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Contamination, risk, and source apportionment of potentially toxic microelements in river sediments and soil after extreme flooding in the Kolubara River catchment in Western Serbia

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Abstract

Purpose Climate change is contributing to an increase in extreme weather events. This results in a higher river flooding risk, causing a series of environmental disturbances, including potential contamination of agricultural soil. In Serbia, the catastrophic floods of 2014 affected six river basins, including the Kolubara River Basin, as one of the larger sub-catchments of the large regional Sava River Basin, which is characterized by large areas under agricultural cultures, various geological substrates, and different types of industrial pollution. The main aim of this study was to establish the sources of potentially toxic elements in soil and flood sediments and the effect of the flood on their concentrations.

Materials and methods Field sampling was performed immediately after water had receded from the flooded area in May 2014. In total, 36 soil samples and 28 flood sediment samples were collected. After acid digestion (HNO_3), concentrations of the most frequent potentially toxic elements (PTE) in agricultural production (As, Cd, Cr, Cu, Ni, Pb, Zn) and Co which are closely related to the geological characteristics of river catchments, were analyzed. The origin, source, and interrelations of microelements, as well as background values of the PTE of the river catchment, the pollution index (Pi), enrichment factor (Ef), and geological index (Igeo), were determined, using statistical methods such as Pearson correlations, principal component analysis (PCA), and multiple linear regression (MLRA).

Results and discussion The content of the hot acid-extractable forms of the elements, PCA, and MLRA revealed a heavy geological influence on microelement content, especially on Ni, Cr, and Co, while an anthropogenic influence was observed for Cu, Zn, and Cd content. This mixed impact was primarily related to mines and their impact on As and Pb content. The pseudo-total concentrations of all the analyzed elements did not prove to be a danger in the catchment area, except for Cu in some samples, indicating point-source pollution, and Ni, whose pseudo-total content could be a limiting factor in agricultural production. For the Ef, the Ni content in 59% soil and 68% flood sediment samples is classified into influence classes.

Conclusions The similar pseudo-total contents of the elements studied in soil samples and flood sediment and their origin indicate that the long-term soil formation process is subject to periodic flooding in the Kolubara River Basin without any significant

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changes taking place. This implies that floods are not an endangering factor in terms of the contamination of soil by potentially toxic elements in the explored area.

Keywords Flood · Multiple linear regression analysis · Principal component analysis · Potential toxic elements · Sediments · Soil

1 Introduction

Potentially toxic elements (PTE), including heavy metals, are usually found in low concentrations in soils and rocks. Sources of PTE are usually considered to be of anthropogenic origin and the degree and extent of pollution have been studied in environmental science, with it being particularly important in agricultural soils because of the quick introduction of PTE into the food chain due to intensive plant production (Adriano 2002). The distribution of PTE in soils is controlled by parent-rock geochemistry, climatic and geomorphologic conditions, the time of weathering exposition, soil texture, living organisms, and anthropogenic inputs, such as industrial pollution and mining, as well as some characteristic activities linked to agricultural production, e.g., manuring and the use of protective measures (Hutchinson and Rothwell 2008; Cakmak et al. 2010; Roca et al. 2012; Cabral Pinto et al. 2014). Concern about the presence and accumulation of these PTE in soil and plants has been ongoing due to their adverse effects on both the environment and human health (des Santos-Araujo and Alleoni 2016). Flash floods cause landscape degradation due to the removal of soil and flood material sedimentation, as well as mechanical pollution and water polluted with PTE, resulting in a series of environmental disturbances (Lauer 2008; Milačič et al. 2017). In addition, the content of potentially toxic microelements in flood-related soils changes (Guo et al. 2014), whether they are of anthropogenic (e.g., Martínez-Santos et al. 2015) or geological origin (e.g., Liu et al. 2016). These changes affect agricultural land in river valleys in particular (Du Laing et al. 2009). Soils that are under the direct influence of flood sediments can represent a pollution source in themselves or through interacting with other factors across multiple spatial and temporal scales (Erftemeijer et al. 2012). Therefore, river sediments become an important indicator for characterizing sources of pollution and the anthropogenic impact (Xu et al. 2014).

However, due to the physical and chemical changes which occur during flooding, the content and total form of PTE in sediments cannot be the only measure of their impact on agricultural soils. Hence, it is necessary to establish their background levels and their levels compared to the total PTE content at the sampling sites. In this way, the coefficients and indices obtained give a more realistic picture of pollution and the anthropogenic impact. Besides this, in the wider spatial context, the relationship between certain coefficients can point very clearly to the extent of the impact of certain pollutants (N'guessan et al. 2009). Climate change is contributing to an increase in extreme weather events, including greater intensity storm rainfall, in many parts of the world, leading to higher risks of river flooding (Bates et al. 2008). Since the 1960s, there have been 298 floods in EU countries, accounting for 12% of all global floods (Green et al. 2013). In Serbia, from 1915 to 2013, 848 flash floods were registered (Petrović et al. 2014), with one of the biggest occurring in 2014, covering six river catchments: the Danube, Sava, Velika Morava, Western Morava, Drina, and Kolubara. Over 200-mm precipitation fell between May 15 and 24, more than the 3-month precipitation average for that time of year, which resulted in 482,700 ha of land flooding. After the water receded, flood sediment had to be removed from 335,400 m^2 of land (Serbian Government Report on Floods 2014).

In this regard, this study aimed to evaluate the possible effects of the 2014 flooding on environmental disturbances and arable soil pollution in the Kolubara River Basin by measuring and analyzing the quantities of hot acid-extractable forms of potentially toxic elements in soil and flooded sediments immediately after flood water receded. The collected samples were analyzed for the hot acid-extractable forms of potentially toxic elements for those elements that most often represent an endangering factor in agricultural production (As, Cd, Cr, Cu, Ni, Pb, Zn) and Co which is closely related to the geological characteristics of the river catchment. So as to determine the degree of pollution and the possible environmental impact of flooding, background values of potentially toxic metals and pollution indicators were determined: the pollution index (Pi), enrichment factor (Ef), and geoaccumulation index (Igeo), only for flood sediments that indicate the degree of pollution in relation to national legal norms, the natural background of certain harmful microelements, and the degree of contamination of the sediments themselves. For data processing, the Pearson correlation, principal component analysis (PCA), and multiple linear regression (MLR) analyses were applied.

2 Materials and methods

2.1 Study area

The Kolubara River (127 km long) flows into the Sava River, which is part of the Black Sea Basin via the Danube. The Kolubara Basin covers 3618.6 km^2 between 44° 04′ and 44°

39′ N and 19° 34′ and 20° 34′ E (Fig. 1), its boundaries coincide with the boundaries of the Jadar block terrane, and it was geologically very active in the past. In terms of geomorphological classes in the Kolubara River Basin, sands, sandy clays, sandy limestones, and conglomerates are found over half the area, while somewhat less common are marlstones, marly limestones, micaceous sandstones, clayey sandstones, and clays. These forms of geological deposits are found in the valley region of the Kolubara Basin. As opposed to the lower-lying areas of the catchment, its western and southern edges are characterized by massive limestone with flows of diabase-hornstone formations as well as sections of serpentinite. On the eastern edge of the catchment, there is more pronounced fragmentation of the geological formations with a large proportion of marlstone, clayey schist sandstones, diabase-hornstone formations, harzburgite, lherzolite, and serpentinite The characteristic Jurassic formations of this belt of diabase-hornstone formations with basic and ultrabasic rocks are the main sources of metallic minerals (Geolis 2010). The diversity of the geological substrate and its intermixing conditioned the mountains, such as Povlen, Maljen, and Rudnik, on the edge of the basin. They abound in Pb, Zn, and Cu ore deposits near ultramafic rocks, which caused high Ni, Cr, and Co concentrations (Anderson et al. 1973; Antić-Mladenović et al. 2017), as well as deposits of lignite in the catchment area (Filipović 2005). The effect of such a geological substrate on soil is pronounced due to water erosion, with 30.44% of the Kolubara River Basin under the influence of moderate and very strong erosion processes (Belanovic-Simic et al. 2013). The soil cover here is mainly Stagnosol and Fluvisol in lower areas, while Cambisols are mainly found in the intrazones between Fluvisol and Stagnosol. Along the edges of the Basin, where altitude increases, there are undeveloped Leptosols and Regosols (WRB 2006; Mrvić et al. 2013; Pavlović et al. 2017). The climate of this area is characterized as continental. The amount of precipitation in the Kolubara Basin is similar to the Central European and Danubian region with a mean annual rainfall of less than 700 mm in the lower parts of the Kolubara and Tamnava basins. As altitude increases, mean annual precipitation rises to more than 900 mm and even over 1000 mm (Đukanović 2000).

2.2 Sampling

Immediately after the floodwater had receded, samples of arable soil were collected at certain distances from the riverbed depending on the flood wave, with the sampling points being on the boundary of this wave. A total of 445 samples (274 soil and 171 flood sediment) were taken from the entire flooded area in Serbia and their basic fertility parameters (soil acidity, percentage of $CaCO_3$ and organic matter, and content of available potassium and phosphorus) and content of PTE were analyzed. Out of these samples, 36 soil samples and 28 flood sediment samples were taken from the Kolubara River Basin and the levels of some PTE they contained are presented in this study (Fig. 1 and Table S1 (Electronic Supplementary Material)). The flood sediment was sampled at a depth corresponding to the thickness of the sediment layers (the maximum thickness of the sediment was 30 cm). The soil samples were taken directly below the flood sediment layer.

2.3 Analytical procedures

After sampling, samples were air-dried, ground, and sieved through a 2-mm mesh. The following analyses were performed: the content of hot acid-extractable forms of PTE (As, Cd, Co,

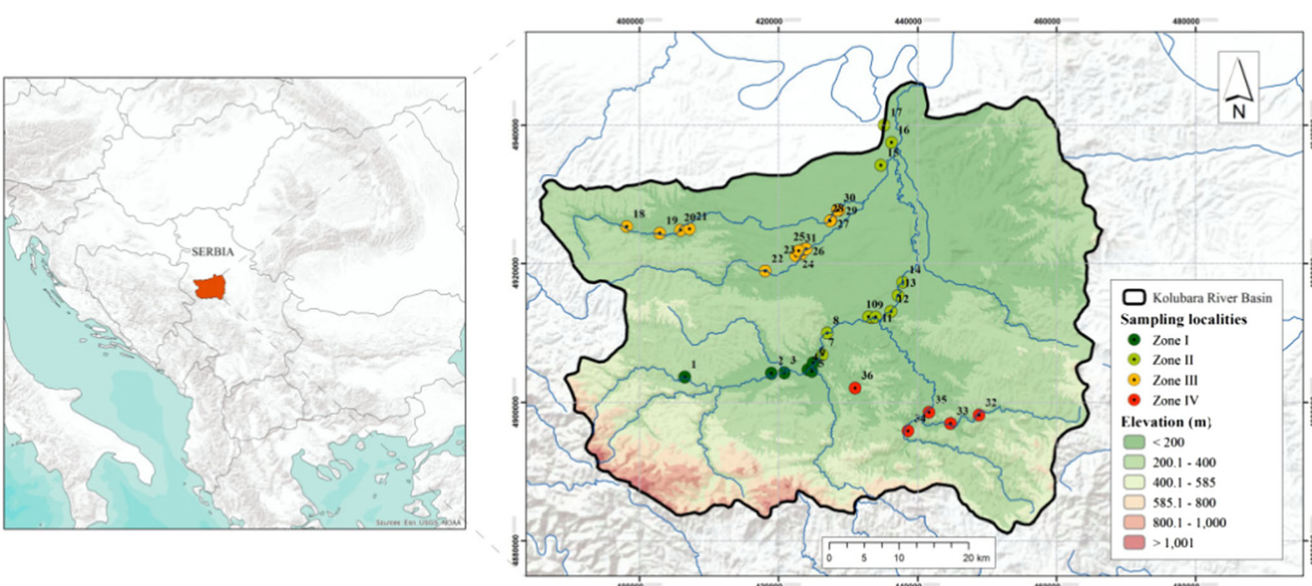

Fig. 1 Sampling localities/sites in the Kolubara River Basin catchment

Cr, Cu, Ni, Pb, and Zn) in soil and flood sediment was determined with an ICAP 6300 optical emission spectrometer (Thermo Electron Corporation, Cambridge, UK) after digestion with nitric acid (HNO_3, 65%) + hydrogen peroxide (H_2O_2, 30%) (US EPA Method 3050B, 1996). In 250-mL digestion vessels, 10 mL HNO_3 was added to a 2-g sample, heated to 95 °C, and refluxed. After cooling, 5 mL of concentrated HNO_3 was added and the cover was replaced and it was refluxed for 30 min. If brown fumes were generated, indicating oxidation of the sample by HNO_3, this step was repeated (with the addition of 5 mL of concentrated HNO_3) until no brown fumes were given off, indicating a complete reaction with HNO_3. After boiling for 2 h, 2 mL of water and 3 mL of 30% H_2O_2 were added. The vessel was covered with a watch glass and returned to the heat source for warming and to start the peroxide reaction. After cooling, it was diluted to 100 mL with water. Particulates in the digestate were then removed by filtration. For result verification, the referent soil (ERM-CC141 loam soil, Belgium) was analyzed. The recovery ranged from 89 to 112%. Detection limits for the elements were as follows: 0.6436 mg kg^{-1} (As), 0.0326 mg kg^{-1} (Co) 0.0166 mg kg^{-1} (Cd), 0.2897 mg kg^{-1} (Cr), 2.3233 mg kg^{-1} (Cu), 0.2239 mg kg^{-1} (Ni), 2.8597 mg kg^{-1} (Pb), 8.5106 mg kg^{-1} (Zn), and 81.4905 mg kg^{-1} (Fe). For each element, the relative standard deviation (RSD) was lower than 5%.

2.4 Indicators of soil and sediment pollution with potentially toxic microelements (PTE)

The pollution level for a given PTE was evaluated with the Pi, using:

$$\mathrm{Pi} = \frac{\mathrm{Ci}}{\mathrm{Si}} \tag{1}$$

where Pi is the pollution index, Ci the metal concentration in the sample, and Si the reference value (Regulation of the Government of the Republic of Serbia, SG RS88/2010 pp. 226–231, 2010): Pi pollution class: I Clean, 0–1; II Slightly polluted, 1–2; III Moderately polluted, 2–4; IV Heavily polluted, 4–6; and V Extremely polluted, > 6 (Cao et al. 2013).

The Ef of PTE were calculated to assess quantitatively the contribution of anthropogenic sources to those concentrations observed in surface soils. The following equation was used:

$$\mathrm{Ef} = \frac{{}^{\mathrm{Ci}}/_{\mathrm{Cr}}}{{}^{\mathrm{Bi}}/_{\mathrm{Br}}} \tag{2}$$

where Ci and Cr are the target metal and reference metal (Fe) concentrations in the soil sample and Bi and Br the target metal and reference metal (Fe) background concentrations in the same region. Iron has commonly been used as a reference metal due to its geochemical characteristics (Summer et al. 1996; Schiff and Weisberg 1999; Sterckeman et al. 2002; N'guessan et al. 2009; Giri et al. 2017). In our study, using Fe was justified due to the significant impact of deposits of lead ore and serpentinite rocks in the study area which naturally contain high levels of iron (Brooks 1987; Adriano 2002; Massoura et al. 2006; Alexander et al. 2007), as is confirmed by the highly significant correlation with Co, As, and Pb in the flood sediments. Ef classification is as follows: I No influence, up to 1; II Minor influence, 1–3; III Moderate influence, 3–5; Moderate to severe influence, 5–10; IV Severe influence, 10–25; V Very severe influence, 25–50; and VI Extremely influence, 50–100 (Guo et al. 2014).

Table 1 Percentage of PTE sample that exceeds MAC in its content

Elements	As	Cd	Cr	Cu	Ni	Pb	Zn
mg kg^{-1}							
MAC[a]	25	3	100	100	50	100	300
Kolubara—samples above MAC %							
Soil	0.00	0.00	15.38	2.85	65.38	0.00	0.00
Flood sediments	0.00	0.00	21.43	3.60	48.57	0.00	0.00

[a] Maximal allowed concentrations (SG RS 23/94, pp. 553–554)

The arithmetical median method was used to calculate the background concentrations (MAD—median of absolute deviations from data median), where a log-transformed modification was performed for Cr and Ni due to the dispersion of the results (Reimann et al. 2005; Mrvić et al. 2011). The reference metal for calculating this factor was Fe (Guo et al. 2014).

The Igeo was calculated to evaluate sediment pollution, using:

$$Igeo = \log_2 {}^{\mathrm{Ci}}/_{1.5\mathrm{bi}} \tag{3}$$

where Ci is the concentration of element *i* and bi the geochemical background value. The factor 1.5 is incorporated in the equation for possible variations in the background data due to the lithogenic effect (Reddy et al. 2004; N'guessan et al. 2009). Igeo pollution classes are as follows: I Unpolluted, < 0; II Unpolluted to moderately polluted, 0–1; III Moderately polluted, 1–2; IV Moderately to strongly polluted, 2–3; V Strongly severe polluted, 3–4; and VI Strongly to extremely polluted, 4–5 (Yin et al. 2013).

2.5 Statistical analyses

In order to define the spatial impact of PTE in the Kolubara Basin, it was divided into four zones: the first (I) is the upper course of the Kolubara (samples 1–7); the second (II) the lower course of the Kolubara (samples 8–17); the third (III) the sub-basin of the Tamnava and Ub rivers (samples 18–31) in the south-western part of the Basin; and the fourth (IV) the River Ljig in the south-western part of the catchment (samples 32–36).

Table 2 Percentage of samples exceeding certain limit values of individual indexes and factors

Class	Soil								Flood sediments							
Pi	As	Cd	Cr	Co	Cu	Ni	Pb	Zn	As	Cd	Cr	Co	Cu	Ni	Pb	Zn
I	100	94	86	3	97	44	100	100	100	79	86	3	92	32	100	96
II	0	3	14	94	0	22	0	0	0	17	14	92	4	25	0	4
III	0	3	0	3	0	22	0	0	0	4	0	4	0	29	0	0
IV	0	0	0	0	3	11	0	0	0	0	0	0	3.6	14	0	0
Ef	As	Cd	Cr	Co	Cu	Ni	Pb	Zn	As	Cd	Cr	Co	Cu	Ni	Pb	Zn
I	69	75	50	11	53	42	97	8	71	0	46	21	64	32	100	64
II	31	22	44	89	44	39	3	89	29	89	50	79	32	54	0	32
III	0	0	6	0	0	14	0	3	0	7	3.6	0	0	14	0	4
IV	0	3	0	0	0	6	0	0	0	4	0	0	4	0	0	0
V	0	0	0	0	3	0	0	0	0	0	0	0	0	0	0	0
Igeo									As	Cd	Cr	Co	Cu	Ni	Pb	Zn
I									100	71	89	100	93	64	100	93
II									0	25	11	0	4	32	0	7
III									0	4	0	0	4	4	0	0

PCA was used to determine the pollution sources more precisely by reducing the total set of PTE data to smaller sets of independent variables. In doing so, clusters were defined which indirectly pointed to the origin of the individual analyzed elements. The absolute principal scores obtained from PCA for each of the individual factors were analyzed by multiple linear regression analysis (MLRA) as independent factors compared to the analyzed individual elements as dependent factors, and as such, the percentage proportion of the factors and the origin of each of the elements were obtained.

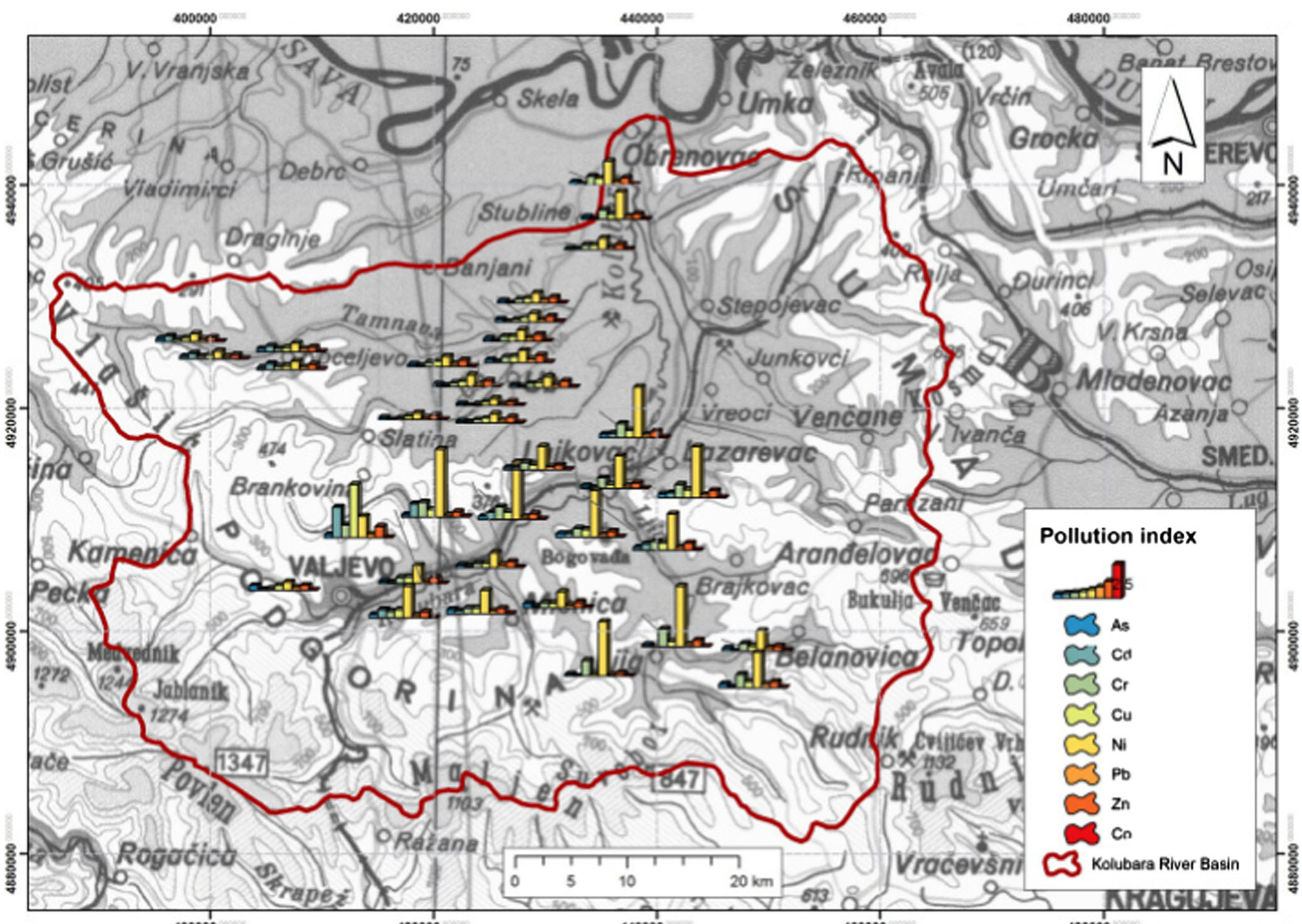

Fig. 2 Pollution index for soil

Statistical analyses (Pearson correlation, PCA, and MLRA) were performed with SPSS version 20 software (SPSS, v21). Pearson correlation coefficients are given in Table S3 (Electronic Supplementary Material).

3 Results

3.1 Pollution classes

The PTE whose concentrations exceeded the maximum allowed concentration (MAC) (Regulation of the Ministry of Agriculture and Water Management of the Republic of Serbia, 1994) in soil and sediment were sequenced as follows: Ni > Cr > Cu, according to the number of samples, while As, Cu, Pb, and Zn did not exceed the MAC (Table 1). Spatially, the highest Ni, Cr, and Co concentrations were observed in the south-eastern part of the catchment, at the confluence and downstream of the River Ljig. For Cu and Zn, spotted pollution was observed in sample 2 (zone I), while slightly higher Pb and As levels were found in the upper Kolubara Basin in Table S1 (Electronic Supplementary Material).

Pi values for As, Pb, and Zn in 100% of samples, for Cu in 97%, and for Cd in 94% classify the soils as clean (unpolluted). For Co, 94% of samples were slightly polluted, while 3% were clean and 3% moderately polluted. For Cr, 86% was classed as clean, while the remainder was slightly polluted (Table 2). Nickel showed the lowest percentage of samples in the first class (44%), while 11% of samples were classed as heavily polluted (Table 2).

In flood sediments, a certain decrease in the percentage of "unpolluted" samples was found for Zn and especially for Cd where an increase in those classed as slightly polluted (17%) was observed. For Ni, a lower percentage of soil (32%) in the unpolluted class was observed, where the other classes characterizing contaminated soils increased proportionately (Table 2).

The spatial distribution of soils according to Pi values for all the elements in the Kolubara catchment coincides with pseudo-total content distribution in Fig. 2 and Table S1 (Electronic Supplementary Material). It indicates elevated Co, Cr, and Ni levels in zones I, II, and IV. Elevated values for Cd, Cu, and Zn were found around Valjevo, while for As and Pb, greater Pi values were found upstream (Fig. 3).

According to the enrichment factor, the percentage of samples in the lowest category (no influence) ranged from 8% for

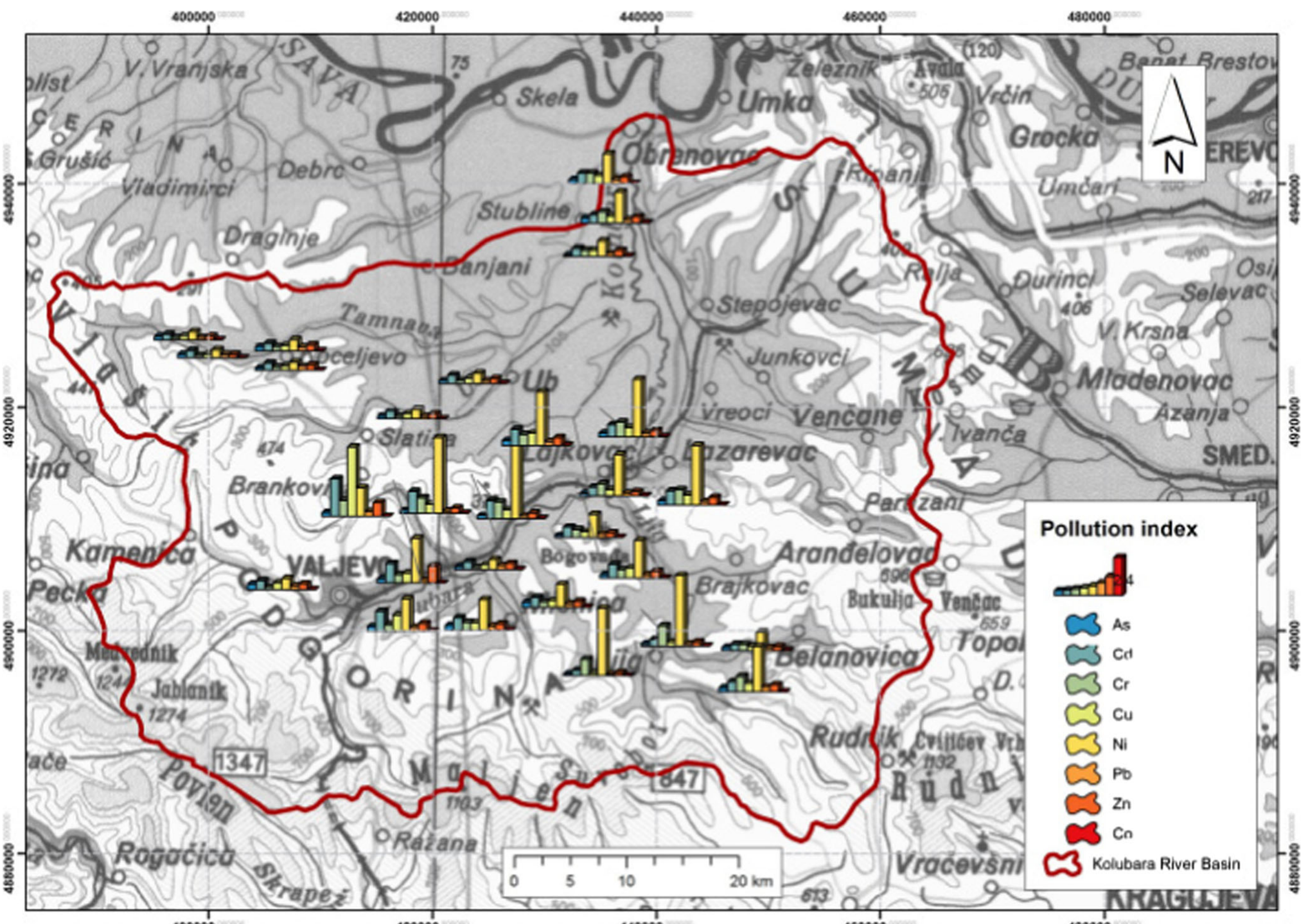

Fig. 3 Pollution index for flood sediment

Zn to 97% for Pb. For Ni, the highest percentages were in the moderate and moderately severe influence classes (Table 2). In flooded sediments, some changes were observed, with the percentage of the lowest category decreasing for Cr and especially Ni and Cd. However, for Zn and Pb, there was a certain increase in the percentage of the first class (Table 2). The spatial distribution of Ef for particular elements indicates that the highest values of Cd were found downstream of Valjevo, in the zone of the Kolubara itself for Cu, in the south-eastern part of the Basin and the lower Kolubara River for Cr, Ni, and Co (Fig. 4), and in the upper stream of the Basin for As and Pb. The Ef values for soil and flood sediment generally coincide in spatial terms (Figs. 4 and 5).

The Igeo for As, Pb, and Co classifies all sediment samples in the same unpolluted category (Table 2). The percentage of samples in this category is sequenced as follows: Cu = Zn > Cr > Cd > Ni.

3.2 Pollution sources

In the PCA of soil and flood sediment, three components were derived, explaining 87 and 84.13% of the variance, respectively. The first component with 42.29% variance for soil and 41.23% for sediment indicates the common origin of Ni, Co, and Cr in the samples analyzed, i.e., a prevailing geological origin, while the second component with 29.35% for soil and 28.39% for sediment indicates Cu, Zn, and Cd are of predominantly anthropogenic origin. The third component explaining 14.40 and 14.06% respectively of the total variance reveals the mixed origin of As and Pb (i.e., both geological and anthropogenic) with the influence of natural deposits of Pb ore and satellite As on the peripheral mountains of the basin in Figs. 6 and 7 and Table S2 (Electronic Supplementary Material).

In terms of spatial distribution, the influence of Cr, Ni, and Co in the soil was mostly seen in the downstream section of the River Kolubara (zone II) and in the south-eastern part of the Basin, near the River Ljig (zone IV). That of Cu, Zn, and Cd was observed in the area of the upper course of the Kolubara (zone I), partially in the downstream section of the Kolubara (zone II), and in the western part of the Basin along the River Tamnava (zone III). Point-source pollution with the highest value in PC2

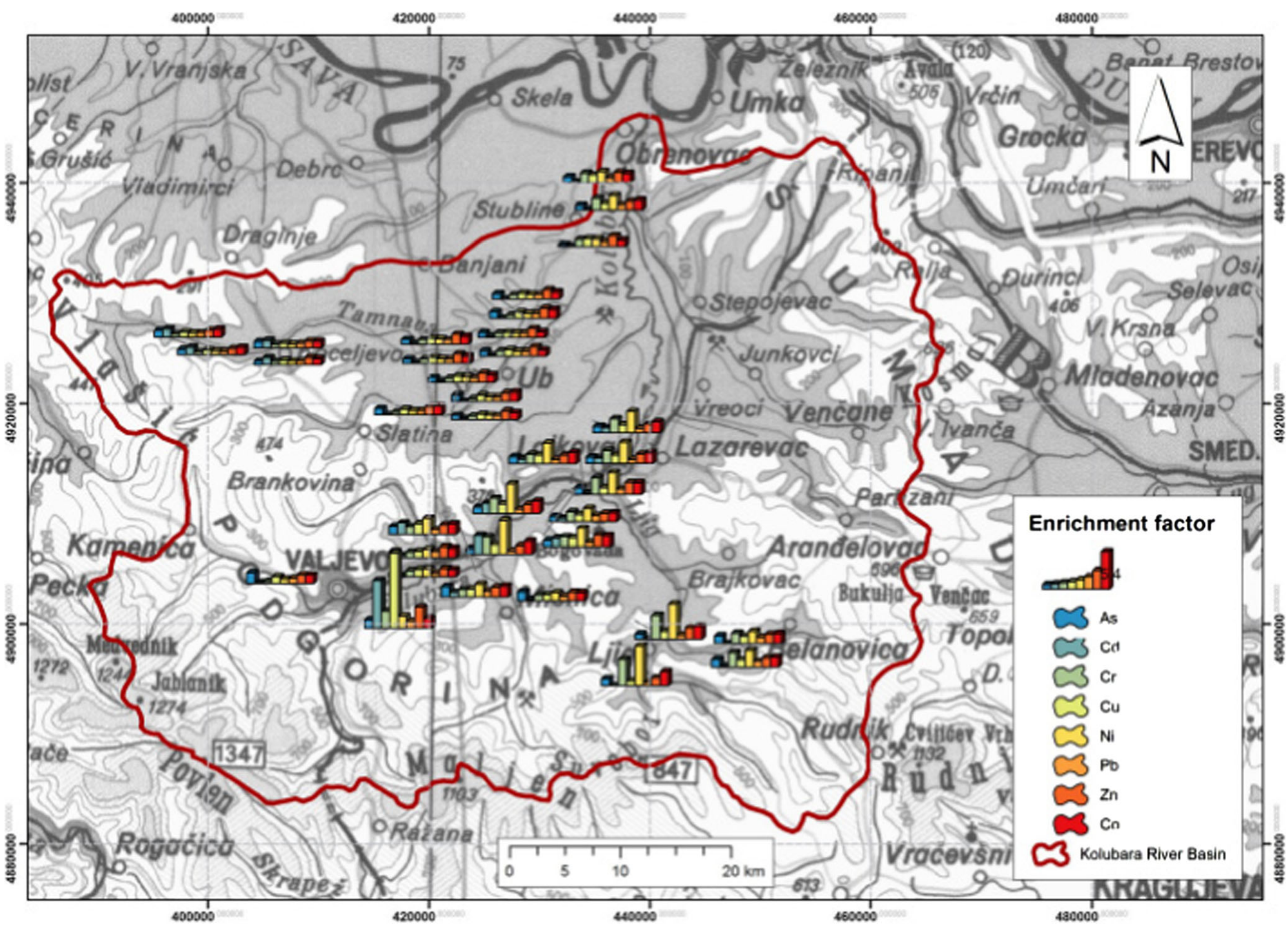

Fig. 4 Enrichment factor for soil

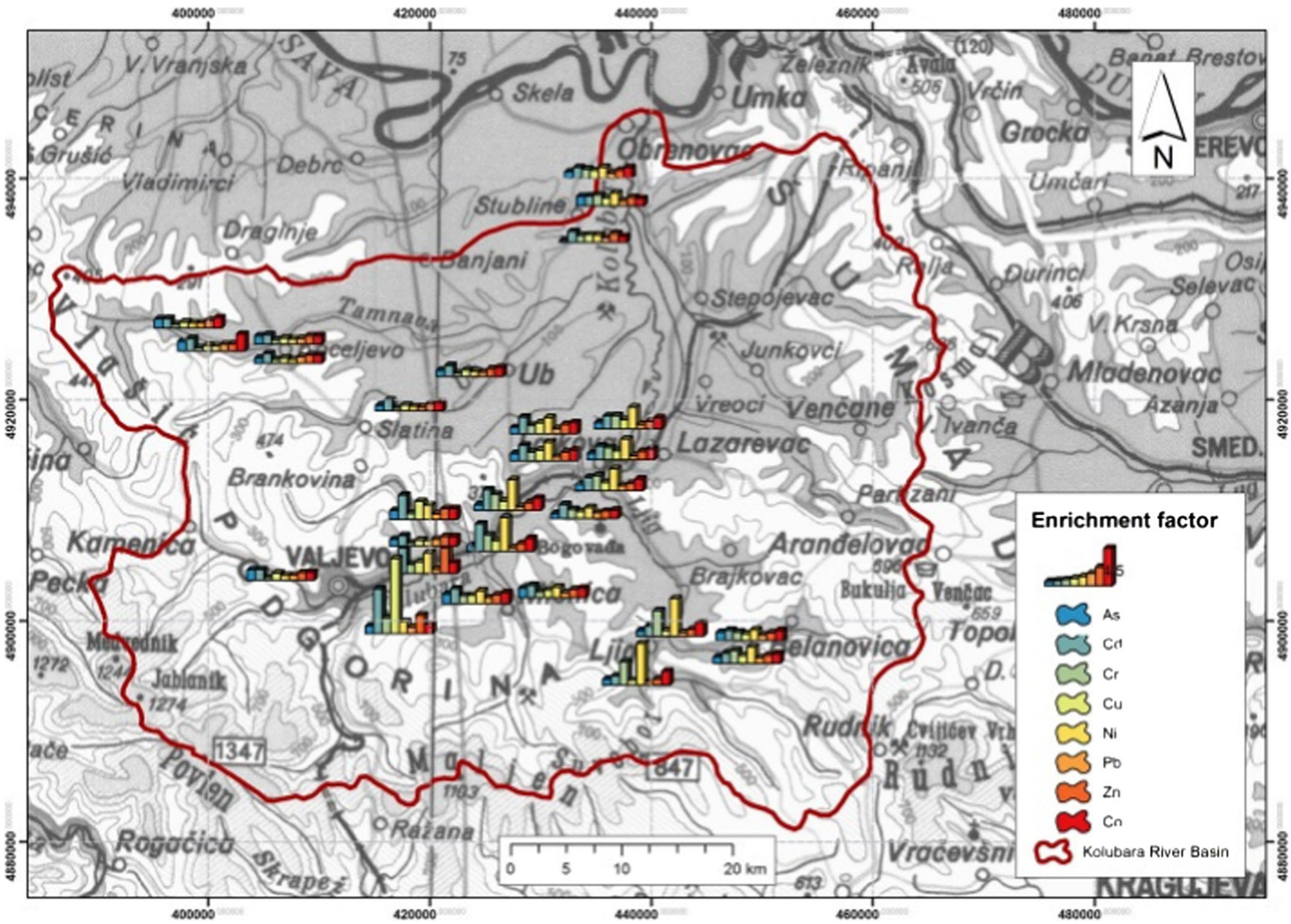

Fig. 5 Enrichment factor for flood sediment

was observed in the upper course of the Kolubara. Pb and As influence is most prevalent in the upper part of the Kolubara Basin, partially including areas in the upper course of the Kolubara (zone I), the entirety of zone III in the south-western part of the Basin, and partially zone IV, encompassing the River Ljig area. A similar spatial distribution for the influence of individual PTE upon locations was established for flood sediment (Figs. 6 and 7).

For most of the elements, PC-MLR analysis showed that the influence of factors not belonging to the major components is higher in flood sediment than soil, which is especially marked for As (Fig. 8).

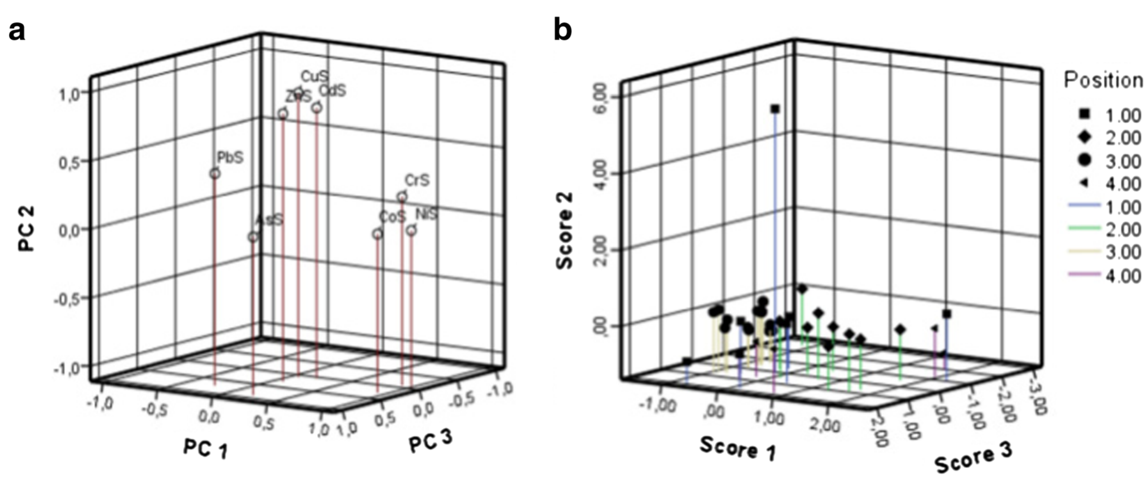

Fig. 6 a PCA loading plot for soil. b Graphic score for soil. 1, samples 1–7, zone I; 2, samples 8–17, zone II; 3, samples 18–31, zone III; 4, samples 32–36; zone IV; MS, metal and metalloid in soil

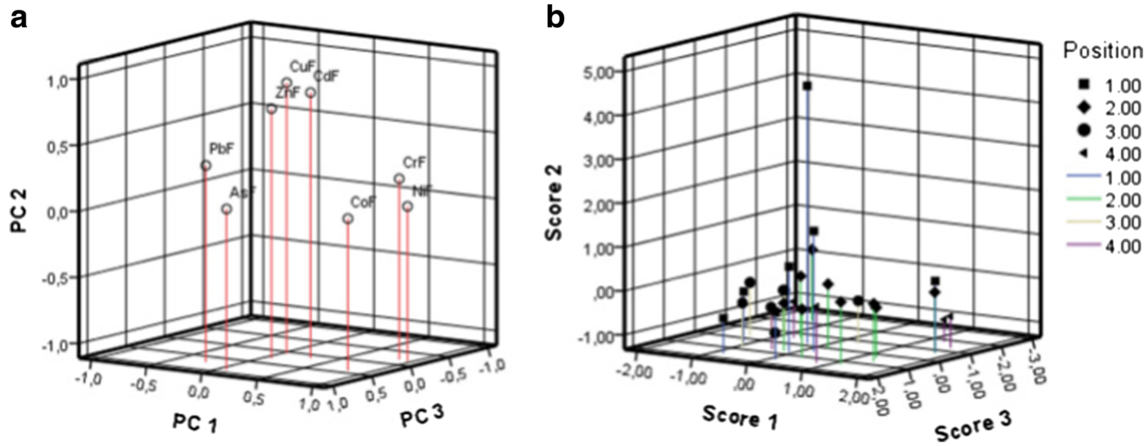

Fig. 7 **a** PCA loading plot for flood sediment. **b** Graphic score for flood sediment. 1, samples 1–7, zone I; 2, samples 8–17, zone II; 3, samples 18–31, zone III; 4, samples 32–36, zone IV; FS, metal and metalloid in flood sediment

4 Discussion

For the Kolubara Basin, the background value of As in soil was 10.30 mg kg^{-1} (based on 247 analyzed samples). The average value in world soils is 10 mg kg^{-1} (O'Neill 1995), while in Serbian soils, it is 11 mg kg^{-1} (Mrvic et al. 2009; Pavlović et al. 2017). Average As levels in the Kolubara sediments were 6.52 mg kg^{-1}, which is within the range for the River Sava (4–10 mg kg^{-1}, Milačič et al. 2017) and considerably less than values for the Danube (70 mg kg^{-1}, Comero et al. 2014).

The predominant influence of ore deposits can be clearly seen in the MLR analysis and is also reflected in the Ef, where almost a third of the samples are categorized as "minor impact" (Table 2 and Fig. 7). The prevalent influence of lead ore is clear on Mts. Maljen and Rudnik (Filipović 2005; Mrvic et al. 2009; Antić-Mladenović et al. 2017; Pavlović et al. 2017) as a source of Pb and also As (O'Neill 1995), which is confirmed by the highly significant positive correlation of these two elements in both soil and flood sediment in Table S3 (Electronic Supplementary Material). The spatial distribution of higher As levels is marked primarily in the upper course of the Kolubara, which is confirmed by PC analysis (Figs. 6 and 7) and Ef (Figs. 4 and 5). However, the anthropogenic influence is also noticeable at point 2 in Table S1 (Electronic Supplementary Material), downriver from Valjevo, most likely due to the influence of the metal industry (Krušik Holding Corporation, Valjevo) (Kabata-Pendias 2011). The evident increase in the influence of those factors not defined as significant in the MLRA on the As content in flood sediment results from increased As solubility in the redox conditions caused by flood water stagnation (Adriano 2002).

In world soils, the background value for Cd is 0.40 mg kg^{-1} (Berrow and Reaves 1984), while the average content in Serbian soils is 0.80 mg kg^{-1} (Mrvic et al. 2009). In the Kolubara Basin, background levels are in line with the global average, at 0.45 mg kg^{-1}. Specificities relating to Cd were also observed in the investigated area: its relatively high solubility in sediments compared to other PTE (Mitchell et al. 2016) and its possible geochemical origin from Zn, Zn-Pb, and Pb-Cu-

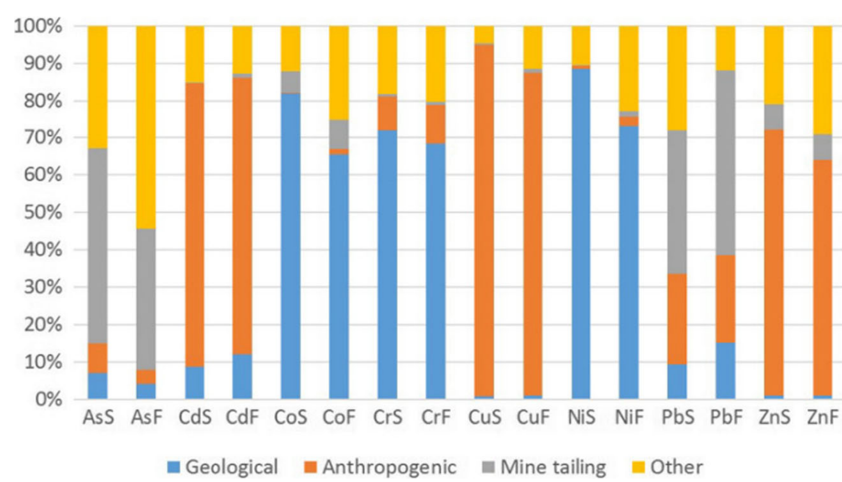

Fig. 8 Apportionment percentage of possible source types based on observed PTE concentrations. MS, metal and metalloid in soil; MF, metal and metalloid in flood sediment

Zn mines (Adriano 2002), as well its anthropogenic origin related to the metal industry and urban areas (Kabata-Pendias 2011). In our study, elevated Cd concentrations reflect an increase in Ef for soil and flood sediment from "no influence" to "minor influence," with the highest pseudo-total content values established downriver from Valjevo (Supplementary 1), where the metal industry is located. According to PCA, point-source soil and sediment contamination in sample 2 (zone I) is related to this site. Obviously, the greatest impact of anthropogenic pollution was observed downriver from Valjevo, indicated by its significant correlation with Zn both in soil ($r = 786^{**}$) and flood sediment ($r = 533^{**}$) in Table S3 (Electronic Supplementary Material). The lower correlation between Zn and Cd in flood sediment is down to greater Cd solubility and its transport along the river course (Mitchell et al. 2016; Wei et al. 2016). Although the MLR analysis mainly indicates the anthropogenic origin of Cd (Fig. 8), its origin is also conditioned by natural sources from the boundaries of the Jadar block (Filipović 2005; Mrvic et al. 2009), which dictates the background of the Basin to a large extent. The extensive impact of anthropogenic factors on Cd content in sediment can be closely related to the Tamnava-West Field lignite mine in zone III (Fig. 7). Although Cd content in lignite is low (Pavlović et al. 2004), its high solubility (Mitchell et al. 2016; Wei et al. 2016) affects its overall content in flood sediment under specific flood conditions—hence, the increase in the percentage of the "minor" Ef category, caused by the average Cd content in sediment rising (0.60 mg kg^{-1}) compared to the determined background levels. However, compared to Cd content found in the sediment of Serbia's major rivers (1.28–10.50 mg kg^{-1} (Sakan et al. 2015), including the Sava (0.99 mg kg^{-1}, Vidmar et al. 2017) and the Danube (> 3 mg kg^{-1}, Comero et al. 2014), the content in the Kolubara is low. The low content of Cd of anthropogenic origin indicates that this element is not a limiting factor for agricultural production after flood waters recede.

Average Co content in world soils is 10 mg kg^{-1} (Kabata-Pendias 2011), while the background value for the Kolubara Basin is 14.49 mg kg^{-1}. In the flood sediment, the average value of 13.21 mg kg^{-1} is similar to background soil values and is towards the lower end of the established value range for levels in Serbian river sediment (8.22–36.2 mg kg^{-1}) (Sakan et al. 2015). Regardless of the very high percentage of samples in the category "slightly polluted" for Pi and "minor effect" for Ef (Table 2), in the PCA, cobalt is in the same cluster as Cr and Ni with most influence in PC1. Similarly, the MLR analysis and the mutual correlations of these three elements in Figs. 5 and 6 and Table S3 (Electronic Supplementary Material) clearly show the geological origin of Co (Anderson et al. 1973). Earlier studies pointed to sources of serpentine in the Mts. Rudnik and Maljen regions (Mrvic et al. 2009; Antić-Mladenović et al. 2017), where elevated Co concentrations were recorded in the upper course (zones 1 and IV), and partially in the lower course of the Kolubara, especially in the sediments, caused by its movement along the river course (Figs. 6 and 7).

Average Cu content for world soils is 30 mg kg^{-1} (Adriano 2002), but levels are lower in Serbian soils (22.24 mg kg^{-1}). The average Cu content in flood sediment was 21.14 mg kg^{-1}, which is towards the lower end of the established value range for levels in Serbian river sediment (11.5–870 mg kg^{-1}) (Sakan et al. 2015) and for the Danube (28.3–193.7 mg kg^{-1}) (Woitke et al. 2003). The Pi value for Cu shows that only in one sample were Cu concentrations found at the moderately polluted level. Considering the low background levels, the Ef reveals the somewhat greater impact of anthropogenic factors or an increased percentage of the "minor" Ef class (Table 1). Igeo also indicates that individual samples in the "moderately polluted" class are associated with point-source pollution in areas downriver of Valjevo due to the developed metal industry and city traffic (Adriano 2002). The PCA showed the crucial impact of anthropogenic factors, highlighting this point-source pollution. This was also confirmed by the MLR analysis with Cu content mostly influenced by anthropogenic factors. Its total content in soil and flood sediments indicates that the flooding did not affect the productive capacity of the studied agricultural soils.

The background Ni content in the Kolubara River Basin is 54.87 mg kg^{-1}, which is similar to the world average (50 mg kg^{-1}, Adriano 2002). In the flood sediments, the somewhat higher concentrations were still within the range established for Serbian rivers (33.2–274 mg kg^{-1}) (Sakan et al. 2015) and for the Danube (23.2–89.8 mg kg^{-1}, Woitke et al. 2003) but significantly higher than in the Sava at the confluence with the Kolubara (100–250 mg kg^{-1}, Vidmar et al. 2017). In our study, the increased solubility of Ni in serpentine compared to chromium (Quantina et al. 2008) probably resulted in its percentage in the first Pi, Ef, and Igeo categories being lower. There is also a difference in the Ef for soil and flood sediment, with the percentage of the "no influence" Ef class higher for soil (42%) than sediment (32%). This is probably due to the high intensity erosion found in those areas with high Ni content (Belanovic-Simic et al. 2013), which under the influence of extreme precipitation is washed out into the river courses in the Kolubara Basin (Serbian Government Report on Floods, 2014). The PCA and MLR analysis showed that Ni content was mostly dependent on its geological origin, which is identical to Co and Cr and explains the very high significant correlations between these three elements in Table S2 Electronic (Supplementary Material) and Figs. 6, 7, and 8. Moreover, the action of Ni is most pronounced in areas characterized by higher Cr and Co levels in the upper part of the Kolubara River Basin (based on PCA, Supplementary 1). However, in areas of the lower part of the Kolubara, near Obrenovac (Supplementary 1), its content is also higher due to Ni-bearing clay minerals formed during the first stage of ultramafic rock weathering (Raous et al. 2013), which can be transported large distances by rivers (Lim et al. 2012). Although Ni is of geological origin, its increased solubility in changed oxido-redox conditions (Antić-Mladenović et al. 2017) can be a limiting factor in plant production in areas affected by flooding.

The background Pb value in the studied soil is 40 mg kg^{-1}, which is more than in world soils (10–30 mg kg^{-1}, Alloway 2013) but identical to average values for Serbian soils (Mrvic et al. 2009). Average Pb values for sediment are 17.7 mg kg^{-1}, which is significantly less compared to Serbian river sediment (57.8–318 mg kg^{-1}, Sakan et al. 2015) and that in the Danube (18.2–85.0 mg kg^{-1}, Woitke et al. 2003). However, its total levels, and the Pi, Ef, and Igeo values, were at the non-polluted level, except for the Ef value in soil sample 2 (zone I), which is again affected by industry in Valjevo in Table S1 (Electronic Supplementary Material). Its high background level is mainly due to geological sources as Pb and As generally have the same origin, which is confirmed by the significant positive correlation between these two PTE in Table S3 (Electronic Supplementary Material), as well as the cluster formation with As in the PCA. The partial overlap with Cu, Zn, and Cd, compared to the other component, indicates its slightly elevated content in the vicinity of Valjevo due to the anthropogenic impact. The MLR analysis indicates the high impact of anthropogenic factors on its content, but PC1 and PC3 suggest that partial geological origin predominates in sediment, indicating historical Pb pollution, which resulted in the percentage in the "unpolluted" EF class for flood sediment being higher than for soil. The absence of any correlation between Pb and Ni, and Pb and Cr, implies that they are not of common origin, but the proximity of their sources has led to a large proportion of PC1 in recognizing its origin in the MLR analysis.

The background Zn value in the Kolubara River Basin is 69 mg kg^{-1}, which is similar to the average for the Earth's crust (Krauskopf 1979), while the value established for flood sediment (55.84 mg kg^{-1}) is within that range but much lower than the values for the Danube (99–398 mg kg^{-1}, Woitke et al. 2003). The Pi and Igeo values fall into the lowest class, except for the Ef for soil. The common origin of Zn and Pb was established by their correlation in Table S3 (Electronic Supplementary Material), while the natural source of these elements has a lower Ef in flood sediment than in soil. However, in the PCA, its content is closely related to Cu and Cd and greatly influenced by anthropogenic sources. Such a differentiation is the result of industry in Valjevo, including the combustion of fossil fuels (Adriano 2002). The mine's influence was established by the MLRA, i.e., the relatively high percentage of the third component (about 7%) in soil and flood sediment, as well as its significant correlation with Pb in Table S3 (Electronic Supplementary Material).

5 Conclusions

This study found that individual levels of all the harmful microelements were below the MAC for PTE for agricultural soil except for Ni, Cr, and Cu, with only Cu concentrations exceeding the MAC in a single soil and flood sediment sample.

For most of the elements, individual indicators of the impact of PTE on soil and flood sediment contamination show they have no impact or only minor impact, with only individual cases falling into higher classes, indicating the absence of pollution in the Kolubara River Basin. Ni is in the higher categories for flood sediment, which was directly reflected in Igeo and relatively few samples are in the "without influence" class. This results from its solubility in the changed oxido-redox conditions. However, given the total content, in these conditions, only Ni may be a limiting factor in plant production in the Kolubara River Basin.

The geological origin of Ni, Cr, Co, and the mixed (both geological and anthropogenic) origin of As and Pb was clearly defined, with their levels mainly related to the nature of the rocks in the mountains in the peripheral parts of the river basin, where their natural deposits are found. However, Cd, Zn, and Cu are mostly of anthropogenic origin arising from cities with a developed metal industry (Valjevo and Obrenovac).

Based on all these indicators, the 2014 flooding did not result in changes to the state of PTE; instead, the observed changes were already a part of the natural soil formation processes in the basin with minimal anthropogenic impact. Therefore, the floods did not result in significant soil pollution in the Kolubara River Basin and the soil is safe for agricultural production.

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