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Impact of a severe flood on large-scale contamination of arable soils by potentially toxic elements (Serbia)

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Abstract Extreme flooding in May, 2014 affected the sub-catchments of six major rivers in Serbia. The goal of the study was to evaluate the contents of potentially toxic elements (PTEs) As, Cd, Pb, Cr, Ni, Cu, and Zn in flood sediments and arable soils within the affected sub-catchments using regulatory guidelines and background levels. The sub-catchment of West Morava was selected to assess the degree of sediments and soils contamination and environmental risk [using the Pollution index (P_i), Enrichment factor, Geo-accumulation index, and Potential ecological risk index (PERI)] as well as to identify main PTEs sources by Principal component (PCA) and cluster analysis. Contents of Ni, Cr, As, Pb, and Cu above both guidelines and background levels, and of Zn and Cd above background levels were detected in the sediments and soils from all the sub-catchments. P_i indicted that about 95% of the soils and sediments were extremely polluted by Ni and about 65% slightly polluted by Cr, whereas about 90% were not polluted by As, Cd, Pb, Cu, or Zn. E_f indicated minor to moderate enrichment of the soils and sediments by Ni, and Cr. PCA differentiated a geogenic origin of Ni, Cr, As, and Pb, a mixed origin of Cd and Zn, and a predominantly anthropogenic origin of Cu. PERI of the soils and sediments suggested a low overall multi-element ecological risk. The ecological risk of the individual elements (E_r^i) for soils was Zn < Cr < Pb < Ni < Cu < As < Cd.

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Introduction

For a decade, observational studies have consistently reported an increase in the intensity of extreme rainfall on a global scale (Alexander et al. 2006; Trenberth 2011; Westra et al. 2013). Such extreme rainfall will significantly affect the magnitude and frequency of urban and rural flash floods (Westra et al. 2014), which might cause enormous damages to both agglomerations and farmland. Storm rainfall events might also lead to rising water level of rivers and their tributaries, causing severe floods and landslides not only in mountainous regions, but also in floodplain ecosystems. During the period from 1960 to 2009, there were 3539 floods registered in the world, of which 298 (12%) occurred in the European Union (Green et al. 2013).

Storm rainfall and flood events cause material damage, degradation of the landscape, and water and soil pollution, all of which result in a series of environmental disturbances (Westrich and Förstner 2007). These forms of soil degradation are of particular relevance to highly fertile arable soils in intensive agriculture, such as soils in large river valleys (Rinklebe et al. 2007; Du Laing et al. 2009; Ličina et al. 2010). A relationship between flooding and soils/sediments pollution with potentially toxic elements (PTEs) has been identified in a number of studies (e.g., Majerová et al. 2013; Guo et al. 2014; Foulds et al. 2014; Martínez-Santos et al. 2015; Jiménez-Ballesta et al. 2016). There are three commonly used soil contamination indices: Contamination factor (CF) (equivalent to pollution index (P_i), Geo-accumulation index (I_{geo}), and Enrichment factor (E_f) (Antoniadis et al. 2017). Flooding has generally been recognized as a diffuse source of soil/sediment contamination by PTEs (Zhao and Marriott 2013; Guo et al. 2014; Todorovic and Breton 2014). In this respect, anthropogenic contributions to the PTEs content of floodplain soils/sediments have been reported (Foulds et al. 2014; Frohne et al. 2014; Rinklebe and Shaheen 2014; Martínez-Santos et al. 2015; Shaheen et al. 2017). At the same time, significant non-anthropogenic pollution of soils by various PTEs might be connected to natural occurrences of ore bodies (e.g., Raous et al. 2010; Rajapaksha et al. 2012; Liu et al. 2016). Majerová et al. (2013) emphasized the usefulness of floodplains as pollution archives of widespread regional to continental pollution signals.

In May 2014, there was a severe flood event in Serbia following the heaviest rainfalls recorded in at least 120 years across portions of South East Europe's Balkan region. From May 12 to 18, the amount of precipitation reached 170–220 mm in western Serbia (Lekić and Jovanović 2015). Officials in Serbia declared the event as a minimally 1-in-100 year scenario, after one-third of the total annual rain fell in a matter of days. That severe flood affected the sub-catchments (drainage areas) of six major rivers in Serbia: the Danube, Sava, Great Morava, West Morava, Drina, and Kolubara (Fig. 1a). The West Morava River (319 km long) flows east to west, partly through the eastern fringe of the Dinaride Ophiolite Zone (Dimitrijević 1992; Dill et al. 2008). As a result, the soils in the West Morava Valley naturally abund in Ni and Cr (Rinklebe et al. 2016). In addition, large-scale occurrences of high contents of geogenic As, Cd, Pb, Cu, and Zn in soils in the West Morava Valley have been reported, though anthropogenic sources of these PTEs, such as road and railroad traffic, metal, chemical and textile industries, and agriculture could not be excluded (Mrvić et al. 2009). During extreme floods, it is possible for material from the West Morava sub-catchment to be transported to the other investigated sub-catchments by erosion processes and/or flood waves. This occurs as a result of specific geographic and topographic features of the West Morava sub-catchment. The extreme flood event in May 2014 provided a unique opportunity to evaluate contamination of flood sediments and soils by PTEs in remote sub-catchments immediately after the withdrawal of flood waters from the points of maximum inundation. In addition, it was an opportunity to evaluate the impact of flood-driven diffuse sources of prevailing geogenic PTEs on soil pedogenesis. Geogenic PTEs may pose a potential risk to the environment (e.g., Rajapaksha et al. 2012; Antić-Mladenović et al. 2017). However, the level of their flood-driven discharge into the environment and their contribution to large-scale contamination and/or soil pedogenesis has generally received less attention. This necessitates research, especially in the context of

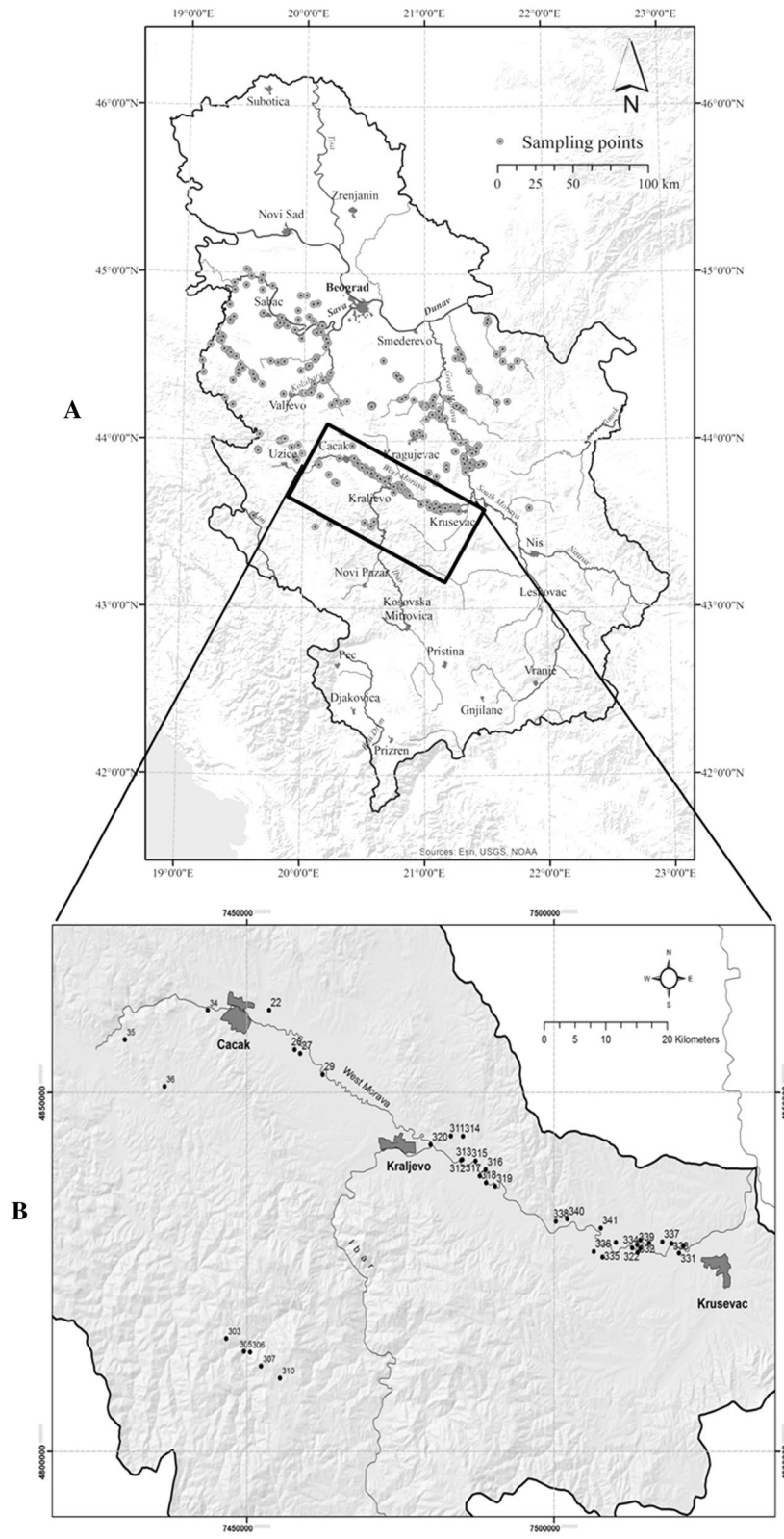


Fig. 1 Sampling sites of the soils and flood sediments at various locations severally flooded in May 2014, Serbia (**a**); sampling sites of the soils and flood sediments from the West Morava sub-catchment (**b**)

climate change and frequent occurrence of extreme floods worldwide.

Consequently, the main objective of the present study was to evaluate the contents and spatial distribution of As, Cd, Pb, Cr, Ni, Cu, and Zn in flood sediments and arable soils within the sub-catchments of six rivers: the Danube, Sava, Great Morava, West Morava, Drina, and Kolubara (Serbia), severely affected by the extreme flood in May 2014, using regulated quality guidelines and respective geochemical background levels. The sub-catchment of the West Morava River was selected as representative for: (1) assessing the degree of flood sediment and soil contamination and consequent ecological risk by means of sediment/soil regulated quality guidelines and quantitative indices (Pollution index-P_i, Enrichment factor-E_f, Geo-accumulation index-I_{geo}, and Potential ecological risk index-PERI), and (2) identifying the contribution of geogenic and anthropogenic sources to PTEs contents in the sediments and soils using multivariate statistical analysis. The results contribute to a novel understanding of the impact of extreme flood-driven diffuse sources of geogenic PTEs on soil pedogenesis, contamination, and environmental risk in the West Balkan rivers catchments and similar areas.

Materials and methods

Study area

The study area belongs to the Black Sea drainage basin, which occupies about 92% of the territory of Serbia. From Serbia, the Danube and its tributaries: the Great Morava River (created by the confluence of the South Morava and the West Morava) and the Sava River (with its tributaries-the Drina and the Kolubara) drain materials that originate from Mesozoic flysch, igneous rocks, Paleozoic schist, Tertiary volcanic rocks, Quaternary loess and Mesozoic ultramafic serpentinite and peridotite, where the latter two are on the fringes of the Dinaride Ophiolite Zone (Dimitrijević 1992; Dill et al. 2008). The sub-catchments of the six main rivers in Serbia: the Danube, Sava, Great Morava, West Morava, Drina, and Kolubara (Fig. 1a) were affected by the severe flood in May 2014.

Sampling of soils and sediments

In all, a total of 445 composite samples (274 of soil and 171 of flood sediment) were collected immediately after flood waters withdraw from the points of maximum inundation (Fig. 1a). The composite samples were bulked from three single soil/sediment samples at each sampling site. At 171 sites, samples were collected from the flood sediment and the soil below, such that sediment/soil pairs were formed. Since the flood occurred in May, the land was already under crops and, the border line between soil and sediment was highly visible. Namely, it was the beginning of root system. Sediment samples were collected above the roots, whereas soil was sampled below the roots from a depth of 0 to 30 cm. At 103 sampling points, the sediment and soil were not separated during sampling due to a sediment thickness of less than 1 cm. Those samples were further addressed as soil. The exact geographic position of each sampling point (Fig. 1) was determined using the Global Positioning System (*GPS*).

Soil and flood sediment pretreatment and analyses

After air-drying, grinding and sieving through 2 mm mesh the following analyses were performed: soil and sediment reaction (pH) was measured with a WTW pH meter 330i in soil/water and soil/1 M KCl (1:2.5) suspensions; organic carbon (org. C) was determined by wet oxidation using potassium dichromate as the oxidizing agent, the unreacted oxidant was determined with iron (II) ammonium sulfate. Distribution of the grain size fractions (sand (< 2–0.063 mm), silt (0.063–0.001 mm), and clay (< 0.001 mm) was determined by a combination of wet sieving and pipette methods, after ultrasonic dispersion at 40 MHz (120 W) without prior destruction of PTEs binding sites such as organic matter or (hydr)oxides, as described by Hereter et al. (2002). The determined physical and chemical properties of the soils and sediments (grain size distribution, pH and organic carbon) are given in Supporting Information 1. Pseudo-total contents of As, Cd, Cr, Pb, Ni, Zn, Cu, and Fe were determined by inductively coupled plasma optical emission spectrometry (*ICP-OES*) (Thermo Scientific *iCAP* 6300) after digestion with nitric acid (HNO_3, 65%) + hydrogen peroxide (H_2O_2, 30%) (US EPA Method 3050B, US EPA 1996). All

measurements were performed in triplicate; the maximum allowable relative standard deviation between replicates was 5%. Certified standard solutions (As—J.T. Baker Analyzed reagent; Cr, Cu, Zn—Accustandard; Ni, Pb, Cd—Panreac) were measured to assess measurement accuracy. Detection limits, calculated as concentration greater than three times the standard deviation of ten measurements of the blank solution, were: 0.6 mg As kg^{-1}, 0.07 mg Cd kg^{-1}, 0.2 mg Cr kg^{-1}, 0.75 mg Pb kg^{-1}, 0.3 mg Ni kg^{-1}, 0.07 mg Zn kg^{-1}, 0.1 mg Cu kg^{-1}, and 0.25 mg Fe kg^{-1}. The reference soil (ERM-CC141 loam soil, Belgium) was analyzed to verify the results; PTEs recovery ranged from 89 to 112%. The 3050B digestion method disregards the fact that a certain portion of the total PTEs may remain in the residuum. Nevertheless, near-total extraction can be achieved in many cases, such that digestion is suitable for routine assessment of soil contamination by metals (Amacher 1996). Accordingly, the obtained pseudo-total contents will be referred to as total contents hereafter.

Pollution evaluation methods and risk indexes

Pollution index (P_i)

To assess the degree of soil and sediment pollution by a particular PTE, the single-factor pollution index (P_i) was calculated as the ratio of the measured PTE content (C_i) in the soil/sediment to its reference value (S_i), according to Cao et al. (2013):

$$P_i = C_i/S_i \quad (1)$$

The maximum permissible PTEs contents in soil according to national legislation (Regulation on Permissible Amounts of Hazardous and Harmful Substances in Soil and Water for Irrigation, and Methods for their Determination (Official Gazette of the Republic of Serbia 23/94), were used as reference values (S_i) in this study.

The P_i classifies the following pollution levels: $P_i \leq 1.0$ = clean (safe); $1.0 < P_i \leq 2.0$ = slightly polluted; $2.0 < P_i \leq 4.0$ = moderately polluted; $4.0 < P_i \leq 6.0$ = heavily polluted, and $P_i > 6.0$ = extremely polluted.

Enrichment factor (E_f)

To quantitatively assess the contribution of anthropogenic sources to PTEs contents in the soils and sediments, the Enrichment factors (E_f) were calculated using the following equation (Guo et al. 2014):

$$E_f = (C_i/C_r)/(B_i/B_r) \quad (2)$$

where C_i and C_r are the measured contents of the targeted PTE and the reference element in the soil/sediment, respectively, and B_i and B_r are the background levels of the targeted PTE and the reference element, respectively. The [Median + 2MAD] method (MAD-median of absolute deviations from the data's median) was used to calculate PTEs background levels in the soils for each sub-catchment (Reimann et al. 2005; Mrvić et al. 2011). Iron (Fe) was selected as the reference element. The iron content in the soils and sediments was determined following the same procedure as for PTEs contents (Sect. 2.3). The calculated background levels are given in Supporting Information 2.

According to the E_f values, PTE content can be classified under one of the following levels of enrichment: $E_f \leq 1$ = no enrichment; $1 < E_f \leq 3$ = minor enrichment; $3 < E_f \leq 5$ = moderate enrichment; $5 < E_f \leq 10$ = moderately severe enrichment; $10 < E_f \leq 25$ = severe enrichment; $25 < E_f \leq 50$ = very severe enrichment; and $E_f > 50$ = extremely severe enrichment.

Geo-accumulation index (I_{geo})

The levels of flood sediment pollution were evaluated by the Geo-accumulation index (I_{geo}). According to Guo et al. (2014), I_{geo} was calculated as:

$$I_{geo} = \log_2[C_i/1.5B_i] \quad (3)$$

where C_i is the measured content of PTE "i", and B_i is the geochemical background level of PTE "i".

According to I_{geo}, sediment can be classified as follows: $I_{geo} \leq 0$ = unpolluted; $0 < I_{geo} \leq 1$ = unpolluted to moderately polluted; $1 < I_{geo} \leq 2$ = moderately polluted; $2 < I_{geo} \leq 3$ = moderate to strongly polluted; $3 < I_{geo} \leq 4$ = strongly polluted; $4 < I_{geo} \leq 5$ = strongly to extremely polluted, and $I_{geo} > 5$ = extremely polluted.

Potential ecological risk index (PERI)

The potential ecological risk index (PERI) grades the overall multi-element environmental risk by merging toxic-response-based ecological risks of individual PTEs (Hakanson 1980). The risk index was calculated as follows:

$$RI = \Sigma E_r^i = \Sigma T_r^i \left(C_s^i / C_n^i\right) \quad (4)$$

where RI is the sum of individual potential ecological risks of all PTEs, E_r^i is the PERI of an individual element, T_r^i is the toxic-response factor for a given PTE, C_s^i is the measured content of a given PTE, and C_n^i is the reference value of the given PTE, in this case the respective background level (see "Enrichment factor (Ef)" section). The toxic-response factors for As, Cd, Pb, Cr, Ni, Cu, and Zn are 10, 30, 5, 2, 5, 5, and 1, respectively (Hakanson 1980).

Hakanson (1980) suggested the following ecological risk grading for E_r and RI values: (1) $E_r < 40$ = low ecological risk; $40 < E_r \leq 80$ = moderate ecological risk; $80 < E_r \leq 160$ = appreciable ecological risk; $160 < E_r \leq 320$ = high ecological risk; and > 320 = serious ecological risk; and (2) $RI < 150$ = low ecological risk; $150 < RI < 300$ = moderate ecological risk; $300 < RI < 600$ = high ecological risk; and $RI \geq 600$ = significantly high ecological risk.

Statistical analyses

Statistical analyses (maximum, minimum, Student's *t* test, Pearson's correlation coefficient r, cluster analysis (CA) and principal component analysis (PCA)) were carried out using StatSoft Statistica 10 software. The strength of the correlation coefficients was interpreted according to Fowler et al. (2006). PTEs were clustered applying the Euclidean distance method and using complete linkage. Prior to PCA, the normality of the datasets was evaluated by means of the Quantiles–Quantiles (Q–Q) plot; all variables showed an approximately normal distribution. Further, the Kaiser–Meyer–Olkin (KMO) test for sampling adequacy revealed values of ~ 0.8, whereas Bartlett's sphericity test yielded p values < 0.01, both indicating that multivariate statistics provided reliable results for further consideration (Kaiser 1974; Cerny and Kaiser 1977; Snedecor and Cochran 1989). Principal components with Eigenvalues > 1 were plotted. Varimax rotation was implemented to improve interpretability. Loadings > 0.7 were significant.

Results

PTEs contents and spatial distribution in soils and flood sediments

In all the studied sub-catchments, the contents of certain PTEs in the soils (Table 1) exceeded regulated maximum permissible values. In particular, high soil Ni was detected in five, Cr in four, and As in three of the six sub-catchments (Table 1). The maximum measured contents of Ni were 9, 5, 4, 3.5, and 2 times higher than the regulated threshold value (50 mg Ni kg^{-1}) in soils from the West Morava, Drina, Great Morava, Kolubara, and Sava sub-catchments, respectively. The Ni contents were also higher than the regulated threshold value in most of the individual soils (Fig. 2a). The maximum measured Cr contents were detected in soils from the West Morava, Great Morava, Kolubara, and Drina sub-catchments and were 2.5, 1.3, 1.3, and 1.2 times higher than the threshold value (100 mg Cr kg^{-1}), respectively. The number of individual soils with Cr contents above the threshold value was smaller than in the case of Ni (Fig. 2a). The maximum measured As contents exceeded the regulated limit (25 mg kg^{-1}) in soils from the Drina (three times higher) and the West Morava sub-catchments (1.6 times higher) (Table 1). Similarly to As, the maximum measured Pb contents were higher than the threshold value (100 mg kg^{-1}) in soils from two sub-catchments (the Great Morava river—two times, and the West Morava River—1.3 times). The number of soils with As and Pb contents above the regulated limit was even smaller compared to both Ni and Cr (Fig. 2a). In contrast, Zn and Cd contents in the soils from all the sub-catchments were below threshold values.

High Ni, Cr, and As contents were detected in flood sediments from the same sub-catchments as in the case of the soils (Table 1). The maximum measured Ni, Cr, and As contents were similar in the soils and sediments, except those from the Drina sub-catchment. The contents of Ni, Cr, As, and Pb higher than threshold value were found in a similar number of

Table 1 The content of potentially toxic elements (PTEs) in soils and flood sediments at various locations severally flooded in May, 2014

Location	Sample type	*n*		As (mg kg^{-1})	Cd	Pb	Cr	Ni	Cu	Zn
The Danube sub-catchment	Flood sediment	13	Min[a]	1	0.12	8	7	6	3	31
			Max[b]	10	0.81	39	47	41	158	120
	Soil	15	Min	3	< 0.05	12	13	13	13	33
			Max	14	0.66	33	47	42	199	148
			t test[c]	−2.96**	−3.14**	ns	ns	ns	ns	ns
The Great Morava sub-catchment	Flood sediment	53	Min	2	0.27	9	19	18	7	31
			Max	28	1.09	191	129	181	42	152
	Soil	82	Min	1	< 0.05	10	17	16	8	26
			Max	29	1.14	201	135	198	145	156
			t test	ns	− 2.57*	ns	ns	ns	ns	ns
The West Morava sub-catchment	Flood sediment	39	Min	5	0.43	15	51	91	16	59
			Max	37	1.66	127	207	372	64	230
	Soil	63	Min	3	0.13	14	30	32	8	40
			Max	40	2.08	126	250	468	108	271
			t test	ns	− 2.14*	ns	ns	ns	ns	ns
The Kolubara sub-catchment	Flood sediment	28	Min	2	0.06	9	14	18	7	28
			Max	10	1.89	27	129	166	157	150
	Soil	36	Min	1	< 0.05	9	14	18	7	36
			Max	10	1.88	24	134	178	21	84
			t test	2.01*	− 4.30**	ns	ns	ns	-2.04*	ns
The Drina sub-catchment	Flood sediment	9	Min	10	0.48	25	15	24	15	66
			Max	54	1.37	122	52	77	44	198
	Soil	34	Min	4	0.07	10	10	20	11	59
			Max	75	0.82	54	121	258	146	126
			t test	− 2.96**	− 3.06**	− 3.71**	ns	ns	ns	− 3.41**
The Sava sub-catchment	Flood sediment	29	Min	2	0.36	11	32	29	14	55
			Max	33	0.91	56	69	105	40	175
	Soil	44	Min	3	< 0.05	8	24	23	13	44
			Max	13	0.90	58	72	100	38	131
			t test	ns	−2.17*	ns	ns	ns	ns	ns
Maximum permitted content in a soil[d]				25	3	100	100	50	100	300

[a]Minimum

[b]Maximum

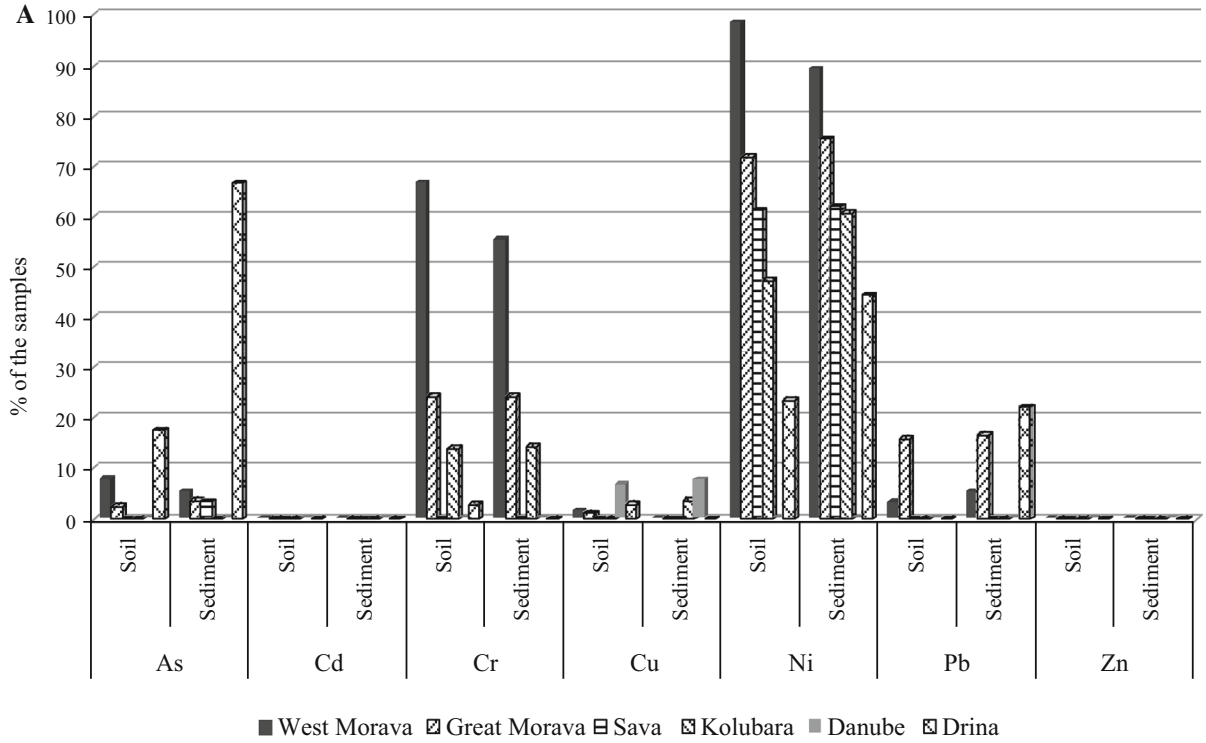
[c]Student's t test between PTE content in the soil and flood sediment

[d]Ordinance of permitted amounts of hazardous and harmful substances in soil and water for irrigation and methods of their determination (Official Gazette of the Republic of Serbia (Sl. RS in Serbian). No 23/94)

*Significant at $p < 0.05$

**Significant at $p < 0.01$, ns not significant

individual sediments as in the cases of the soils (Fig. 2a). In the present study, the PTEs threshold value and their background levels used to evaluate the flood sediments were the same as for the soils since: (1) flood sediment covered arable land, and (2) in preparation for the next cropping season, farmers had plowed the sediment along with the soil.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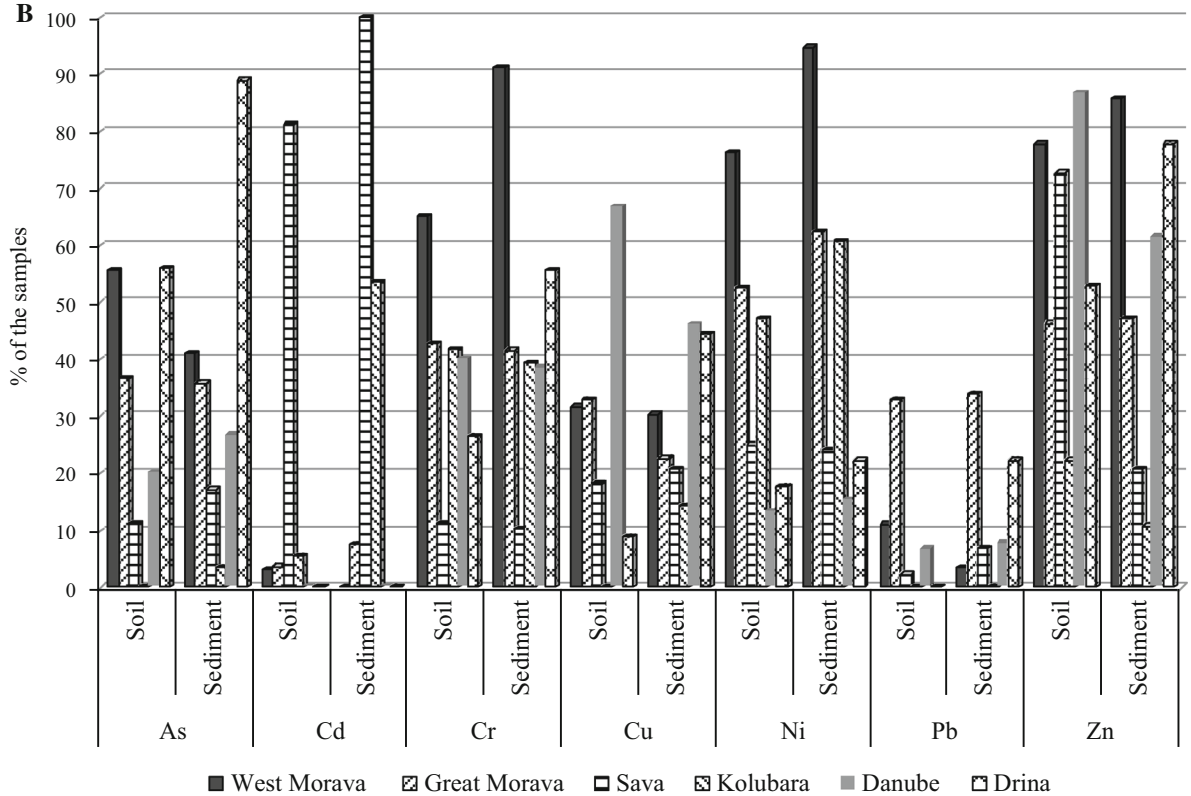
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Zn
West Morava
Great Morava
Sava
Kolubara
Danube
Drina

◀**Fig. 2** The percentage of soil and flood sediment samples with PTEs contents above their regulated threshold values according to legislation in Serbia (**a**), and the percentage of the soil and flood sediment samples with PTEs contents above their respective background values (**b**)

For a more in-depth evaluation, the PTEs in the soils and sediments were compared with the respective background levels (Supporting Information 2). The comparison indicated that Ni, Cr, and Zn contents in the soils were above background levels in all the sub-catchments, while Pb and Cd contents exceeded background levels in four, and Cu and As in five sub-catchments. At the same time and in all cases, the number of soils with PTEs contents above background levels was significantly higher than indicated by the comparison with threshold values, except for Ni (Fig. 2a, b).

The difference in the results depending on the normalization mode was also notable when the maximum measured PTEs contents were compared with their background levels. For example, in the case of Ni, the maximum measured contents in the soils from the West Morava and Great Morava sub-catchments were 4.5 and 2.7 times higher than the background levels, respectively. On the other hand, the maximum measured Zn contents in the soils were below the regulated limit (300 mg kg^{-1}), whereas they exceeded background levels in all the sub-catchments, by factor of 1.5 (Kolubara and Drina) to 3.4 (West Morava). Similarly to the soils, the PTEs contents in the flood sediments were higher than their respective background levels in most of the samples from all the sub-catchments (Fig. 2b).

The West Morava sub-catchment (Fig. 1b), was selected for more detailed evaluation of the level of soils and flood sediments contamination. This sub-catchment was chosen because of the highest measured Ni and Cr contents and, consequently, the greatest potential environmental threat compared to the other sub-catchments. The PTEs contents of the sediment/soil pairs from the West Morava sub-catchment ($n = 39$) are shown in Supporting Information 3.

Pollution indices

Based on the P_i classification of Ni contamination, about 95% of both soils and flood sediments from the West Morava sub-catchment belonged to moderately and extremely polluted categories and there were no samples in the clean category (Table 2). In the case of Cr, the majority of the soils and sediments belonged to the slightly polluted category (67 and 64% of the samples, respectively), followed by the clean category (28% of soils and 30% of sediments). The P_i classification indicated that about 90% of the analyzed soils and sediment fell into the clean category with regard to contamination by As, Cd, Pb, Cu, and Zn.

However, E_f indicated minor and moderate enrichment of the soils and sediments with Ni, and Cr, to a lesser extent with As, Pb, Cu, and Zn, and mostly no enrichment with Cd (Table 2). The lowest percentage of the soils and sediments in the no enrichment category was found in the case of Ni (soils-5.1% and sediments-5.2% of the total number of samples).

The I_{geo} indicated that about 82% of the flood sediments could be considered polluted by different levels of Ni. Over 90% of the sediments were found unpolluted by Cd, Pb, and Cu, whereas nearly 2/3, 1/2, and 1/2 of the sediments belonged to this category in the case of As, Cr, and Zn, respectively.

The calculated E^i and PERI of the soils and sediments are summarized in Table 3 and shown in detail in Supporting Information 4. The results suggest low overall multi-element ecological risk at all the studied sites. The same was indicated by the potential ecological risk index for individual PTEs (mean values of E_r^i). The outcome of the mean E_r^i was Zn < Cr < Pb < Ni < Cu < As < Cd from the soils, and Zn < Cr < Pb < Cu < Ni < Cd < As from the sediments.

Multivariate statistical analysis

Pearson's correlation analysis

This analysis revealed strong significant correlations (Pearson's r) between the As, Cd, Pb, Cr, Ni, and Zn contents in the soils and flood sediments from the West Morava sub-catchment (0.86, 0.80, 0.93, 0.95, 0.95, and 0.87, respectively, $n = 39$, $p < 0.01$). The correlation between the Cu contents in the soils and sediments was moderate ($r = 0.52$, $n = 39$, $p < 0.05$).

Table 2 Pollution level of the soil/sediment pairs in the West Morava sub-catchment (n = 39)

Pollution level	As		Cd		Pb		Cr		Ni		Cu		Zn	
	Soil	Flood sediment	Soil	Flood sediment	Soil	Flood sediment	Soil	Flood sediment	Soil	Flood sediment	Soil	Flood sediment	Soil	Flood sediment
	Pollution index (P_i)													
Clean	87.2	92.3	100	100	97.4	97.4	28.2	30.8	0.0	0.0	97.4	100	100	100
Slightly polluted	12.8	7.7			2.6	2.6	66.7	64.1	5.1	5.1	2.6			
Moderately polluted							5.1	5.1	28.2	30.8				
Heavily polluted									53.9	53.8				
Extremely polluted									12.8	10.3				
	Enrichment factor (E_f)													
No enrichm.	23.1	20.5	94.9	92.3	51.3	41.0	7.7	7.7	5.1	5.2	53.8	30.8	10.3	5.1
Minor enrichment	71.8	76.9	5.1	7.7	48.7	59.0	89.7	79.5	64.1	46.1	43.6	66.7	84.6	79.5
Moderate enrichment	5.1	2.6					2.6	12.8	30.8	46.1	2.6	2.6	5.1	15.4
Moderately severe enrichment										2.6				
	Geological index (I_{geo})													
Unpoll.		74.4		100		97.4		46.1		17.9		92.3		43.6
Unpoll. to moderately polluted		25.6				2.6		53.9		76.9		7.7		56.4
Moderately polluted										5.2				

Data refer to the percentage of samples in a particular pollution level

Table 3 The results of potential ecological risk assessment of the soils and flood sediments from the West Morava sub-catchment (n = 39)

E^i								RI
	As	Cd	Pb	Cr	Ni	Cu	Zn	
Soil								
Min	4.27	2.38	0.86	1.26	4.11	2.17	0.54	18.10
Max	29.61	36.79	6.28	5.09	17.15	17.54	3.39	96.63
Average	12.27	11.48	3.18	3.09	10.41	4.79	1.43	46.66
Flood sediment								
Min	3.83	7.59	0.94	1.27	4.35	2.65	0.74	22.35
Max	27.80	29.38	7.96	5.16	17.80	10.39	2.88	86.87
Average	12.05	14.72	3.07	3.04	10.38	4.78	1.52	49.57

Principal component analysis (PCA)

The PCA of the PTEs contents in the soil from the West Morava sub-catchment revealed two principal components with Eigenvalues > 1, which explained 83.14% of the total variances (Fig. 3a). The first component (PC 1) accounted for 63.05% of the total variance and had a high positive loading of Ni, Cr, Pb, and As. The second component (PC 2) had a high positive loading of Zn and Cd and accounted for

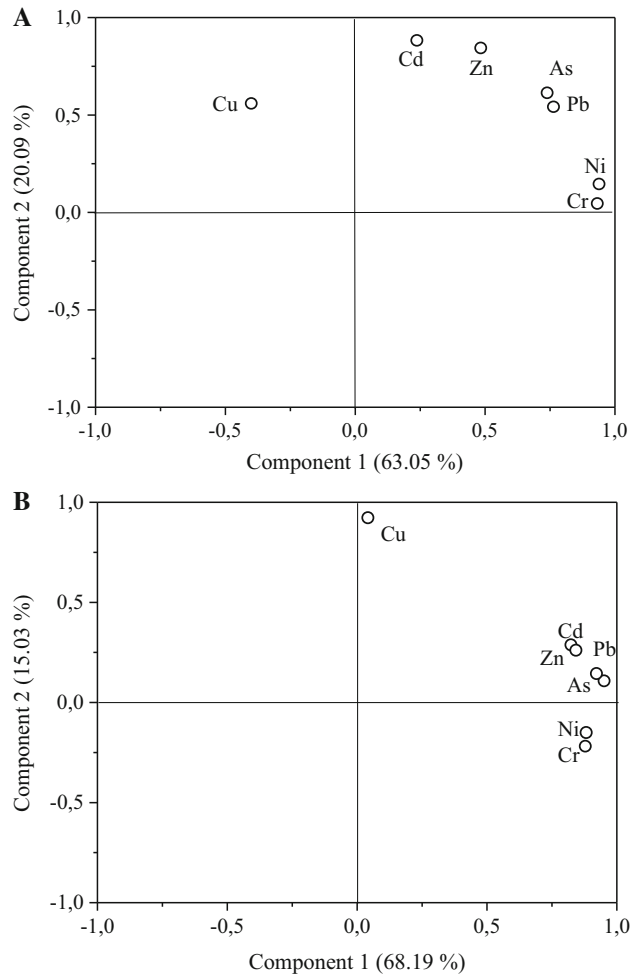


Fig. 3 The principal component analysis of PTEs in the soils (**a**), and flood sediments (**b**) from the West Morava sub-catchment. The measured PTEs contents were normalized by Varimax rotation before plotting. The cooper loadings in the soils were insignificant (factor loadings < 0.7)

20.09% of the total variance. The factor loadings for Cu were insignificant (< 0.7 in PC 1 and PC 2).

Two principal components were also found for PTEs in the sediments from the West Morava sub-catchment, explaining 83.22% of the total variance (Fig. 3b). The first component had high positive loadings of As, Pb, Ni, Cr, Zn, and Cd and explained 68.19% of the total variance. The second component accounted for 15.03% of the total variance and had a high positive loading of Cu.

Cluster analysis (CA)

The dendrogram of the cluster analysis of the soils from the West Morava sub-catchment showed three major clusters: cluster I (locations 303–341, Fig. 4a), cluster II (310–318), and cluster III (305–327). The sites within cluster I were mainly characterized by Ni content close to 200 mg kg^{-1} and As contents close to the 10–18 mg kg^{-1} interval. Cluster II comprised sites with the highest Ni and As within the class (> 250 mg Ni kg^{-1} and > 20 mg As kg^{-1}). The sites in cluster III were mainly characterized by the lowest Ni and As contents within the class (< 200 mg Ni kg^{-1} and < 10 mg As kg^{-1}).

The dendrogram of the cluster analysis of the flood sediments showed two major clusters: cluster I (locations 303–36, Fig. 4b) and cluster II (310–335). The sites in cluster I were mainly characterized by Ni content below 200 mg kg^{-1} and As content below 20 mg kg^{-1}, while the sites in cluster II primarily contained above 200 mg Ni kg^{-1} and above 20 mg As kg^{-1}.

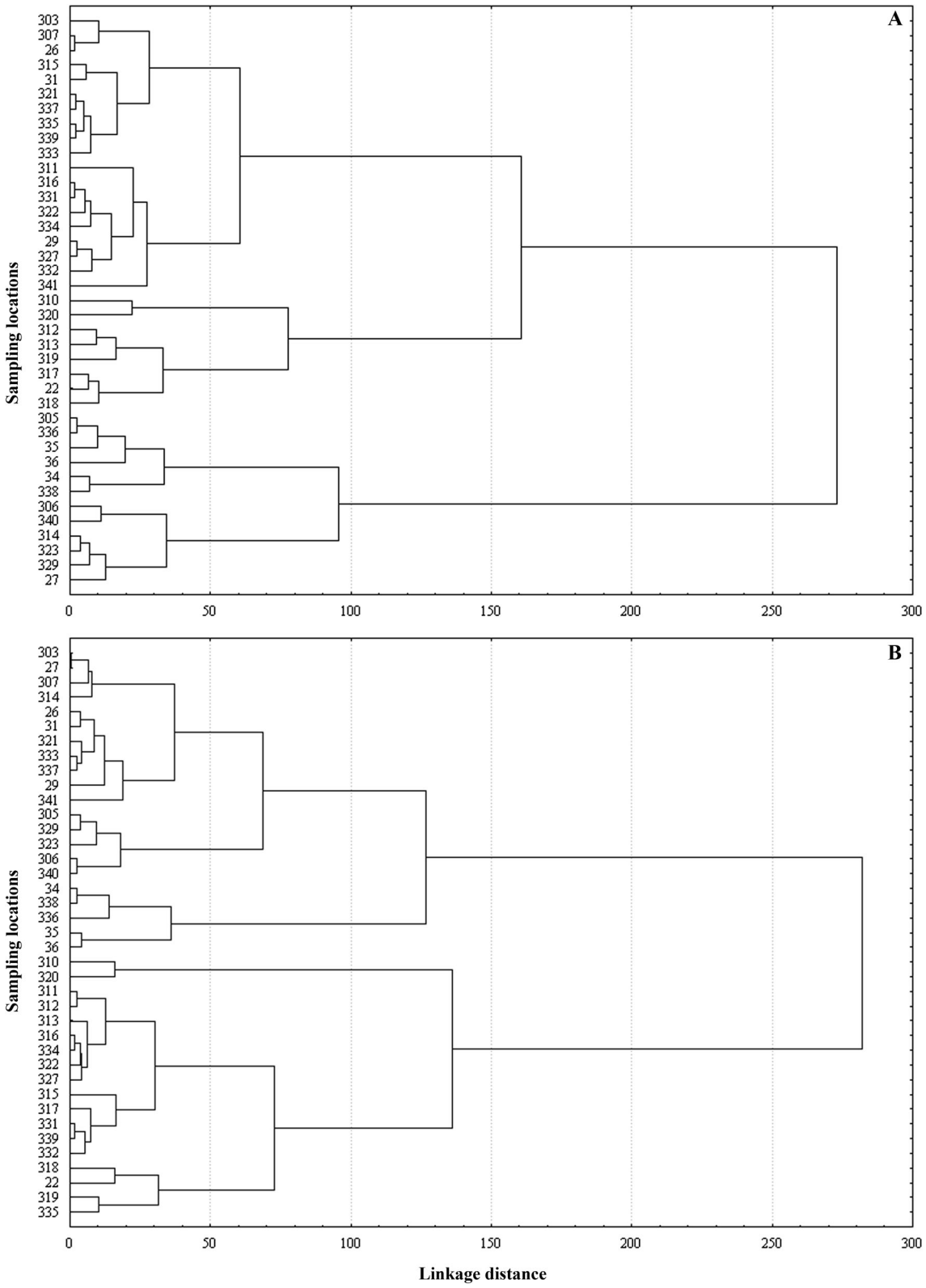
Discussion

PTEs contents in soils and sediments

The PTEs contents in the soils and sediments varied over a very wide range, showing spatial variability within and among the sub-catchments. These variations are attributable to, *inter alia*, soil pedogenesis in the floodplains and physical and chemical processes that govern sediment transport, sorting and deposition (Berner et al. 2012). The PTEs contents in the soils were found to be above regulated limits and/or background levels for remote sub-catchments (Fig. 2a, b). However, these results are generally in line with previous reports on soils across the study area (Mrvić et al. 2009; Antić-Mladenović et al. 2011, 2017). In addition, the contents of nearly all the PTEs in the soils were mostly similar to those in the sediments from all the sub-catchments. These findings imply that their sources in the soils might be similar to those of the flood sediments in the study area. The high and positive correlation coefficients among the PTEs, except for Cu, for the soils on one hand and the sediments on the other hand additionally support such a hypothesis. During flood events materials from both, geogenic and anthropogenic sources are carried by flood waves and deposited in flooded areas. The contents and origin of Ni and Cr contents in the soils might be directly related to ultramafic peridotite and serpentinite on the fringes of the Dinaride Ophiolite Zone in western Serbia (Dill et al. 2008; Antić-Mladenović et al. 2017). Arsenic, Pb, Cd, and Zn in the soils and sediments from the studied sub-catchments might originate from point sources such as ore bodies, mixed with anthropogenic diffuse sources like agriculture, road and railroad traffic, and the metal, chemical and textile industries as previously reported by Mrvić et al. (2009). The modest correlation of Cu content between the soils and sediments suggests that Cu sources and accumulation in the soils and sediments might differ from those of the other PTEs. Copper in the drained material might be associated with erosion of arable land and thus connected to more pronounced anthropogenic sources from agriculture than the other PTEs. In addition, point source pollution of the soils by Cu-based pesticides is indicated for sites with multiple exceedance of Cu contents in the flood sediment (individual data for all sub-catchments are not shown. The PTEs contents in the soil/flood sediment pairs from the West Morava sub-catchment are given in Supporting information 3).

The spatial occurrence of high PTEs contents in the soils and sediments that belonging to different sub-catchments indicates that there is a permanent PTEs load in the study area. Further, similar PTEs contents in the soils and sediments connect the PTEs loading of

Fig. 4 Dendrogram showing clustering of the Ni and As contents in the soils (**a**), and flood sediments (**b**) from the West Morava sub-catchment according to the Euclidean distance method by complete linkage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Sampling locations
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Linkage distance

the soils with flood events. Accordingly, soil contamination by PTEs might be result of a flood-driven geohistorical deposition of suspended materials of different origin, not a single flood event. This is in line with Majerová et al. (2013) who suggest that floods might be considered as a diffuse source of contamination. It is also consistent with the conclusions of Predić et al. (2016), that the May 2014 flood, which affected some parts of Bosnia and Herzegovina, did not cause soil contamination by trace elements. On the other hand, periodic flooding and sedimentation of different materials coincide with long-term soil formation processes in flood-prone areas (Čakmak et al. 2017).

Risk assessment indices

The pollution index (P_i) indicated that the highest pollution of the soils and flood sediments is attributable to Ni, Cr, and, to a lesser extent, As, which is consistent with risk indications according to the regulated limits (Fig. 2a, Table 2). However, the P_i clearly indicates the level of pollution, which is not visible from the normalization of PTEs contents by the regulated limits. In the case of Ni, the level of the sediments pollution is slightly higher than the pollution of soils, which might be related to "a dilution effect" in soils as well as to mineral weathering and soil pedogenesis. The trend is not as distinct for Cr, probably due to the refractory nature of Cr-reach spinels and their incomplete digestion (Rodgers 1972; Matys Grygar and Popelka 2016). The indicated level of soils pollution by As, Cd, Pb, Cr, Cu, and Zn is analogous to that of the sediments (Table 2). Overall, the P_i results are consistent with the geochemical nature of the soils in western Serbia (Dill et al. 2008; Antić-Mladenović et al. 2017) and suggest diffuse spreading of the PTEs within the West Morava sub-catchment.

Characterization of PTEs contents according to E_f and I_{geo} takes into account PTE background levels and, as such, qualitatively differs from P_i. The two might be more reliable risk assessment indexes than P_i. In the present study, E_f classification notably reduced the pollution risk of Ni as indicated by P_i. Sites heavily to extremely polluted by Ni according to P_i might be considered moderately enriched, due to the high geochemical background level of Ni (104 mg kg^{-1}). Accordingly, when the results of E_f are combined with the geology of the study area, the focus shifts primarily toward the geogenic origin of Ni in both soils and sediments. Knowledge of the geological material that might be transported and accumulated via flood waves and/or erosion is therefore of critical importance for interpreting pollution indices.

In the case of background levels lower than threshold values, as for As, Cd, Pb, and Cu in the present study, according to E_f, the influence of anthropogenic loadings on their total contents declines in the order: As > Cu > Pb > Cd. For Zn, both P_i and E_f probably overestimate the clean and minor to moderate enrichment categories, due to a very large difference between the background level (80 mg kg^{-1}) and the regulated limit (300 mg kg^{-1}). In the case where a background level approaches the regulated limit, as for Cr in the present study, the E_f minor enrichment might cover P_i classes clean + slightly polluted. Similarly to Ni, E_f reduced the pollution level indicated by P_i. Resulting I_{geo} categories for the flood sediments are in line with the E_f classification.

The predominantly geogenic origin of PTEs in the soils and sediments in the West Morava sub-catchment is reflected in the low overall multi-element environmental risk (mean RI), as well as in the low risk of the individual elements (E^i). The E^i for Ni was lower than for Cd and As, regardless of very high Ni contents (up to 468 mg kg^{-1}, Table 1). In contrast, Cd contents in the soils and sediments did not exceed permissible value, and the As contents exceeded them rarely. Thus, the E^i suggested low environmental risk from PTEs of geogenic origin (Rinklebe and Shaheen 2017), on the one hand, and confirmed Cd and As mobility and toxicity on the other hand (e.g., Lombi et al. 2000; Farooq et al. 2016).

Multivariate statistical analysis–identification of sources

Three primary sources of the PTEs in the soil could be identified according to PCA. High factor loadings of Ni, Cr, Pb, and As in the PC 1 indicated that they have been predominantly hosted in geogenic phases. This is in line with geology of western Serbia (Dill et al. 2008; Antić-Mladenović et al. 2017). PC 2 could differentiate Zn and Cd from the others PTEs. They mostly originate from mixed geogenic–anthropogenic

sources, which are consistent with their contents lower than maximum permissible values but, higher than the respective background levels (Fig. 2). This confirms the findings of Mrvić et al. (2009) regarding the origin of Zn and Cd in the soils of the West Morava sub-catchment. On the other hand, the insignificant factor loadings of Cu (< 0.7) corroborate with the hypothesis of soil contamination from anthropogenic point sources. This also explains the P_i and E_f for Cu, as well as the higher E^i for Cu in relative to Ni.

The PTEs with the high positive loadings in the components 1 and 2 for the soils are grouped in a single component for the sediments (Fig. 3b). This corroborates that the soils in the West Morava sub-catchment might be formed by accumulation of materials/phases which generated sediment in the 2014 flood. It further implies that geohistorical erosion and/or flood-driven sediment deposition might be: (a) a significant source of PTEs in the soils, and (b) an important soil-forming factor in the West Morava sub-catchment.

The cluster analysis grouped both soil and flood sediment from distant locations within the West Morava sub-catchment into similar classes according to the variability of Ni and As contents. The PTEs dispersal within a sub-catchment by sediment transport would primarily be governed by the mineral composition of the transported materials, as well as sediment sorting by hydraulic transport that might cause higher PTEs contents in laterally deposited sediments than in distal floodplain sediments (Matys Grygar et al. 2013). Since Ni contents exceeded As contents multiple times, Ni had a greater effect on the linkage between distant locations than As. Minerals highly enriched with Ni can roughly be separated into two groups. The first group comprises heavy density minerals, such as hematite, magnetite, sphene, and spinels (Rinklebe et al. 2016). The density of these minerals suggests relatively short transport before sedimentation (Berner et al. 2012). The second group includes Ni-bearing clay minerals formed in the first stage of ultramafic rock weathering (Raous et al. 2013; Bani et al. 2014). Light density clay minerals indicate relatively long transport before sedimentation (Ciszewski and Matys Grygar 2016). Consequently, different transport of Ni-enriched minerals with differing densities explains similar Ni contents in remote locations within the sub-catchment. In addition, sedimentation might be controlled by a hydraulic equivalence, which balances the opposite influence of the grain size and density of the deposited materials (Berner et al. 2012). Spatial variability of the other PTEs in the soils and sediments with a low mutual geochemical or mineralogical affinity might be attributable to comparable physical and chemical processes.

Conclusions

The study presented the contents and spatial distribution of PTEs (As, Cd, Pb, Cr, Ni, Cu, and Zn) in soils and flood sediments collected from six major river sub-catchments (Serbia), which were severely flooded during May 2014. The results revealed high PTEs contents, especially of Ni and Cr, and to a lesser extent of As, Pb, and Cu in flood sediments and arable soils from the all sub-catchments. The contents of Ni, Cr, As, Pb, and Cu above both regulated guidelines and background values, and the contents of Zn and Cd above background levels, were found in the sediments and soils from all the studied sub-catchments.

According to the pollution index (P_i), about 95% of soils and sediments from the sub-catchment of the West Morava River were extremely polluted by Ni and about 65% of all the samples were slightly polluted by Cr, whereas about 90% of soils and sediments were not polluted by As, Cd, Pb, Cu, and Zn. However, according to the Enrichment factor (E_f), the enrichment of the soils and sediments with Ni and Cr was minor to moderate. Further, the contents of nearly all the PTEs in the soils were mostly similar to their contents in the sediments. The results strongly indicated that: (1) the severe flood event in May 2014 did not cause significant contamination of arable soils by PTEs, and (2) flood-driven processes of PTEs transport and sedimentation might be an integral part of soil pedogenesis in the affected areas. At the same time, floods might be considered as a long-term secondary/diffuse source of soil contamination by PTEs in the affected areas.

The PCA differentiated the prevailing geogenic origin of Ni, Cr, As, Pb, the mixed origin of Cd and Zn, and the prevailing anthropogenic origin of Cu in the soils and sediments within the West Morava sub-catchment. The origin of PTEs in synergy with their contents and biogeochemical behavior in the soils and flood sediments, as well as their toxic response,

resulted in low overall environmental risk in the order Cd > As > Ni ≥ Cu > Pb > Cr > Zn. The higher ecological risk (E^i) of lower contents of more toxic PTEs (As, Cd) than E^i of higher contents of less toxic PTEs (Ni, Cr) suggests that the regulated threshold values might not always be reliable for assessing the level of soil pollution or the environmental impact of a particular PTE.

In the future, a soil monitoring program should be implemented to detect differences on a temporal scale, for instance to discriminate between the pre- and post-flood status of PTEs. In addition, biological monitoring of the studied sub-catchments and similar places should be included as an integral part, to enable assessment of the environmental risk, regulatory and geochemical guidelines, and pollution indices.

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