_{bg}])$$

where k = 1.5 is the background matrix correction factor introduced to account for possible differences in the background values due to lithospheric effects. The geoaccumulation index consists of seven grades or classes: Igeo ≤ 0, Class 1 (unpolluted); Igeo = 0–1, Class 2

(unpolluted to moderately polluted); Igeo = 1–2, Class 3 (moderately polluted); Igeo = 2–3, Class 4 (moderately to strongly polluted); Igeo = 3–4, Class 5 (strongly polluted); Igeo = 4–5, Class 6 (strongly to extremely polluted), (Yin et al., 2012).

The arithmetical median method was used for calculating background concentrations of the elements for soils in Serbia (Mrvić et al., 2010), Slovenia (Slovenian Environment Agency ARSO, 2017) and Croatia (Halamić et al., 2012), and the obtained value of Mn for the River Sava was 772.96 mg/kg.

To evaluate the ecological risks of heavy metals and their mobility, the risk assessment code (RAC) was calculated by the ratio of the concentration of exchangeable and carbonate fractions to the sum of the concentrations of all the fractions according to Jain (2004):

$$RAC (\%) = 100 \times F1 / (F1 + F2 + F3 + F4)$$

When this percentage is < 1%, the sediment is of no risk to the environment, 1–10% reflects a low risk, 11–30% a medium risk, 31–50% a high risk, and above 50% a very high risk.

The individual contamination factors (ICF) for the sediment and soil samples from the various sampling sites were calculated from the results of the fractionation study by dividing the sum of the first three extractions (i.e. the exchangeable, acid-reducible and oxidisable-organic forms) by the residual fraction for each site. The global contamination factor (GCF) for each site was calculated by summing the ICF obtained for the examined elements at the site (Ikem et al., 2003). The ICF and GCF were calculated using the equations:

$$ICF_{metal} = F1 + F2 + F3 / F4$$

$$GCF = \sum_{i=1}^n CF_i$$

### 2.5. Statistical analysis

Spearman Rank Order correlation coefficients were calculated using SPSS 20 software (IBM SPSS Statistics, 2016). The correlations were calculated for two data sets (sediment, soil), as well as for each analysed element in a different matrix. Correlation was assumed to be statistically significant at  $p < 0.05$ .

The possible sources of heavy metals were identified by a correlation matrix and multivariate analyses, including principal component analysis (PCA), (Wu et al., 2014). Raw data was normalised according to the Varimax method. Components with Eigen values > 1 were further plotted.

## 3. Results and discussion

### 3.1. Physico-chemical properties of riparian soil

The pH values ranged from 7.08 at the BOH site to 7.73 at BEO. The measured values were mostly within the neutral range (pH 6.6–7.3) upstream of SLB, whereas a weak alkaline reaction was found downstream of SLB (pH 7.4–7.8).

The examined soil samples were predominantly composed of sand, followed by silt and clay. However, amounts varied among the samples: higher sand content (66–79%) was measured upstream of SLB, from which point it reduced significantly (29–36%), especially at the ZUP site (only 8.8%); the silt fraction varied from 14% at ZAG up to 55.7% at the ZUP site; and the clay fraction ranged from 5% at LIT to 35% at ZUP, with an increasing trend downstream of SLB. Soil organic matter content varied irregularly within a narrow range, from 1.2% at LIT to 2.8% at ZUP, while the C content varied in a similar manner (Table 1). High flow events as well as floods contribute to constant flushing activity, which supports the low percentage of organic carbon in the riparian soil.

### 3.2. Potentially toxic elements content in sediment and riparian soil

To estimate the environmental status of sediment, Canadian Environmental Quality Guidelines (CCME, 2001) were used. The Interim Sediment Quality Guidelines (ISQG) correspond to the threshold level effects below which adverse biological effects are not expected (TEL), while probable effect levels (PEL) characterise contents of pollutants that may affect aquatic life. Levels above the PEL are denoted in bold (Table 2). Concentrations above the TEL were measured for As (at CAT, SLB, SRM, and BEO), Cd (at SLB and BEO), Cr and Cu (at SLB, SRM and BEO), and for Pb at all the sites. Levels above the PEL were measured for As (at BEO), Cr (at SRM and BEO), and Ni (at SLB, SRM and BEO). All the measured values for Cd and Zn were below the TEL and PEL, and below the PEL for Cu.

In general, sediment in the lower reaches of this stretch of the River Sava, including SLB, SRM and BEO, is potentially polluted by As, Cr and Ni, supporting the previously established spatial gradient of pollution (Markovics et al., 2010; Ščančar et al., 2015; Milačić et al., 2017). The environmental status of River Sava sediment is comparable to other moderately polluted rivers in Europe if rivers impacted by mining activities are not taken into account. For instance, levels of Cd, Cr, Cu, Pb and Zn in sediment are far lower in comparison to earlier findings for the Sava (Sakan et al., 2011) and the River Danube (Woitke et al., 2003; Pavlović et al., 2016). Copper content was also found to be lower in comparison to earlier findings for the River Sava (Sakan et al., 2011), the Danube (Woitke et al., 2003; Pavlović et al., 2016), and the Tisza (Sakan and Đorđević, 2010). Conversely, chromium content was found to be higher than for the Tisza (Sakan and Đorđević, 2010). The Ni range was found to be lower in comparison to earlier findings for the River Sava (Sakan et al., 2011), but higher in relation to the Tisza (Sakan and Đorđević, 2010) and the Danube (Woitke et al., 2003; Pavlović et al., 2016).

Data on total trace element content in riparian soil is shown in Table 3. In order to estimate the environmental status of riparian soils, several guidelines (the mean values of the background levels of trace metals in two common soil types worldwide by Kabata-Pendias and Pendias (2001) and background values in European soils as proposed by Gawlik and Bidoglio (2006)) were used. Concentrations above the threshold levels are denoted in bold. Levels above the mean values described for global soils (Kabata-Pendias and Pendias, 2001) were measured for As (at SLB, ZUP, SRM and BEO), Cd and Cr (at ZUP), Cu (at ZUP and BEO), Ni (at SLB, ZUP, SRM and BEO), Pb (at all sites) and Zn (at SRM). At the same time, all the concentrations measured for all the elements were within the range proposed for European soils, while there is no data on background values for As in European soils.

### 3.3. Partitioning of selected elements in sediment and soil samples

Figs. 3 and 4 show the partitioning of As, Cd, Cr, Cu, Ni, Pb and Zn in sediment and soil samples for each step of the BCR sequential extraction procedure.

Arsenic in sediment and soil samples mainly occurred in the residual (on average 70.32% and 39.35% respectively) and oxidisable (on average 25.98% and 53.45% respectively) fractions, but it also occurred in the reducible fraction at several sites, mostly in the lower stretches of the River Sava. Arsenic fractionation revealed that the soluble fraction of As in sediment and soil was 0% since the content of extracted arsenic was below the limit of quantification (LoQ) in the first fraction.

The average content of extracted cadmium in the residual fraction of sediment and soil samples was 63.08% and 74.66%, whereas the contribution of all other fractions was significantly lower. In the soil and sediment from SLB, ZUP, SRM and BEO, a significant extraction of Cd in the reducible fraction can be noted (17–22%), as well as in sediment from RAD (58.36%).

The highest Cr content in sediment and soil was observed in the residual (an average of 66%) and oxidisable fractions (31%), showing

**Table 1**  
The main physico-chemical properties of riparian soils.

Site	Soil texture				Soil organic matter (%)		Soil type
	pH (H <sub>2</sub> O)	Sand (%)	Silt (%)	Clay (%)		C (%)	
BOH	7.23	68.04	24.47	7.49	2.339	1.357	Sandy loam
RAD	7.28	77.55	16.65	5.80	1.641	0.952	Loamy sand
LIT	7.21	77.10	17.99	4.91	1.231	0.715	Loamy sand
CAT	7.15	66.29	25.14	8.57	2.755	1.599	Sandy loam
ZAG	7.40	79.09	14.00	6.91	1.746	1.013	Loamy sand
JAS	7.17	68.60	23.94	7.46	2.021	1.173	Sandy loam
SLB	7.47	36.73	41.40	21.87	1.733	1.006	Loam
ZUP	7.17	8.80	55.76	35.44	2.888	1.676	Silty clay loam
SRM	7.38	32.07	46.21	21.72	2.170	1.259	Loam
BEO	7.49	29.57	44.95	25.48	1.880	1.091	Loam

**Table 2**  
Total trace element concentrations in sediment. Mean levels with standard deviation in parenthesis. Concentrations in mg/kg.

Site/element	As	Cd	Cr	Cu	Ni	Pb	Zn
RAD	5.68 (0.79)	0.59 (0.14)	19.94 (0.28)	21.04 (0.55)	20.18 (0.33)	85.44 (5.12)	36.29 (0.40)
LIT	4.72 (0.67)	0.34 (0.01)	13.17 (0.14)	23.49 (0.15)	12.78 (0.11)	<b>91.39</b> (6.85)	44.06 (0.34)
CAT	6.02 (0.37)	0.32 (0.01)	12.81 (0.15)	17.13 (0.15)	17.06 (0.15)	72.50 (7.37)	41.96 (0.48)
ZAG	5.79 (0.47)	0.25 (0.01)	8.51 (0.06)	10.25 (0.07)	10.82 (0.87)	78.49 (3.11)	23.46 (0.24)
SLB	14.08 (0.78)	0.63 (0.01)	72.43 (0.45)	42.07 (0.16)	<b>101.58</b> (0.62)	36.75 (3.89)	72.06 (0.54)
SRM	16.77 (0.97)	0.60 (0.00)	<b>103.98</b> (0.32)	39.85 (0.11)	<b>165.50</b> (0.59)	55.53 (3.82)	100.81 (0.55)
BEO	<b>21.70</b> (0.71)	0.68 (0.01)	<b>116.32</b> (0.30)	94.84 (0.29)	<b>177.86</b> (0.22)	66.06 (7.16)	101.48 (0.44)
TEL <sup>a</sup>	5.9	0.6	37.3	35.7	18.0	35.0	123.0
PEL <sup>a</sup>	17.0	3.5	90.0	197.0	36.0	91.3	315.0

Source

<sup>a</sup> Smith et al. (1996).

**Table 3**  
Total trace element concentrations on a dry mass basis in riparian soil. Mean levels with standard deviation in parenthesis. Concentrations in mg/kg.

Site/element	As	Cd	Cr	Cu	Ni	Pb	Zn
BOH	4.20 (0.45)	0.13 (0.00)	15.22 (0.07)	13.81 (0.12)	26.06 (0.17)	<b>37.80</b> (5.14)	4.31 (0.15)
RAD	5.76 (0.63)	0.30 (0.01)	6.97 (0.10)	16.34 (0.12)	10.11 (0.14)	<b>180.34</b> (9.57)	26.44 (0.28)
LIT	7.56 (0.65)	0.23 (0.01)	10.55 (0.03)	12.66 (0.08)	11.57 (0.06)	<b>97.39</b> (16.01)	18.12 (0.17)
CAT	7.75 (0.32)	0.28 (0.01)	13.50 (0.06)	16.94 (0.12)	14.02 (0.13)	<b>72.56</b> (11.24)	27.93 (0.25)
ZAG	7.56 (0.19)	0.22 (0.01)	12.13 (0.04)	16.78 (0.19)	23.11 (0.25)	<b>67.00</b> (15.13)	56.88 (0.44)
JAS	6.51 (0.64)	0.18 (0.06)	9.43 (0.03)	9.72 (0.06)	11.83 (0.09)	<b>71.27</b> (14.34)	15.01 (0.12)
SLB	<b>8.87</b> (0.36)	0.36 (0.02)	24.47 (0.21)	16.16 (0.06)	<b>32.46</b> (0.24)	<b>44.70</b> (8.29)	16.66 (0.33)
ZUP	<b>15.26</b> (0.28)	<b>0.49</b> (0.01)	<b>74.15</b> (0.61)	<b>32.53</b> (0.38)	<b>116.41</b> (0.45)	<b>60.56</b> (8.05)	45.46 (1.83)
SRM	<b>15.63</b> (0.58)	0.39 (0.01)	45.60 (0.36)	22.10 (0.18)	<b>70.32</b> (0.46)	<b>55.81</b> (6.32)	<b>73.30</b> (1.18)
BEO	<b>12.67</b> (0.63)	0.40 (0.01)	45.17 (0.30)	<b>25.28</b> (0.16)	<b>65.90</b> (0.38)	<b>49.14</b> (5.28)	54.68 (0.54)
Mean <sup>a</sup>	4.8–8.4	0.37–0.45	47–51	13–23	13–26	22–27	45–60
EU soils <sup>b</sup>	–	1–3	50–100	50–140	30–75	50–300	150–300

Source

<sup>a</sup> Kabata-Pendias, A., Pendias, H., 2001. Trace Elements in Soils and Plants. CRC Press LLC, Boca Raton, London, New York, Washington.

<sup>b</sup> Gawlik, B.W., Bidoglio, G., Eds., 2006. Background values in European soils and sewage sludges PART III, Conclusions, comments and recommendations. European Commission, Directorate-General Joint Research Centre, Institute for Environment and Sustainability (Directive 86/278/EEC (6 < pH < 7)).

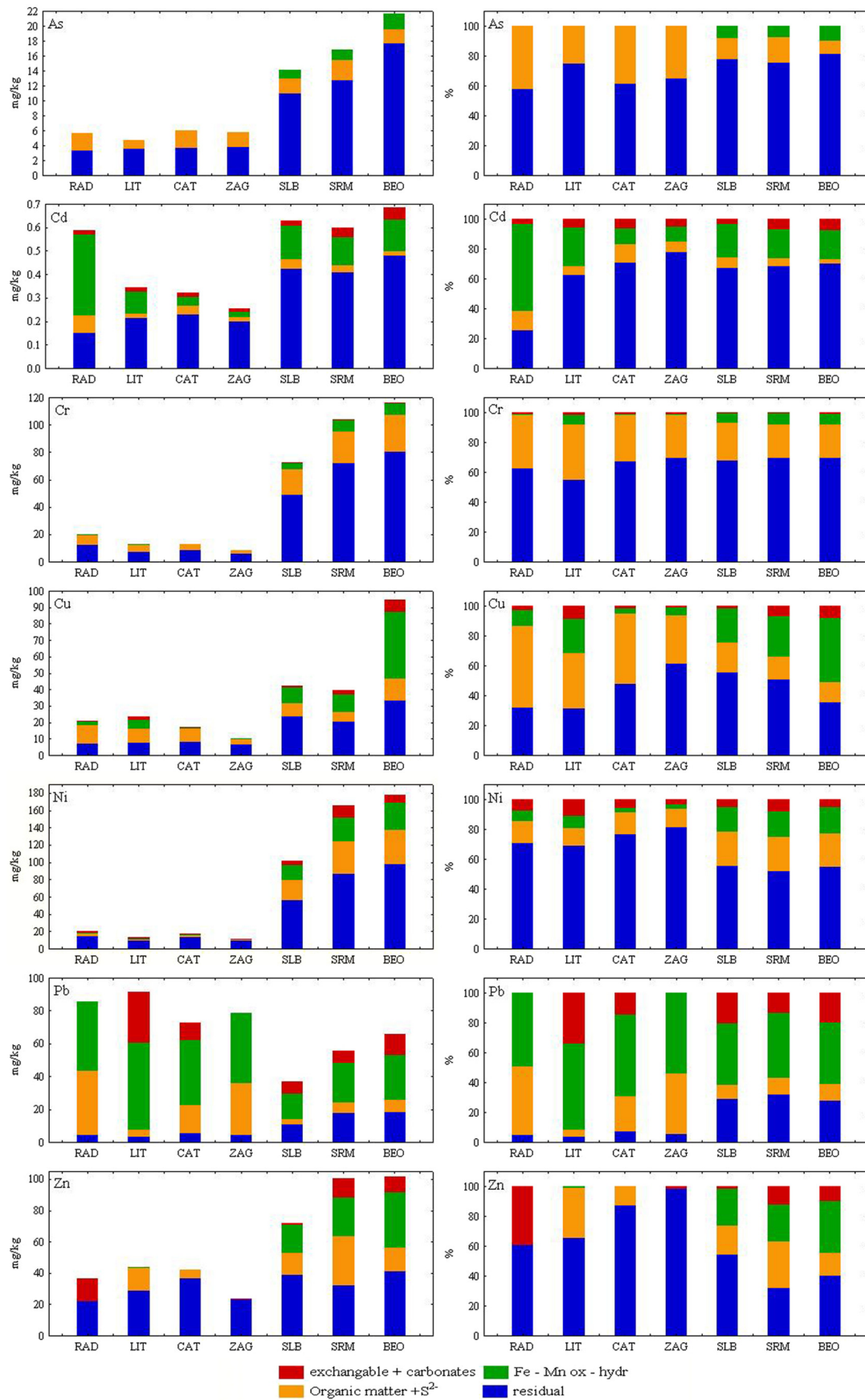


Fig. 3. Partitioning of As, Cd, Cr, Cu, Ni, Pb and Zn in sediment samples.

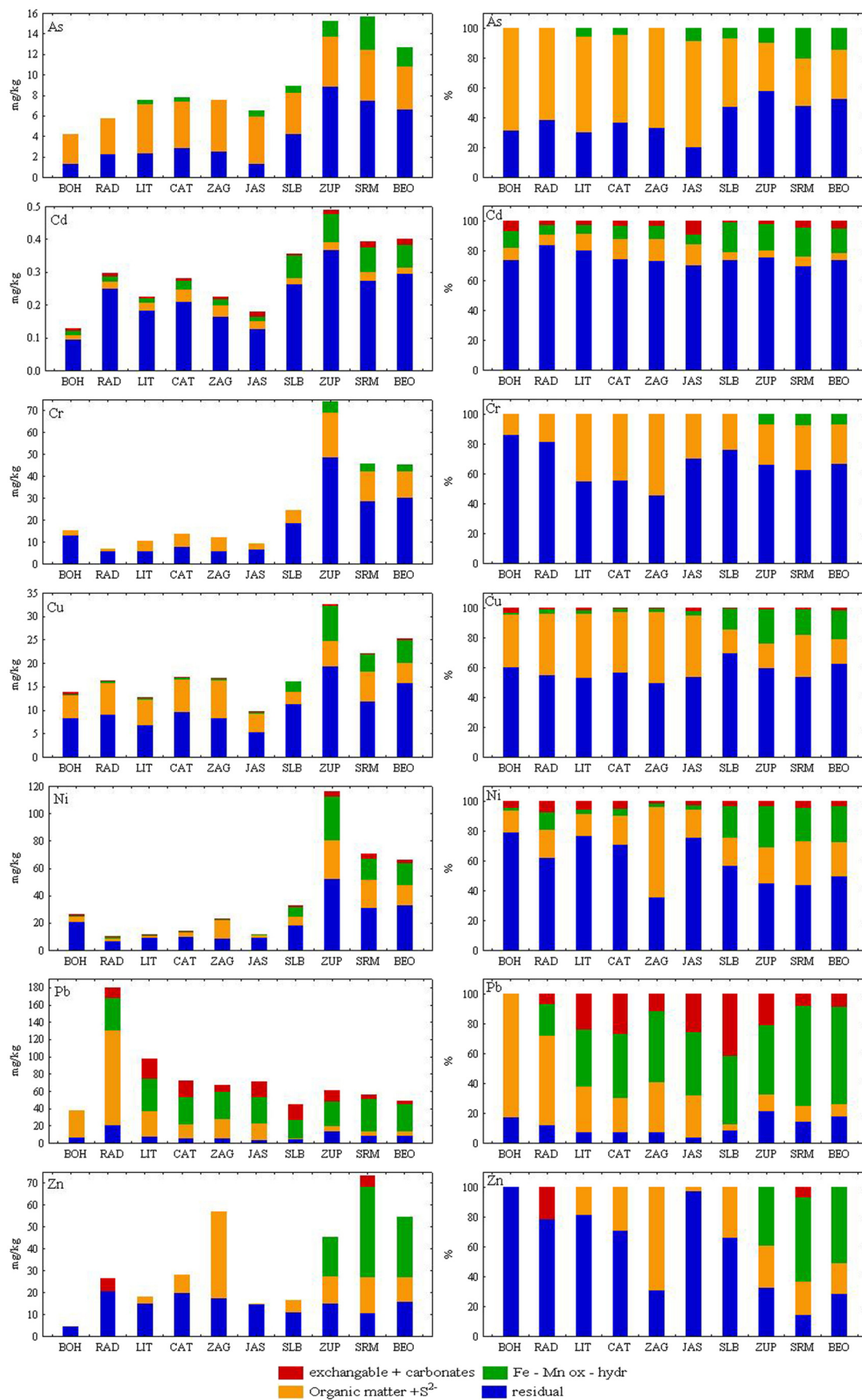


Fig. 4. Partitioning of As, Cd, Cr, Cu, Ni, Pb and Zn in riparian soil samples.



levels of the total content of extracted Ni can also be detected when compared to other sites.

The lowest levels of lead occurred in the extractable and residual fractions (an average of 15%), while a very high content of Pb was noted in the reducible fraction (an average of 49% in sediment and 42% in soil). A higher content of extracted lead in the soil at SLB (40%) and CAT and JAS (27% and 28% respectively) was measured in comparison to other localities. Large amounts of Zn are mainly associated with the residual fraction (approximately 60%), with the lowest contribution of this fraction in the lower reaches of the examined stretch of the Sava. At some localities (SRM and BEO) a significant extraction of Zn was noted in the oxidisable and reducible fractions, as well as the extractable fraction (at RAD), which indicates that Zn is potentially bioavailable and mobile and represents a high potential risk for the surrounding environment at these localities.

In this study, soluble As, Cd, Cr, Cu and Ni fractions < 10% in sediment and soil indicated their low mobility. The exceptions were readily soluble Pb and Zn in the sediment and soil at some sampling sites. For instance, at SLB and BEO, the Pb in the sediment was indicative of a medium environmental hazard (RAC > 20%), while at LIT the average Pb content in sediment was higher than the PEL (91.39 mg/kg), revealing a high environmental hazard (RAC > 30%). The highest ICF values for Pb (27.4%) and GCF values (32.3%) were found at this site (Table S1). These pollution factors for Pb in soil indicated a medium environmental hazard in the upper and middle stretch of the Sava (at LIT, CAT, JAS and ZUP) and a high environmental hazard at some sites in the lower stretches (RAC = 41.8% at SLB), (see Supplementary information, Tables S3 and S4). However, total Pb content in soil in lower stretch is within the range proposed for European soils. Although the RAC for Zn in both soil and sediment is > 10% at some sites (RAD, ZAG and SRM), it does not indicate an environmental hazard due to its normal range at all the examined sites (< TEL).

### 3.4. Identification of sources of potentially toxic elements in sediment and soil

In this study, the PCA of chemical elements in sediment and riparian soil showed three principal components (PC1, PC2 and PC3) that explained 94.89% of all data variation (Supplementary information, Table S5; Fig. 5). Considering that water-level fluctuations control the structure and functioning of aquatic ecosystems and that water fluctuation intensity can influence the precise identification of the origin of trace elements (Zhao et al., 2014), high water levels were singled out as a particular factor in this study. Namely, PC1 is defined as a natural factor, a high water event, PC2 relates to anthropogenic factors, while PC3 is based on the variability of elements controlled by natural factors such as the geological substrate. In the rotated component matrix, the PC1 variance of 76.20% included Cd in soil as well as, Cd, Cr, Cu, Ni

and Zn in sediment, indicating that their accumulation mostly in sediment is largely due to high water events, but also to a lesser degree to natural factors such as the geological substrate, which is proved by the significant influence of Al on PC1 (Supplementary information, Table S5). The PC2 variance of 9.83% included anthropogenic sources of As, Cr, Ni, Cu and Zn in soil as well as the significant accumulation of Ni in sediment at the ZAG, SRM and BEO sampling sites. The PC3 variance of 8.55% included As and Cd of lithological origin in sediment, explained by the influence of Al on PC3 at SLB. Likewise, there is a clear overlap of Pb and Cd content in soil at RAD, as well as Pb and As content in soil at LIT and CAT.

### 3.5. Assessment of potentially toxic elements contamination in sediment and soil

In the present study, the resulting EF-sediment values demonstrate that As, Cd, Cr and Zn are either not enriched or enriched to a minor extent in the sediment of the River Sava. The EF-sediment values for Pb are the highest among the metals and it exhibits minor, moderate (at RAD and CAT) to moderately severe enrichment (at LIT and ZAG). The EF-sediment values also indicate that Cu displays minor to moderate enrichment at LIT and moderately severe enrichment at BEO, while Ni exhibits minor enrichment in the upper reaches and moderate to moderately severe enrichment in the lower stretch (SLB, SRM and BEO), (Table 4; Fig. 6). Clearly, those sampling sites located closer to the various industries have a higher EF. The differences between the EF-sediment values for the different metals in the surface sediment may be due to differences in the magnitude of input for each metal and/or differences in the removal rate of each metal (Ghrefat et al., 2011). Igeo-sediment values classify almost all the examined sites as unpolluted; however, there are several sites in the category of moderately polluted, including SLB (Cu and Ni), SRM (Cu and Ni) and BEO (As, Cr, Cu, Ni and Pb) (Supplementary information, Table S6).

Similarly, the resulting EF-soil values demonstrate no enrichment for As (except at JAS) or Cr and Zn (except at ZAG), while values for Cd, Cu and Ni show that they are either not enriched or enriched to a minor extent. However, EF-soil values for Pb are also the highest among the metals and it displays minor, moderate (at CAT), moderately severe (at LIT, ZAG and JAS) to severe enrichment (at RAD), (Table 4; Fig. 7). Riparian soils fall into the class of moderately polluted at sites from RAD to JAS (Pb) and ZUP, SRM and BEO (Ni).

Along the Sava, there is an increase in As content in sediment with the highest content measured at BEO as a result of transport, transfer and deposition of As downstream (Dennis et al., 2009) from industrial discharge (on the right bank of the Sava, there are two thermal electric power plants “Nikola Tesla A and B” and two huge ash deposit sites with a total surface area of approximately 1000 ha, Pavlović et al., 2004; Mitrović et al., 2008; Kostić et al., 2018), as well as the transfer downstream of finer particles of soil, to which As is bound (Lim et al.,

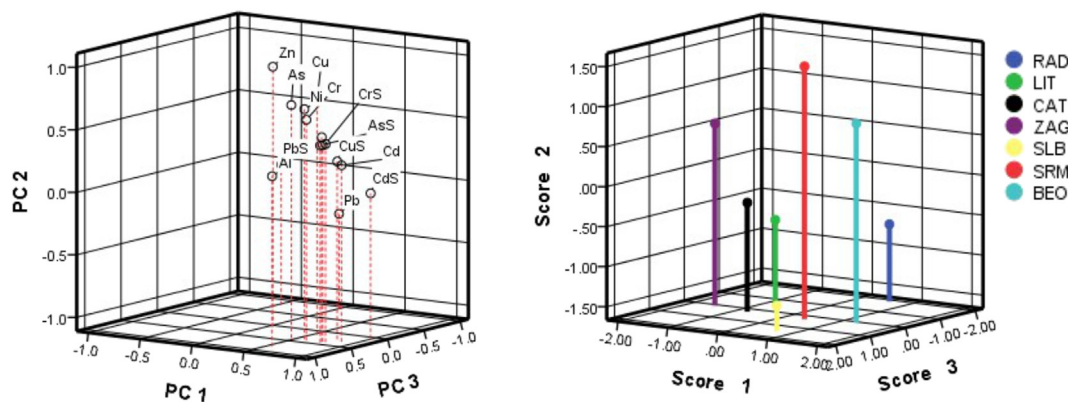


Fig. 5. PCA loading plot for soil and sediment (A); Graphic score for soil and sediment (B).

**Table 4**  
Enrichment factor (EF) in sediment and soil.

Site/Element	As	Cd	Cr	Cu	Ni	Pb	Zn
<b>Sediment</b>							
RAD	1.20	2.12	0.67	2.13	1.19	4.74	0.97
LIT	1.38	1.69	0.61	3.28	1.04	7.01	1.62
CAT	1.41	1.27	0.48	1.92	1.12	4.46	1.24
ZAG	1.78	1.30	0.42	1.51	0.93	6.32	0.91
SLB	2.41	1.83	1.97	3.44	4.85	1.65	1.55
SRM	1.75	1.06	1.72	1.99	4.82	1.52	1.32
BEO	2.64	1.40	2.25	5.49	6.03	2.10	1.55
<b>Soil</b>							
BOH	0.75	0.39	0.43	1.18	1.30	1.77	0.10
RAD	1.22	1.08	0.23	1.65	0.60	10.00	0.70
LIT	2.21	1.14	0.49	1.77	0.94	7.47	0.67
CAT	1.82	1.11	0.50	1.90	0.92	4.46	0.83
ZAG	2.32	1.15	0.59	2.47	1.98	5.39	2.20
JAS	3.78	1.25	0.61	1.90	1.35	7.65	0.77
SLB	1.52	1.05	0.67	1.32	1.55	2.00	0.36
ZUP	1.19	0.65	0.92	1.21	2.54	1.24	0.45
SRM	1.63	0.69	0.76	1.10	2.05	1.52	0.96
BEO	1.54	0.82	0.87	1.31	2.23	1.56	0.84

2012). The increased anthropogenic impact downstream is confirmed by the higher EF-sediment values at SLB and BEO, which indicates a mixed anthropogenic and geological origin, as does the higher Igeo at these sites (Table 4; Fig. 6).

The As content in soil changes spatially with higher levels in the lower stretches of the river, which is mainly the result of the high water level as PCA showed that all sites downriver from JAS were affected markedly by the high water level factor (PC1). The lower percentage of the residual fraction in soil generally points to the washing away of finer fractions of soil particles into the river. These are characterised by a strong bond with As due to their greater surface area and higher content of Fe oxides (Lombi et al., 2002). The noticeable increase in the percentage of the residual fraction in soil downstream from JAS also points to a change in the character of As, whereby the anthropogenic impact on its levels starts to be more marked. This impact on soil samples from JAS is also confirmed by the higher EF-soil values. At SLB, despite the fact that PCA suggests that As content is influenced by high water levels, its anthropogenic origin is visible through its higher

percentage in the reducible fraction, pointing to the effects of intensive agricultural production, i.e. the use of herbicides and insecticides (Sarmani, 1989; Zulkifli et al., 2010), as well as the use of phosphatic fertilizers containing As (Jayasumana et al., 2015), and P and As ion antagonism in soil (Davenport and Peryea, 1991; Peryea, 1998). The high As content in the soil samples from SRM, as well as the proportion of the reducible fraction, is the result of the activities of numerous metallurgical and chemical industries in the region (Adriano, 2001; Milačić et al., 2017; Vidmar et al., 2017). All these factors, as well as the total As content, show that As does not pose a threat to the riparian zone, i.e. the sediment and riparian soil of the River Sava (Table 4; Supplementary information, Table S6; Fig. 7).

Total Cd content in sediment and its high concentration in the residual phase points to it being of mainly geological origin (Chlopecka et al., 1996; Hickey and Kittrick, 1984). The exception is at RAD, where an extremely low percentage of the residual fraction was noted, with such a ratio of the fractions being conditioned by a high water level, i.e. reducing conditions lead to an increase in Cd solubility in the presence of carbonate (Mitchell et al., 2016; Ashraf et al., 2012) and its binding to amorphous forms of Mn and Fe oxides. The results suggest that Cd is the most labile metal because of its stronger affinity to the non-residual fraction at this particular site. It is clear that its levels are significantly affected by metal mining, which is also a source of Cd in the region. The total Cd content in soil generally increases with distance downstream. However, there is a deviation from this which sees a slight decrease in Cd levels in samples from ZAG and JAS, as well as sudden spikes specific to SLB and ZUP, where the highest total Cd content was measured. These deviations are primarily the result of industrial discharge from the metallurgical and chemical industries (Adriano, 2001) in the region above CAT, combined with developed agricultural production in the vicinity of the SLB and ZUP sampling sites, including the use of phosphatic fertilizers, which are one of the most ubiquitous sources of Cd contamination in agricultural soils throughout the world (Alloway and Steinnes, 1999). The absence of anthropogenic contamination along the majority of the river is shown by the EF-soil and Igeo-soil values (Table 4; Supplementary information, Table S6; Fig. 7). This might be explained by the fact that Cd has a special affinity for clay mineral structures due to its ionic radii and tends to combine with carbonate minerals at high pH (Modak et al., 1992; Förstner and Wittmann,

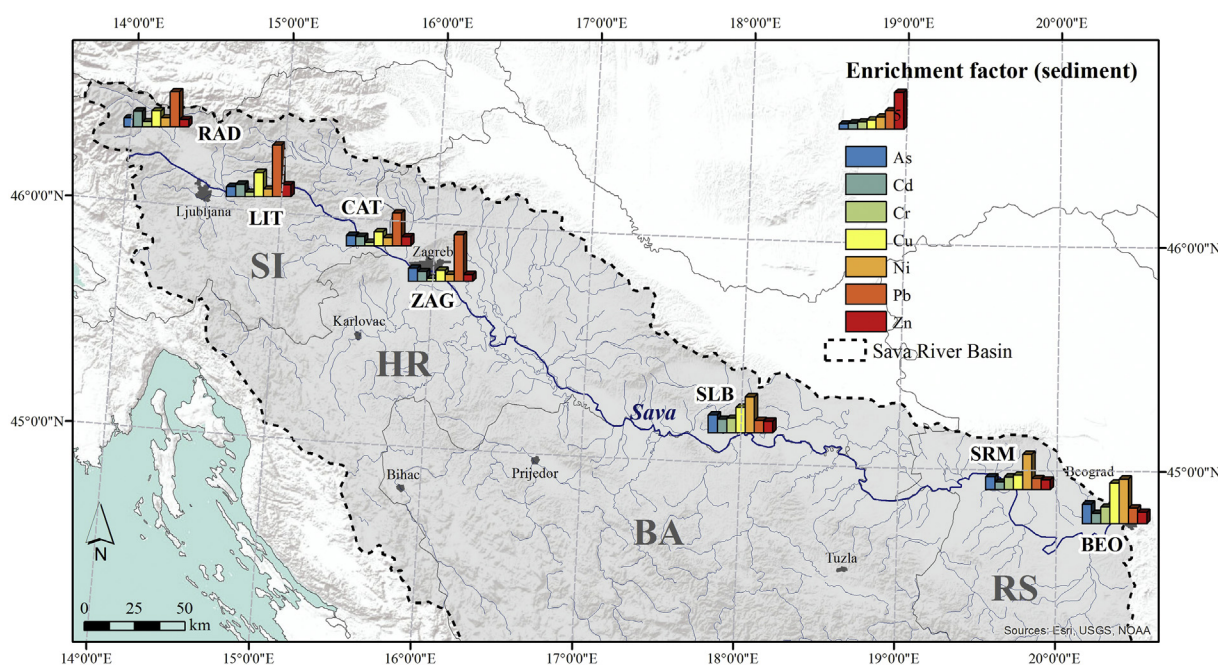


Fig. 6. Examined sites categorized on the basis of the enrichment factor (EF) for selected elements in sediments.

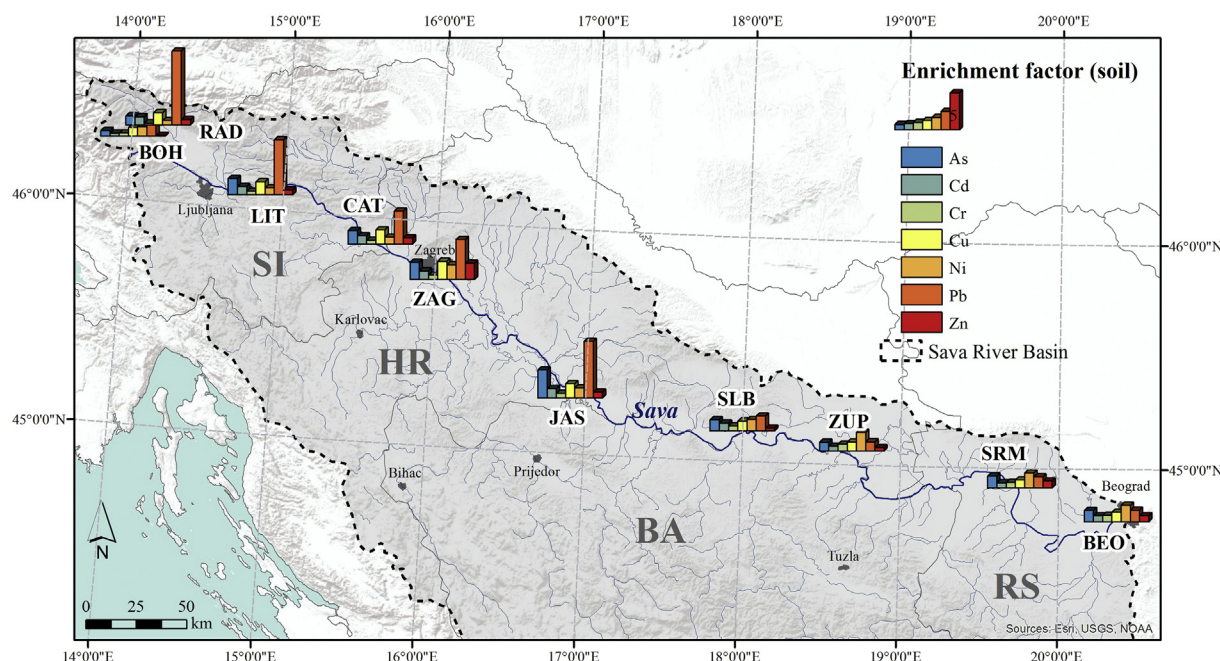


Fig. 7. Examined sites categorized on the basis of the enrichment factor (EF) for selected elements in riparian soils.

1981). In the upper reaches of the river, the Cr content in sediment is  $< 20$  mg/kg, but from SLB onwards, this ratio changes considerably with levels 3–5 times higher (at SLB, SRM and BEO), which points to the transfer of finer fractions from the tributaries that come from areas that are geologically rich in Cr, while this tendency intensifies when flooding occurs. Spatially, it is also noticeable that the residual fraction proportion is significantly higher in the sediment in the lower reaches of the Sava, which points to the geological origin of Cr regardless of its presence in the first fraction. This is confirmed by the position of Cr in sediment on PC3 at SLB (Fig. 5). EF-sediment points to the geological origin of Cr and Igeo-sediment shows that sediment is not contaminated by this element (Table 4; Fig. 6). As with Cr, total Ni levels can be divided spatially, into the upper stretch with a Ni content  $< 20$  mg/kg and the lower stretch below SLB with a content  $> 100$  mg/kg. Enrichment with Ni is moderate at SLB and SRM and moderately severe at BEO, which is confirmed by Igeo-sediment values at SRM and BEO (Table 4; Supplementary information, Table S6; Fig. 6).

The spatial distribution of total Cr in soil can generally be divided into two zones: from the source to SLB, where levels reach 20 mg/kg, and then from ZUP to the confluence with the Danube, which is marked by an increasing trend with levels  $> 40$  mg/kg. This is a result of the geological substrate in the lower reaches of the Sava, i.e. the Central Dinaric Ophiolite Belt, alluvial flooding by the River Bosna (Grba et al., 2015), and serpentine alluvial flooding by the River Kolubara from the Maljen and Rudnik mountains (Mrvić et al., 2010; Čakmak et al., 2018), as well as erosional processes in the River Kolubara catchment (Belanović et al., 2013). The key factor behind such a trend is the accumulation of Cr in the surface layers of soil due to the effects of weathering, its transfer to the watercourse through erosion and its accumulation downstream under the influence of the river's flow (Oze et al., 2004; Grba et al., 2015). The variables Cr and in particular CrS as the natural geochemical form of Cr have a significant impact on PC1 and correlate to the position of SRM and BEO. However, a more marked anthropogenic impact (industry) is also noticeable in this region (Milačić et al., 2017). In addition, the presence of Cr within PC2 at ZAG was also noted, which is highly likely to be the result of increased discharge of municipal wastewater, with the fact that the residual fraction in the soil in this area is the lowest of all the sampling sites pointing to the effects of the anthropogenic factor. The EF-soil also

points to the geological origin of Cr, with a minor impact noted in soil samples at SLB, SRM and BEO, confirmed by the Igeo-soil showing that soil is not contaminated by this element (Table 4; Supplementary information, Table S6; Fig. 7). It is clear that the dominant influence on Cr along the entire stretch of the River Sava is the geological substrate (Čakmak et al., 2018).

Total Ni levels in soil can also be divided spatially, into the upper stretch with a Ni content  $< 30$  mg/kg and the lower stretch below SLB with a content  $> 30$  mg/kg. The similar behaviour of Cr and Ni in soil and sediment is dictated by their common origin, which is confirmed by their highly significant correlation ( $r = 0.903^{**}$  for soil and  $0.900^{**}$  for sediment). The established difference in the proportion of the different fractions in soil at ZAG compared to upstream and downstream sites, together with the sudden increase in Ni content in both sediment and soil downstream, points to anthropogenic pollution on the one hand (Adriano, 2001) and geological origin (serpentine rocks) in the vicinity of this locality on the other (Zovko and Romić, 2011). The similar behaviour of Cr and Ni in terms of the fractions is characteristic for serpentine, which PCA confirms. However, the solubility of Ni is higher than Cr in serpentine (Quantin et al., 2008), particularly in conditions where the percentage of the soluble/exchangeable and reducible - Fe and Mn oxide bound fractions is higher. This higher solubility of Ni leads to greater transfer in sediment along the river, which leads to an increase in both EF-sediment and EF-soil values with distance downstream (Figs. 6 and 7). Total Cu in sediment has a similar spatial distribution to the elements mentioned previously with an increasing trend downstream. This is conditioned by local sources of Cu, but also the possible deceleration of the current downriver, which leads to greater deposition of suspended particles in sediment considering that Cu binds easily to organic material (McLaren and Crawford, 1973; Milačić et al., 2017). The increase in the reducible fraction can also be the result of processes of the mineralization of suspended organic matter in sediment (Wang et al., 2010) and the binding of Cu to the reducible - Fe and Mn oxide bound fraction, primarily to Mn (McLaren and Crawford, 1973).

Total Cu content in riparian soil is site-specific, with the highest level measured at ZUP and the lowest at JAS, with an increasing trend downstream from SLB. Its higher percentage in the reducible - Fe and Mn oxide bound fraction in the lower stretch of the river is without

doubt the result of point-source pollution of anthropogenic origin. At SLB and ZUP, the percentage increase is the result of intensive agricultural production and the use of pesticides and herbicides (Walsh et al., 1972; Thornton, 1979), while at BEO, the cause is industrial and municipal pollution (Adriano, 2001). PCA clearly singles out BEO with a high Cu content in both soil and sediment, while its origin at the other localities was not clearly defined due to the effect of the high water level (PC1). EF-soil values, at the level of minor impact, give a clearer picture of its origin, while EF-sediment revealed an impact that was moderate at LIT and SLB, as a result of agriculture, and moderately severe at BEO, impacted by industry (Fig. 6 and 7).

The results of PCA clearly show that the origins of AlS and MnS coincide, pointing to their lithogenic origin in sediment. However, in soil, analysis suggests a somewhat different situation, with the origin of Mn being linked to the impact of flooding and, to a lesser degree, anthropogenic factors (Supplementary material, Table S5). This can be put down to the properties of Mn, which exhibits varying solubility in changeable redox conditions in periodically flooded riparian soils. It has been proven that the chemistry of elements in soils is governed by many factors, among which, soil redox potential and pH reaction are considered as key drivers in frequently flooded soils (Du Laing et al., 2009; Rinklebe et al., 2016a, 2016b).

Unlike other elements, the accumulation of Pb in sediment is higher in the upper reaches, with the highest content measured at LIT. EF-sediment values reveal that Pb enrichment is moderately severe at this site and that EF values are generally higher in the upper reaches. Igeo shows that sediment is at the level of unpolluted to moderately polluted (Table 4; Supplementary material, Table S6; Fig. 6).

In terms of total Pb content in soil, the upper stretch down to SLB, characterised by levels higher than 70 mg/kg (apart from BOH), can be separated from the lower stretch, where levels do not surpass 60 mg/kg. The highest content was measured at RAD, a result of the proximity to a lead mine and a large municipal tip, with a high level in the residual phase and the highest percentage in the oxidisable - organic matter bound fraction pointing to its relatively limited mobility (Adriano, 2001; Filgueiras et al., 2002; Elsokkary et al., 1995). Elevated Pb levels both in soil and sediment in the upper reaches point to the minor impact of flooding on the migration of this element and its ability to bind quickly to soil particles in the immediate vicinity of pollution sources (Al-Chalabi and Hawker, 2000; Milberg et al., 1980; Page and Ganje, 1970). This is confirmed by PC1, which explains that high water levels have a very low impact on Pb content in soil and sediment. The three statistically significant components barely exhibited any impact on Pb throughout the entire course of the river, given the fact that the elevated levels found in the upper stretch of the Sava were a result of the predominant effect of the mine, i.e. of local character, which resulted in elevated EF values in this part of the river. The accumulation of Zn in sediment is mostly in line with the hydrological characteristics of the river, i.e. accumulation along the river, as well as increased deposition of river sediment as the current decelerates (Dennis et al., 2009). Total Zn content in soil is elevated at those sites which are close to major cities along the river, such as ZAG and BEO, as well as sites related to industrial facilities such as SRM. Given the EF values for all the analysed soil samples, as well as the Igeo-soil values (characteristic for unpolluted soils), and its total content and high percentage in the residual phase at all sites apart from ZAG, SRM and BEO, soil is not contaminated with Zn.

#### 4. Conclusions

In this large-scale study, different useful tools, methods, guidelines and indices have been used to evaluate the contamination of sediment and riparian soils during a high water event along the River Sava. Together with flooding, this evaluation has taken into account the variability of elements controlled by natural factors, such as the geological substrate, as well as anthropogenic sources of contamination of

both matrices along the course of the river. The high water event caused an increase in levels of potentially toxic elements in both the riparian sediment (As, Cr, Ni, and Pb) and soil (Ni) of the River Sava when compared to reference levels for sediments and European soils.

In this study, soluble As, Cd, Cr, Cu and Ni fractions < 10% in sediment and soil indicated their low mobility. The exceptions were readily soluble Pb and Zn in the sediment and soil at some sampling sites. Although the RAC for Zn in both soil and sediment was > 10% at some sites, it does not indicate an environmental hazard due to its normal range at all the examined sites.

It is concluded that, in spatial terms, there was an increase in the content of all the studied elements from the source towards the confluence of the Sava and the Danube, with the exception of Pb and Zn. The high level of Pb in sediment and soil in the upper course of the river is a result of anthropogenic activities (mine tailings) and its ability to bind to soil particles in the immediate vicinity of pollution sources, proven by the highest EF-sediment and EF-soil values for Pb, indicating moderately severe enrichment.

On the basis of our research, it can be concluded that in periods of high water, lead represents an environmental hazard in sediment, which is supported by the pollution indices (a high environmental hazard in the upper reaches, RAC > 30%; the highest ICF and GCF values for Pb) and a medium environmental hazard in the middle and lower stretches (RAC > 20%). Unlike sediment, pollution factors for Pb in riparian soils indicated a medium environmental hazard in the upper and middle stretches of the Sava (RAC > 20%) and a high environmental hazard at some sites in the lower reaches (RAC > 40%), although total Pb content in soil was within the range proposed for European soils.

The results of this study show how high water levels induced by the occurrence of natural flooding during the wet season can result in potentially toxic element enrichment in both the riparian sediment and soil of the River Sava. This indicates that seasonal fluctuations in water levels can lead to the higher mobility of heavy metals due to a change in the physical and chemical conditions in riparian soil, posing a potential threat to the riparian zone.

#### Acknowledgements

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catena.2018.11.034>.

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