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RESEARCH ARTICLE

Distribution and mobility of heavy elements in floodplain agricultural soils along the Ibar River (Southern Serbia and Northern Kosovo). Chemometric investigation of pollutant sources and ecological risk assessment

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Abstract This work investigates the influence of a high-magnitude flood event on heavy elements (HEs) pollution and mobility in the agricultural soils along Ibar River in Southern Serbia and Northern Kosovo. The study area was one of the most important Pb/Zn industrial regions in Europe. Soil samples ($n = 50$) collected before and after the floods in May 2014 were subjected to the sequential extraction procedure proposed by the Community Bureau of Reference (BCR). The results indicated that the floods significantly increased not only the pseudo total concentrations of HEs in the soil but also their mobile and potentially bioavailable amounts. Moreover, higher concentrations (both pseudo total and potentially bioavailable) were found in the agricultural soils closer to the industrial hotspots. Principal component analysis and hierarchical cluster analysis successfully grouped the analyzed elements according to their anthropogenic or natural origin. The floods significantly increased the potential ecological risk of HEs associated with Pb/Zn industrial activities in the study area. The potential ecological risk of Cd after the floods was highest and should be of special concern.

Keywords Heavy elements · Agricultural soil · Floods · Sequential extraction · Multivariate statistical analysis · Potential ecological risk

Introduction

Soil pollution by heavy elements (HEs) from industrial and mining processes has been the main subject of many studies and research in recent years (Borgna et al. 2009; Anju and Banerjee 2012; Popescu et al. 2013; Liu et al. 2013; Sajn et al. 2013; Li et al. 2015). Mining processes, chemical industries, metal ore processes, beneficiation processes, metallurgical operations, generate various categories of industrial waste,

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i.e., mine waste low-grade ore, overburden, barren rocks, tailings, dump and heap leaching, acid mine water, etc. These wastes, disposed off in surrounding land, are major sources of HEs contamination in soil (Ashrafi et al. 2015). Once agricultural soil is polluted by HEs, they could be accumulated into the crops, which occasionally lead to chronic and acute diseases in animal or humans (Liu et al. 2013). The behavior of HEs in soil reportedly depends on the physicochemical properties of the soil, such as pH, organic matter content (OM), cation exchange capacity (CEC), soil texture, and the distribution of the elements among the various soil fractions (Li et al. 2010). The chemical fractionation, i.e., the association of elements with specific soil fractions (e.g., exchangeable/acid soluble, reducible, oxidizable, and residual), determines how strongly they are retained in soil and how easily they may be mobilized to the hydrosphere and biosphere (Nannoni et al. 2011). In order to assess the above, a wide range of sequential extraction procedures (SEP) have been employed (Tessier et al. 1979; Pickering and Shuman 1981; Beckett 1989). One of the most widely applied SEP is that proposed by European Community Bureau of Reference (BCR) which extensively used for the fractionation of HEs in soil (Borgese et al. 2013; Liu et al. 2013), sediment (Huang et al. 2013; Sungur et al. 2014), sludge (Yuan et al. 2015) and dust samples (Zhai et al. 2014).

The extreme and continuous rainfall event (over 200 mm) that affected the countries of the Western Balkans during the period from 14th to 16th May 2014 caused catastrophic floods and landslides (Republic Hydro-meteorological Service of Serbia). A result of this was the deposition of fine-grained sediments across the floodplains of the middle and lower flows of the Ibar River, the land of which is mainly using for agricultural production. In addition to the regular monitoring of HEs distribution in the Ibar River alluvium, the opportunity was created to assess the impact of flooding on the mobility and bioavailability of HEs in the field of research. This region was one of the most important mining districts in Europe where Pb and Zn ores were mined intensively in the past century (Borgna et al. 2009). Furthermore, the industrial district of Kosovska Mitrovica is considered to be one of the largest contaminated areas in the Western Balkans (Sajn et al. 2013).

In this context, the present study aimed at: (i) defining the impact of the floods on contamination and fractionation of As, Cd, Cr, Cu, Ni, Pb, Sb, and Zn in the agricultural soils along the Ibar River Valley; (ii) highlighting their origin by multivariate statistical analysis; and (iii) estimating the potential ecological risk in the area of interest. The novelty of this study and its relevance to the scientific community is based on the fact that it presents findings which combine pollution by HEs and their fractionation in the agricultural soil coupled with applications of multivariate statistics and assessment of environmental implications along the floodplain of the Ibar River.

In addition, the present study provides information concerning the behavior of HEs in arable land hit by high magnitude floods in one of the most important mining districts in Europe. The findings of the present study could be a good reference for health studies and formulation of the priority issues in the fields of environmental protection and food safety.

Materials and methods

Study area and sample collection

The study area is located in Southern Serbia and Northern Kosovo in the middle and the lower flows of the Ibar River through a length of 130 km (Fig. 1). The present study covers the area defined by the coordinates 42° 54'–43° 42' N and 20° 50'–20° 38' E, and the terrain altitude above sea level is between 203 and 500 m. The climate in this area is moderate continental, and annual precipitation ranges from 540 to 820 mm (Republic Hydro-meteorological Service of Serbia). This region hosts one of the most important base metal ore fields in Europe, namely the Trepča district. All Trepča's mines yielded until 1999, when production stopped, approximately 67 million tons of ore (Barać et al. 2006). Six of the Trepča's flotation plants produced a total of 2.3 million tons of lead concentrate, 3.4 million tons of zinc concentrate, 2.5 million tons pyrite (FeS_2) concentrate, and 1.3 million tons pyrrhotite (Fe_7S_8) concentrate (Barać et al. 2006). The legacy of all of these activities in the area of interest are eight tailing ponds, which cover a total area of around 170 ha and a total amount of 44.6 million tons of tailings from the production of lead and zinc concentrates and 2.7 million tons of tailings from the production of copper and magnetite concentrates. The majority of these tailings, with high concentrations of HEs (Barać et al., 2006), are unsecured and located next to the Ibar River flow and directly threaten the environment by leaching into the surface- and groundwater and by wind erosion. Dust particles enriched in HEs from tailing ponds considerably threaten the surrounding land and persist as a real risk to natural vegetation, crops, and public health.

Soil sampling was performed before and after the high-magnitude flood event in May 2014 from crop fields, which were uniform in size, slope, quality, and cultivated plant species. A total number of 50 soil samples from agricultural land were collected from 25 sites selecting locations with approximately the same distance between the sampling sites. About 1 kg of each soil sample was obtained by applying "systematic random sampling" described in IAEA–TECDOC–1415 (2004). Samples were collected from the tilled depth (0–30 cm) with a manually operated stainless-steel auger and transported to the laboratory in sealed polyethylene containers. Prior to processing and analysis of the heavy elements content,

Fig. 1 Map of the study area
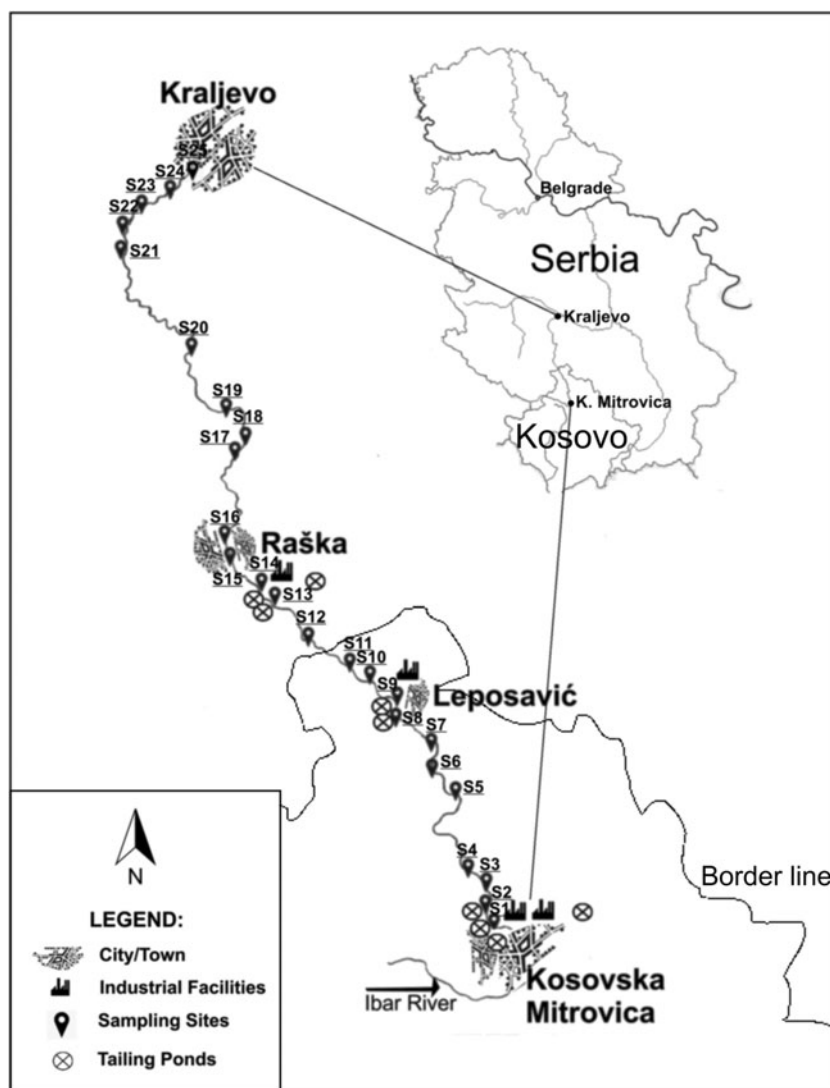
the soil samples were air-dried at room temperature for 3 weeks (Krgović et al. 2015), ground and homogenized in an agate mortar and sieved through a 2-mm stainless steel sieve.

Laboratory treatment and analytical determinations

The soil pH was determined in distilled water at a solid-liquid (S/L) ratio of 1:2.5 using an inoLab pH/Cond 720 instrument. The soil moisture content was determined from the weight loss of air-dried samples after 24 h at 105 ± 5 °C, and the CEC was determined by the ammonium acetate method by extracting NH_4^+ from NH_4^+-saturated samples obtained by soil treatment with 1 mol dm^{-3} ammonium acetate solution. The organic matter (OM) content (%) was determined from the weight loss on ignition (4 h at 550 °C) of 10 g oven dried samples. Once the OM had been removed, the soil samples were weighed and subjected to soil texture analysis (<2 mm) by a combined sieve and pipette technique in order to

determine the following fractions as recommended by the US Department of Agriculture (USDA–United States Department of Agriculture 1999): coarse sand (2–0.5 mm), medium sand (0.5–0.25 mm), fine sand (0.25–0.05 mm), silt (0.05–0.002 mm), and clay (<0.002 mm).

In the present study, modified BCR SEP was used to fractionate the HEs into the exchangeable/acid soluble (f_1), reducible (f_2), oxidizable (f_3), and residual (f_4) fractions according to Rauret et al. (1999). In the first step of the BCR protocol, carbonate-associated HEs were extracted by using acetic acid (40 mL of 0.11 mol L^{-1} CH_3COOH), in the second step, the HEs bound to Mn and Fe oxides/hydroxides were extracted with hydroxylamine-hydrochloride (40 mL of 0.5 mol L^{-1} $NH_2OH \cdot HCl$), in the third step, the HEs associated with organic matter, and sulfides were extracted with hydrogen peroxide (10 mL of 8.8 mol L^{-1} H_2O_2) and ammonium acetate (50 mL of 1.0 mol L^{-1} CH_3COONH_4). After BCR extraction, the residue was microwave digested with *aqua regia*

(HCl:HNO$_3$ in ratio 3:1) in order to quantify the HEs associated with crystalline minerals (ISO 11466: 1995). In the present study, the total amounts of elements in soil were defined as the sum of the concentrations in each four fraction (Borgese et al. 2013). This method results in concentrations normally referred to as "pseudo total," as it does not completely destroy silicates (Facchinelli et al. 2001).

The microwave-assisted digestion procedure was performed using a Milestone ETHOS One Advanced Microwave Digestion System. The HE concentrations in digests and extracts were analyzed by the ICP-OES method on a Thermo Scientific iCAPTM 6500 Duo instrument. All chemicals and reagents were of analytical reagent grade. The instrument was calibrated with a series Multi-Element Plasma Standard Solution 4, Specpure® (Alfa Aesar, Germany). These multielement standards and blanks were prepared in the same matrix as the extracting reagents in order to minimize the matrix effects.

Quality assurance and quality control

The efficiency of the BCR three-step SEP was assessed by analysis of the BCR®—701 certified reference material of the European Commission Institute for Reference Materials and Measurements (Geel, Belgium). For each extraction step, recoveries were calculated as the ratio (%) between determined and certified concentration values. Percentage recoveries varied from 95.8 to 100.3 % for the f_1, from 98.8 to 106.1 % for the f_2, and from 90.3 to 104.1 for the f_3. Calibration was performed every 10 samples. Analytical determinations were carried out in triplicate on all samples. The relative standard deviations of the means of triplicate measurement were less than 10 %.

Data analysis

Potential ecological risk assessment

A potential ecological risk index (RI) was introduced to assess the ecological risk degree of HEs in the agricultural soils of the Ibar River alluvium. This approach, proposed by Håkanson (1980), has been widely used in various environmental studies (Min et al. 2013; Kerolli–Mustafa et al. 2015). The RI value can be calculated according to:

$$C_f^i = C_{HE}^i / C_{bcg}^i \tag{1}$$

$$E_r^i = C_f^i \cdot T_f^i \tag{2}$$

$$RI = \sum_{i=1}^{n} E_r^i \tag{3}$$

where C_f^i is the contamination factor of single HE, C_{HE}^i is the pseudo total HE concentration, C_{bcg}^i is the local background HE level estimated by Borgna et al. (2009) for the floodplain

soils of the Ibar River, considered as a suitable "geochemical average" unaffected by industrial activities (As = 24 mg kg^{-1}; Cd = 0.5 mg kg^{-1}; Cu = 30 mg kg^{-1}; Pb = 84 mg kg^{-1}; Sb = 2.4 mg kg^{-1}; Zn = 150 mg kg^{-1}), E_r^i is the potential ecological risk for the individual HE, and T_f^i is the toxic-response coefficient for a given HE, adopted to be evaluation criteria. According to Håkanson (1980), the corresponding coefficients based on the toxicity of HEs are 5, 5, 30, 1, and 10 for Pb, Cu, Cd, Zn, and As, respectively.

In order to assess environmental implications Håkanson (1980) defined five risk categories of E_r^i: low ($E_r^i < 40$), moderate ($40 \leq E_r^i < 80$), considerable ($80 \leq E_r^i < 160$), high ($160 \leq E_r^i < 320$), and very high risk ($320 \leq E_r^i$), as well four categories of RI: low (RI < 150), moderate ($150 \leq RI < 300$), considerable ($300 \leq RI < 600$), and very high risk ($600 \leq RI$).

Statistical analysis

To investigate the normality of data distribution, the Kolmogorov-Smirnov test and the Shapiro-Wilk test were used at a 0.05 significance level. To test statistical hypotheses, Wilcoxon signed-rank test, the Mann-Whitney U test, the t test, and one-way analysis of variance (ANOVA) were used. Inter-element relationships in the soil samples as well relationships between the properties of the soils were determined by either the Spearman rank or Pearson linear correlation coefficients.

Since the applied techniques of multivariate statistical analysis are conditioned by the requirement that the data are normally distributed, transformation into standardized variables was performed using the log-transformation. Principal component analysis (PCA) was applied with Varimax rotation and Kaiser Normalization in order to distinguish the possible sources of the HEs in soil (Chai et al. 2015). Hierarchical cluster analysis (HCA) was performed using Euclidean squared distances and the Ward linkage method on the pseudo total HE contents in soils to check PCA results. The hierarchical method of the cluster analysis used in the present study has the advantage that it does not require any prior knowledge of the number of clusters, which is a prerequisite of the non-hierarchical method (Martínez–Santos et al. 2015). Statistical analysis of the experimental data was performed using IBM SPSS software Version 20.

Results and discussion

Soil properties

The main physicochemical properties of the soil samples are summarized in Table 1. The analyzed soils were found to be slightly to moderately alkaline with the similar pH average of 7.8 before (BF) and 7.9 after (AF) the floods (Table 1).

Table 1 The main physico-chemical properties of the soil samples

Parameter	Floods	Mean	SD	Median	Min	Max
Moisture (%)	BF	19	2.6	18	14	24
	AF	23	4.8	21	16	32
pH-H_2O	BF	7.8	0.22	7.8	7.4	8.2
	AF	7.9	0.16	7.8	7.6	8.1
OM (%)	BF	5.1	1.3	4.7	3.4	7.7
	AF	4.9	1.5	4.3	2.4	8.0
CEC ($mmol_{(+)}$ 100 g^{-1})	BF	12	5.3	11	4.6	25
	AF	10	4.7	9.6	3.5	25
Sand (%) (0.05–2 mm)	BF	70	5.8	70	55	80
	AF	69	8.0	71	56	83
Silt (%) (0.002–0.05 mm)	BF	23	5.4	22	14	36
	AF	24	6.8	23	13	41
Clay (%) (< 0.002 mm)	BF	7.0	2.1	7.2	4.1	11
	AF	7.1	2.4	7.0	4.3	11

SD standard deviation, *BF* before the flood event, *AF* after the flood event

Particle size distribution shows that the soils from the study area had low clay content, ranging from 4.1 to 11 %. In accordance with the USDA soil texture classification, the soil samples had a loamy sand to loam texture. The OM content in the soils ranged from 2.4 to 8.0 %, and the CEC ranged from 3.5 to 25 $mmol_{(+)}$ 100 g^{-1}. Overall, the OM increased with the percentage of the silt fraction ($r = 0.47$, $p \leq 0.01$) and decreased with the sand fraction ($r = -0.47$, $p \leq 0.01$), while the CEC values increased with the percentage of OM ($r = 0.56$, $p \leq 0.01$). This was expected taking into account that soil CEC is determined by the clay and OM amounts (Borgna et al. 2009). Besides the moisture content (t (14) $= -3.014$, $p \leq 0.01$, ANOVA F (1, 28) $= 8.9$, $p \leq 0.01$), there were no remarkable differences in soil properties between the BF and AF soil samples.

Total content of heavy elements in the agricultural soils

Univariate statistics of pseudo total metal concentrations before (BF) and after (AF) the floods are presented in Table 2 together with the target and intervention thresholds set by the Netherlands Ministry of Housing, Spatial Planning, and the Environment (VROM–Netherlands Ministry of Housing and Spatial Planning and the Environment 2009). Additionally, the determined HEs concentrations by sampling sites in relation to the VROM–Netherlands Ministry of Housing and Spatial Planning and the Environment (2009) thresholds for both sampling campaigns are illustrated in Fig. A1 of the Supplementary material A.

In the present study, the determined pseudo total concentrations of As indicated that the analyzed soil samples were generally polluted with this element, exceeding the corresponding intervention threshold in 21 soil samples (both BF

and AF). Most of the elevated levels of As were recorded in the industrial region from Kosovska Mitrovica to Raška (middle River flow) with values reaching 335 and 474 mg kg^{-1} in AF sampling sites S1 and S7, respectively (Fig. 1; Fig. A1). The obtained results for As are in accordance with those of a previous investigation on the distribution and mobility of this element conducted in the study area (Barać et al. 2015). The results of the mentioned research indicated that the total As content in soil generally decreased with distance from the industrial facilities and Ibar River watercourse (Barać et al. 2015).

The pseudo total Cd concentrations were generally elevated with exceeding intervention value at the sampling site S7 after the floods (Fig. 1; Fig. A1). The highest Sb concentration was recorded after the floods at the sampling sites in the vicinity of industrial facilities which exceeded the intervention value (Fig. 1; Fig. A1). Similar findings were reported by Borgna et al. (2009), who conducted their research from Kosovska Mitrovica City to the industrial zone Leposavić (see Fig. 1) and found the highest Cd and Sb concentrations in the soils around the industrial hotspots of Trepča.

The most elevated Pb concentrations were recorded before the floods, exceeding the intervention value, at sampling sites near to the industrial hotspots (Fig. 1; Fig. A1). Such a situation led to increasing concentrations of Pb after floods downstream in comparison to the concentration before floods, probably by deposition of fine sediment originating from erosion and leaching from industrial tailings located on the bank of the Ibar River. The determined pseudo total Pb concentrations in the soil (both BF and AF) indicated a clear trend of decreasing concentrations downstream with increasing distance from the industrial sources of pollutants (Fig. A1), which shows that the Pb concentration in the soil is mainly influenced by industrial hotspots.

The concentrations of Zn exceeded the corresponding intervention value at seven sampling sites located in the industrial vicinity (Fig. 1; Fig. A1). Generally, the pseudo total content of Zn in the agricultural soils tended to decrease downstream with a few isolated cases before the floods at the most remote sampling sites (Fig. A1). Before the inundations of the Ibar River, the Zn concentrations had a fairly uniform trend downstream (in the pollution area) without exceeding the recommended intervention value at any sampling point. (Fig. 1; Fig. A1).

The highest Cu concentrations were recorded at sampling sites located near the industrial facilities but they did not exceed the intervention value at any sampling point. There was declining trend of the Cu concentrations with increasing distance downstream from the industrial hotspots, but not so intensive as in the case of As, Cd, Pb, Sb, and Zn (Fig. A1).

Most elevated Cr and Ni concentrations were recorded in the northern sector of the study area at sampling points that could not be associated with Pb/Zn industry (Fig. 1; Fig. A1).

Table 2 Concentrations (mg kg^{-1}) of As, Cd, Cr, Cu, Ni, Pb, Sb, and Zn in different fractions of agricultural soil samples from the Ibar River alluvium

BCR steps	Floods		As	Cd	Cr	Cu	Ni	Pb	Sb	Zn
Exchangeable/acid soluble fraction (f_1)	BF	Mean±SD	1.7±1.4	0.43±0.60	0.10±0.16	0.87±0.59	11±5.6	20±51	<LOD	36±32
	n=25	Median (range)	1.2 (0.46–6.3)	0.19 (0.04–2.8)	0.0 (<LOD–0.49)	0.71 (0.04–2.8)	10 (3.3–23)	2.1 (0.56–239)	<LOD	23 (7.9–132)
	AF	Mean±SD	1.6±0.93	1.6±1.7	0.19±0.27	2.6±3.6	14±4.9	23±39	<LOD	185±194
	n=25	Median (range)	1.4 (<LOD–4.1)	1.2 (<LOD–5.9)	0.0 (<LOD–0.92)	1.5 (0.33–15)	12 (5.8–29)	8.6 (1.1–159)	<LOD	124 (6.3–681)
Reducible fraction (f_2)	BF	Mean±SD	6.9±5.8	0.49±0.38	3.2±3.1	4.9±3.2	33±21	265±384	0.02±0.08	66±38
	n=25	Median (range)	5.4 (0.91–22)	0.33 (0.13–1.6)	2.1 (<LOD–13)	4.8 (1.0–12)	28 (9.4–83)	118 (33–1628)	0.0 (<LOD–0.42)	49 (19–170)
	AF	Mean±SD	32±32	0.94±0.91	3.5±2.3	7.5±5.6	31±13	251±263	0.10±0.26	173±147
	n=25	Median (range)	19 (2.9–113)	0.62 (<LOD–3.5)	2.9 (0.66–9.4)	5.5 (2.2–28)	30 (9.9–58)	157 (34–963)	0.0 (<LOD–1.06)	129 (17–514)
Oxidizable fraction (f_3)	BF	Mean±SD	1.9±2.3	0.04±0.08	19±7.8	8.2±4.4	35±18	18.±28	0.28±0.35	15±12
	n=25	Median (range)	1.1 (<LOD–8.9)	0.0 (<LOD–0.32)	19 (5.5–40)	6.6 (3.1–19)	31 (9.4–74)	7.9 (1.3–135)	0.0 (<LOD–0.82)	12 (2.2–54)
	AF	Mean±SD	5.3±7.4	0.13±0.18	16±7.3	13±12	30±10	17±20	0.27±0.35	32±32
	n=25	Median (range)	1.5 (<LOD–26.6)	0.02 (<LOD–0.55)	16 (2.8–35)	10 (1.2–54)	27 (7.0–53)	7.6 (0.88–76)	0.00 (<LOD–0.84)	17 (1.3–117)
Residual fraction (f_4)	BF	Mean±SD	36±30	1.0±1.3	72±40	29±20	116±98	46±39	5.3±3.2	105±96
	n=25	Median (range)	30 (6.7–147)	0.0 (<LOD–3.4)	65 (19–158)	24 (14–112)	89 (26–438)	31 (7.2–150)	4.6 (<LOD–16)	62 (25–485)
	AF	Mean±SD	90±94	1.4±1.6	83±36	28±10	131±107	67±68	7.9±6.0	140±106
	n=25	Median (range)	74 (9.6–440)	1.2 (<LOD–5.5)	88 (19–180)	26 (13–52)	107 (25–553)	37 (7.6–265)	6.8 (2.7–24)	113 (19–487)
Pseudo total Σf_1+f_2+f_3+f_4	BF	Mean±SD	467±34	1.9±1.6	94.±47	43±22	196±122	349±474	5.6±3.3	222±129
	n=25	Median (range)	40 (9.4–165)	2.2 (0.13–5.1)	86 (25–189)	40 (23–132)	163 (50–546)	162 (50–2078)	5.00 (<LOD–16)	205 (55–538)
	AF	Mean±SD	129±114	4.2±3.4	103±42	51±21	206±122	358±360	8.3±6.2	530±415
	n=25	Median (range)	113 (15–473)	3.9 (0.13–12)	100 (25–219)	43 (25–95)	195 (51–687)	235 (50–1320)	6.7 (2.7–26)	365 (50–1374)
VROM (2009) thresholds		Target[a]	29	0.80	100	36	35	52	3.0	140
		Intervention[b]	55	12	380	190	210	530	15	720

LOD limit of detection, *n* number of analyzed soil samples, *BF* before the floods, *AF* after the floods

[a] Target values define the quality of unpolluted soils

[b] Intervention values define the concentration when soil remediation becomes necessary (VROM–Netherlands Ministry of Housing and Spatial Planning and the Environment 2009)

Exactly at these sites, the Ni concentrations exceed the intervention value independently of the floods occurrence (Fig. A1). The Ni and Cr concentrations in these soils could be geogenic enriched taking into account that similar levels of these two metals in this part of study area were found in a previous investigation (paper in preparation) and confirmed by a Report on the State of Land in the Republic of Serbia of the Serbian Ministry of Environment and Spatial Planning (SEPA—Serbian Environmental Protection Agency 2009).

Generally, lower As, Cd, Cu, Pb, Sb, and Zn concentrations, below the corresponding target and intervention values proposed by VROM–Netherlands Ministry of Housing and Spatial Planning and the Environment (2009), were recorded in the samples collected in the lower River flow (northern sector of the study area) at the distant sites from industrial activities (Fig. 1; Fig. A1). Accordingly, significantly higher concentrations of the mentioned HEs (except Cu before the floods), were recorded in the samples collected in the middle River flow (southern sector of the study area). Contrary to this, concentrations of Ni and Cr were significantly higher in the northern sector of the study area, i.e., in the samples collected in the lower flow of the Ibar River (Table B1 Supplementary material).

Here, the high-magnitude flood event significantly increased the As ($Z=-3.8$, $p \leq 0.001$), Cd ($Z=-3.7$, $p \leq 0.001$), Cu ($Z=-2.2$, $p \leq 0.05$), Sb ($Z=-2.8$, $p \leq 0.01$), and Zn ($Z=-3.7$, $p \leq 0.001$) pseudo total concentrations. It is also clear that the Cr, Ni, Pb, and Sb concentrations were also higher after the floods, although these differences were not necessarily significant on a statistical analysis basis (Table 2). It could be supposed that the increase in HEs concentration after the floods was a result of a deposition of contaminated particles eroded from industrial tailings located on the bank of the Ibar River.

Chemical fractionation of the heavy elements in the agricultural soils

The concentrations of the analyzed elements obtained for each step of the BCR SEP are presented in Table 2. In addition, the percentage of the fractions, based on the average is illustrated in Fig. 2, while in the Supplementary material A, Fig. A2 illustrates the results as percentages of the elements extracted in each fraction for all 25 sampling sites in both sampling campaigns.

It was observed that Cd and Zn were the most mobile elements predominantly extracted in f_1 in the samples collected after the floods (Fig. 2). In general, anthropogenic Cd and Zn were preferentially associated with carbonate minerals (Li et al. 2015). The Cd ions can easily substitute Ca ions in $CaCO_3$ in soils, leading to a high proportion of Cd in the carbonate-bound fraction (Li et al. 2015), while Zn was probably related to carbonates such as Zn-rich calcite and/or smithsonite ($ZnCO_3$) (Nannoni et al. 2011). The highest concentration of Cd in f_1 (over 91 %, which corresponds to a concentration of 4.7 mg kg^{-1}) was recorded after the floods at the sampling site S13 located in the vicinity of the former flotation plant Rudnica and two huge unsecured tailing ponds (Fig. 1; Fig. A2). It was determined that the concentrations of Cd and Zn in f_1 significantly increased after the floods ($Z=-3.6$, $p \leq 0.001$ and $Z=-4.1$, $p \leq 0.001$, respectively). In addition, the Cd and Zn concentrations in f_2 (bound to Mn and Fe oxides/hydroxides) were also significantly higher in the AF soil samples ($Z=-2.7$, $p \leq 0.01$ and $Z=-3.8$, $p \leq 0.001$, respectively). Before the high-magnitude flood event, Zn and Cd were mainly associated with soil crystalline minerals (f_4), (Fig. 2). Under natural conditions, metals in this fraction are unlikely to experience significant release (Passos et al. 2010), therefore, do not pose a significant environmental risk. All these facts clarified the significant impact of the floods on the mobility of these two metals in agricultural soils. It should be noted that the Zn concentrations in f_1 were significantly higher than those of Pb in f_1, indicating that Zn is considerably more mobile than Pb, which is in accordance with other fractionation research conducted in Pb/Zn industrial regions (Rodríguez et al. 2009; Nannoni et al. 2011; Popescu et al. 2013).

Pb in the soils was mainly extracted in f_2 fraction for both BF and AF soils (Fig. 2; Fig. A2). In the samples collected in the vicinity of the industrial hotspots, the percent of Pb in f_2 reached 86.9 % (equivalent to 1121 mg kg^{-1}) in S13 for BF soils and 83.4 % (equivalent to 340 mg kg^{-1}) in S2 for AF soils (Fig. A2). The enrichment of Pb in f_2 could be explained by its affinity to Fe and Mn oxides (Li et al. 2015; Mukwaturi and Lin 2015). A similar finding of Pb in the reducible fraction (77 % on average) was reported by Nannoni et al. (2011) in the study conducted in the industrial district of Kosovska Mitrovica. Generally, the results for Pb in f_2 are in agreement with the other studies conducted in industrial areas in which the accumulation of Pb in f_2 was related to anthropogenic origins (Passos et al. 2010; Canuto et al. 2013).

Considering the sum of the first three BCR fractions, the mobility of arsenic was generally increased after floods (Fig. 2). Indeed, the concentrations of As associated with Mn and Fe oxides/hydroxides (f_2) were significantly higher in the AF in relation to the BF samples ($U=170$, $p < 0.01$; $t(48)=3.9$, $p \leq 0.001$; ANOVA $F(1. 48)=15.5$, $p \leq 0.001$). Arsenic can be absorbed onto the surface of iron oxides or form iron arsenate (Mukwaturi and Lin 2015). It could be assumed that the significant amount of As was accumulated in f_2 due to the dissolution Mn and Fe oxides/hydroxides, which were re-oxidized and precipitated as high-adsorbing low-crystalline phases, like ferrihydrite which again absorbed As (Fritzsche et al. 2011). The highest amount of extracted As based on the sum of the first three fractions (up to 51 %) was recorded after the floods at the sampling point S10 in the
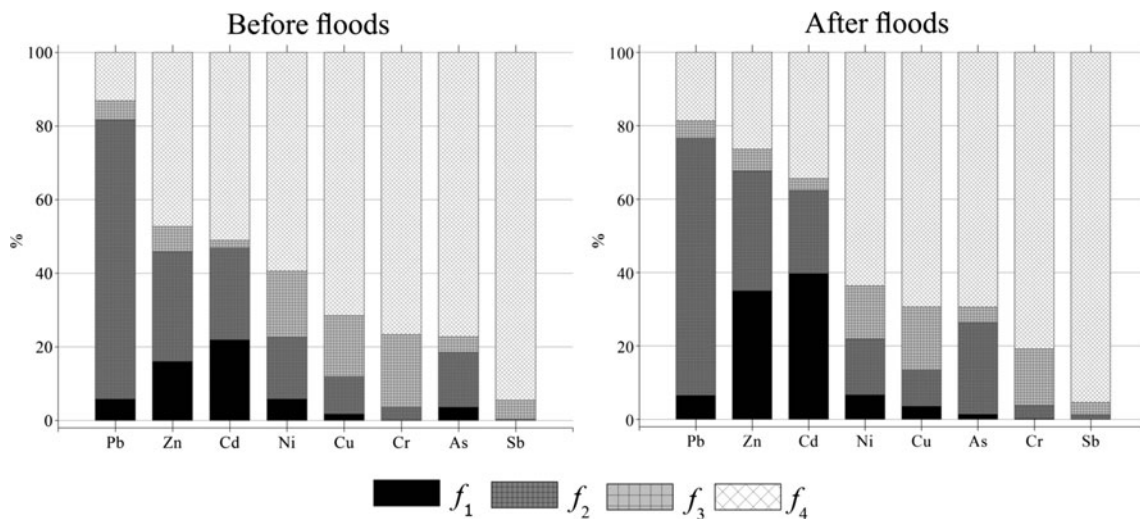
Fig. 2 Fractionation of Pb, Zn, Cd, Ni, Cu, Cr, As, and Sb in agricultural soils along the Ibar River alluvium before and after the high-magnitude flood event in May 2014

vicinity of flotation tailing ponds in the town of Leposavić (Fig. 1; Fig. A2). Additionally, it was determined that the concentrations of As in f_3 and f_4 significantly increased after the floods ($Z=-3.9$, $p \leq 0.001$ and $Z=-3.5$, $p \leq 0.001$, respectively). These results are in broad agreement with a previous investigation on arsenic mobility in this area (Barać et al. 2015). In the mentioned study, taking into account the different localities with respect to the Ibar River flow, the sum of the first three BCR fractions (as well as each fraction separately) was higher in the fluvial soils than in the soils from distant locations (Barać et al. 2015).

In the studied soils, Sb was a less mobile element mainly extracted in f_4 (Fig. 2). Most of the Sb contents in the analyzed soil samples (both BF and AF) were below the detectable limit for the first two fraction of the BCR SEP (Fig. A2). Taking into account that the highest pseudo total Sb concentrations were recorded in the vicinity of industrial hotspots, it could be assumed that the anthropogenically enriched Sb was mainly associated with crystalline minerals of the soil. The obtained results of Sb mobility in the soils are in strong agreement with those of an investigation on the mobility of the HEs in soils from the Pb/Zn industrial district of Kosovska Mitrovica (Nannoni et al. 2011). The results of the mentioned study also recognize Sb as an element in soil with poor mobility.

As shown by the fractionation scheme (Fig. 2), Cu, Cr, and Ni were mainly associated with soil crystalline minerals (f_4) with no significant differences between AF and BF samples. Nevertheless, Cu concentrations in the potentially mobile fractions ($f_1+f_2+f_3$) for AF samples located near industrial hotspots (S1, S2, S10; Fig. A2) were around 70 % of the total content. Additionally, the Cu concentration associated with carbonates (f_1) was significantly increased after the floods ($Z=-3.7$, $p \leq 0.001$). The amounts of potentially mobile Ni and Cr phases in soils ($f_1+f_2+f_3$) exceed 50 and 30 % of the

total contents, respectively, at a few scattered sampling points with generally a steady trend along the Ibar River alluvium (Fig. A2).

According to previously conducted investigations (Passos et al. 2010; Canuto et al. 2013; Li et al. 2015), BCR SEP, besides determining the association of HEs and providing information about their mobility and bioavailability, represents a very useful tool for the determination of the origin of HEs in contaminated soil. In this regard, there is an opinion that the HEs from anthropogenic sources are mainly contained in the earlier extraction steps, while those from lithogenic sources are present in the residual fraction. This suggests that the environmental risk of As, Cu, Cr, Ni, and Sb may be low in the study area because they were mainly associated with soil crystalline minerals unlikely to be released.

Potential origin and sources of heavy elements in the agricultural soils

Correlation analysis (CA)

In order to determine the affinities between the HEs in the collected soil samples and thus improve the understanding of their origin and behavior (Cai et al. 2015; Chai et al. 2015), a Spearman CA was conducted. Significantly positive correlations were found among the pseudo total contents of As, Cd, Cu, Pb, Sb, and Zn in the analyzed soil samples with correlation coefficient values of 0.75–0.91 ($p \leq 0.001$, Table 3). These correlations are in agreement with the geochemical affinity of these elements, which occurs naturally with lead and zinc in the sulfide ores galena (PbS) and sphalerite (ZnS) in the forms of sulfide minerals. Galena and sphalerite are associated in nature, so could be terminologically defined as Pb/Zn polymetallic ores (Barać et al. 2006). This

Table 3 The Spearman correlation matrix for the pseudo total concentrations of heavy elements in the soil samples ($n = 50$)

	As	Cd	Cr	Cu	Ni	Pb	Sb	Zn
As	1							
Cd	0.86***	1						
Cr	−0.41**	−0.26	1					
Cu	0.80***	0.77***	−0.35*	1				
Ni	−0.27	−0.096	0.93***	−0.22	1			
Pb	0.79***	0.70***	−0.67***	0.77***	−0.54***	1		
Sb	0.84***	0.89***	−0.28*	0.80***	−0.14	0.77***	1	
Zn	0.91***	0.87***	−0.34**	0.79***	−0.21	0.75***	0.78***	1

***correlation is significant at $p \leq 0.001$; **correlation is significant at $p \leq 0.01$; *correlation is significant at $p \leq 0.05$

fact suggests a common origin of these elements, and therefore, the mining and smelting activities and industrial waste dumping on the floodplain land of the Ibar River alluvium could be indicated as the sources for the soil pollution by these elements. Similar element affinities were reported in various studies conducted in Pb/Zn industrial areas (Anju and Banerjee 2012; Liu et al. 2013) as well as in the industrial district of Kosovska Mitrovica City (Borgna et al. 2009; Sajn et al. 2013).

A strong relationship was observed between Cr and Ni ($r = 0.93$, $p < 0.001$, Table 3) indicating an independent origin of these two elements in the soil other than Pb/Zn industrial production. Additionally, these elements were significantly negatively correlates with all other considered HEs. Similar correlations were also observed at other Pb/Zn smelting sites, e.g., Cr and Ni were not correlated with As, Cd, Cu, Pb, Sb, and Zn in the soils near smelters in the south western China (Li et al. 2015). It is well known that Cr and Ni could be lithologically influenced, so strong correlation between these element and their high levels could be controlled by parent material for example, the weathering and erosion of Jurassic and Cretaceous serpentinite and ophiolite rocks, Paleogene flysch and Neogene clastic series that are enriched in these elements (Sajn et al. 2013; Cai et al. 2015).

Principal component analysis (PCA)

The mutual relations between the variables were tested using the Pearson correlation coefficient at the level of statistical significance of $p = 0.05$. The results confirm (as well as Spearman correlation, Table 3) the high degree of interdependence between the individual variables. A large number of variables were highly correlated, with correlation factors over 0.80 (between As, Cd, Cu, Zn, and Sb and between Ni and Cr). The Bartlett test of sphericity reached statistical significance of $p = 0.000$ and the Kaiser-Meyer-Olkin measure had a value of 0.81, indicating the efficient performance of a PCA on the dataset. The PCA with Varimax rotation was applied on the whole set of data (50 samples, eight elements) of the

pseudo total HE concentrations. The principal components that had eigenvalues higher than 1 were extracted. According to the Kaiser criterion, two principal components were extracted explaining up to 90 % of total variance. A graphical representation of the two components is given in Fig. 3, which shows the associations among the analyzed HEs.

The PC1 included As, Cd, Cu, Pb, Sb, and Zn which explains 68 % of the total variance. The high loadings of As (0.91), Cd (0.94), Cu (0.94), Pb (0.72), Sb (0.87), and Zn (0.92) in the PC1 and the fact that these elements had significantly positive correlation with each other strongly suggest their common origin. It could be freely said that the PC1 represents an "anthropogenic factor" taking into account that As, Cd, Cu, and Sb usually co-exist with the Pb/Zn ores galena (PbS) and sphalerite (ZnS), historically exploited in the study area (Barać et al. 2006).

The PC2 explains 22 % of the total variance, with high factor loadings of over 0.9 of Ni and Cr. Taking into account that lithogenic Cr and Ni often occur together in primary minerals (Cai et al. 2015; Li et al. 2015), this factor could be assumed as being "lithologically influenced." In the present study, there are a non-point source of contamination by these
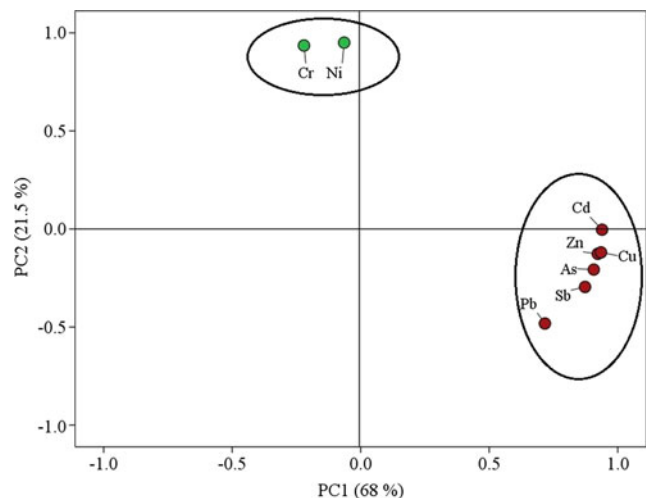

Fig. 3 Loading plot for two rotated components from the PCA analysis

elements, suggesting no significant anthropogenic input of Cr and Ni. Anthropogenic inputs of Cr and Ni in fertilizers, limestone, and manure are generally lower than the concentrations already present in soil (Facchinelli et al. 2001).

Hierarchical cluster analysis (HCA)

A hierarchical clustering by applying the Ward linkage method for determining similarities between the HEs is presented in Fig. 4. The cluster has two subgroups: the first subgroup contains As, Cd, Cu, Pb, Sb, and Zn, and the second one, only Ni and Cr. The results of HCA confirmed those obtained by application of PCA and CA. Both Ni and Cr had a very high factor loading in PC2 and mutual strong significantly positive correlation which suggests that their may derive from lithogenic sources. On the other hand, the As, Cd, Cu, Pb, Sb, and Zn associations (Fig. 4) confirm the assumption that these elements in soils originate from anthropogenic sources.

Environmental implications

The calculated C_f^i values (Eq. 1) for each element associated with Pb/Zn industrial production (As, Cd, Cu, Pb, Sb, and Zn) by sampling sites are given in Table B2 of the Supplementary material B. In general, it can be seen that the floods affected an increase in C_f^i for each considered element considered element but as in the case of pseudo total content, As, Cd, Cu, Sb, and Zn with statistical significance (Table B2 Supplementary material).

The calculated E_r^i values (Eq. 1) of As, Cd, Cu, Pb, and Zn and the RI of each sampling site for both sampling campaigns are presented in Table B3 of the Supplementary material B, together with risk ranges recommended by Håkanson (1980). As listed in Table B2, Cd posed a very high ecological risk (≥ 320) in the soils collected after the floods at seven sampling sites near industrial hotspots. Such a situation was predicted in recent research of assessment of metal risks from the jarosite
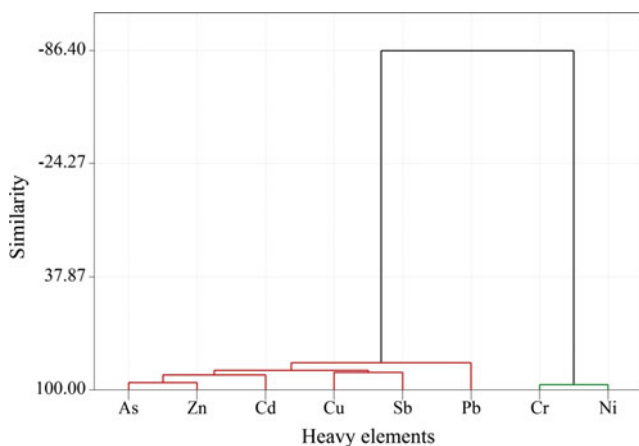

Fig. 4 HCA dendrogram resulting from the Ward method and the Euclidean distance method for the analyzed HEs in the soil samples

tailing waste of Trepča's Zn industry in Kosovska Mitrovica district (Kerolli–Mustafa et al. 2015). In the aforementioned study, the authors concluded that Cd possesses the highest potential ecological risk factor that requires special attention in regard to the potential threat for the surrounding environment (Kerolli–Mustafa et al. 2015).

Calculated RI values indicated that the considered soils before flood were generally in the range of low to moderate risk with three cases suffering from considerable risk at sampling sites S1, S3, and S7 (Table B3 Supplementary material). By applying independent samples t test, it was observed that the flood event in May 2014 significantly increased ($p \leq 0.05$) the potential ecological risk in the study area caused by contamination with As, Cd, Cu, Pb, and Zn. Finally, the most elevated RI values were recorded after the floods at sampling points near industrial hotspots (S1, S2, S3, S7, and S10; Table B3 Supplementary material).

Conclusions

The present study provides valuable information of the concentrations, chemical speciation, and sources of As, Cd, Cr, Cu, Ni, Pb, Sb, and Zn in agricultural soils from Ibar River Valley, which is considered as one of the most important mining districts in Europe. The results showed that the Cd and Zn in the soil collected after the floods were the elements with the greatest percentages in the fraction considered as the most mobile and the most dangerous for the environment (f_1). In the samples collected in both sampling campaigns, before and after the floods, Pb was preferentially associated with Mn and Fe oxides/hydroxides (f_2) which are widely reported as excellent scavengers of this metal in soil. The high-magnitude floods significantly increased the Cd, Cu, and Zn concentrations in f_1 and As and Zn concentrations in the f_2 fractions of the BCR protocol.

The pseudo total concentrations of As, Cd, Pb, Sb, and Zn were found to be the highest in samples collected in the vicinity of industrial hotspots, exceeding the corresponding intervention thresholds proposed by the VROM—Netherlands Ministry of Housing and Spatial Planning and the Environment (2009). In contrast, the pseudo total Ni and Cr concentrations were most elevated in the northern sector of study area that is not associated with Pb/Zn industrial production. In this part of the study area, the Ni concentrations exceeded the corresponding intervention value in the soil samples collected in both sampling campaigns. Here, the high-magnitude flood event significantly influenced the pseudo total concentrations of As, Cd, Cu, Sb, and Zn. The concentrations of Cr, Ni, and Pb in the soil were also found to be higher after floods but not statistically relevantly. Application of the chemometric methods PCA and HCA as well as CA showed that the As, Cd, Cu, Pb, Sb, and Zn in the soils originated from

Pb/Zn industrial production, while Cr and Ni arose from geogenic sources. These conclusions were in agreement with the geochemical affinity of these elements.

It could be concluded that the floods significantly increased the of As, Cd, Cu, Sb, and Zn. The calculated values indicated that Cd posed a very high ecological risk in the soils collected after the floods, and this deserves special attention. The *RI* in the study area caused by contamination with HEs associated with industrial activities before the flooding was in the range of low to moderate ecological risk with three cases suffering from considerable risk at sampling sites near industrial hotspots. A very high *RI* was recorded after the floods at sampling points in the southern sector of the study area, where Pb and Zn ores were intensively exploited and processed in the past century, with a clear decreasing trend downstream. Generally, the occurrence of the high-magnitude flood event resulted in significantly increase of *RI* in the study area indicating serious anthropogenic pollution.

Information provided by this investigation could help in obtaining more insights into the likely adverse effects of contaminated sites and could assist to the decision makers in justifying the need to designate the "contaminated land" with more confidence.

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