



Exploring distribution of potentially toxic elements in soil profiles to assess the geochemical background and contamination extent in soils of a metallurgical and industrial area in Kosovo

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Abstract

This geochemical study explored the distribution of potentially toxic elements (PTEs), such as As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U, and Zn, along soil profiles of a metallurgical and industrial area in Kosovo, with the aim of assessing geochemical background and contamination threshold of PTEs in soil, and defining surface and vertical level and extent of soil contamination by PTEs. The geochemical background was assessed by exploratory data analysis of PTE concentrations in soil profiles. The upper limit of geochemical background (contamination threshold) was used as reference value to calculate the single pollution index and establish the PTE contamination level. Cadmium, Pb, Sb, Zn were the primary soil contaminants and As, Cu, Tl the secondary ones. The main sources of soil contaminants were the Zvecan smelter for Pb, Sb, As, Cu, Tl, and the Treпча industrial complex for Cd and Zn. The highest levels of Pb and Sb contamination were found up to depths between 30 and 60 cm in soil profiles within 5 km north and south-east of the Zvecan smelter. Contamination by Pb and Sb decreased with depth and affected the whole thickness of soil profiles closer the smelter. Cadmium and Zn contamination declined with distance from the Treпча industrial complex and decreased with depth, extending down to depths of 40–90 cm and 30–70 cm, respectively. Anomalous natural concentrations of Co, Cr, and Ni were found in soils collected in the northern part of the study area, where the geology consists mainly of ultrabasic and basic magmatic rocks.

Keywords Potentially toxic elements · Soil · Vertical distribution · Geochemical background · Contamination · Smelter

Introduction

In environmental geochemistry assessment of the geochemical background (or natural background) is a proper approach to establish whether the concentrations of potentially toxic elements (PTEs) in soil are geogenic due to natural factors and processes (e.g. parent rock, morphology, climate, weathering and erosion), or have been affected by human contributions from industrial plants, vehicle traffic, agriculture and so on. Therefore, defining the geochemical background is essential for distinguishing the natural and anthropogenic origin of PTEs in soil, determining their level and extent of contamination, tracing the source of these contaminants, and establishing action levels in environmental legislation

(Matschullat et al. 2000; Salminen and Gregorauskiene 2000; Baize and Sterckeman 2001; Reimann and Garret 2005; Reimann et al. 2005).

In the past 20 years, many studies have assessed the geochemical background of PTEs (e.g. As, Cd, Cr, Cu, Hg, Ni and Pb) in soil in geo-environmental settings such as industrial and mining sites as well as agricultural and urban areas, by applying geochemical and statistical methods (Chiprés et al. 2009; Pérez-Sirvent et al. 2009; Roca et al. 2012; Hao et al. 2014; Galuska et al. 2016; Reimann et al. 2018; Yotova et al. 2018). Geochemical methods estimate the geochemical background of PTEs in soil by means of their concentrations in uncontaminated soils in pristine sectors of the study area and in deep layers of soil profiles in contaminated sites, or by using reference values such their average contents in the bulk/upper earth crust and in soil estimated at regional to global scale (Massas et al. 2009; Yang et al. 2009; Lienard and Colinet 2016). Statistical methods assess the geochemical background through the calculation of statistical indices of analytical datasets or techniques of exploratory and

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spatial data analysis (Reimann et al. 2005; Chiprés et al. 2009; Ander et al. 2013; Reimann and de Caritat 2017).

In metallurgical sites atmospheric emissions from non-ferrous ore smelters are a worldwide environmental issue. The smelting plants release PTEs associated with airborne fine and ultrafine particles that may travel long distances and accumulate in soil by wet and dry deposition (Csavina et al. 2014; Ettlér 2016; Lee et al. 2020). In addition, coarser particles blown by wind from mining and ore processing waste disposal sites, usually located near smelters, may be a secondary source of PTEs (Ettlér et al. 2014).

Many studies have revealed severe contamination by PTEs in surface soil (topsoil) near smelters, extending a few tens of kilometres and decreasing with distance from the metallurgical site (Stafilov et al. 2010a; Kribek et al. 2010; Ettlér et al. 2011; Li et al. 2015; Ghayoraneh and Qishlaqi 2017; Xing et al. 2019). Level and extent of contamination by PTEs in topsoil around smelters depend mainly on the amount, size, physical properties and chemical/mineralogical composition of the particles released, prevailing winds, landscape features and soil characteristics.

Several authors have investigated the vertical distribution of PTEs in soils of metallurgical sites, showing a common pattern consisting in a significant enrichment in the upper part of the soil profile and a decline in concentrations with depth (Kabala and Singh 2001; Yuan et al. 2017; Gelly et al. 2019). However, few studies have established the surface and in-depth level and extent of soil contamination by PTEs around smelting plants in relation to the local geochemical background, usually represented by the element concentrations in selected subsoil layers (Sterckeman et al. 2000; Kribek et al. 2010; Lienard and Colinet 2016; Lee et al. 2020).

In this view, a field geochemical study was performed to explore the top-to-bottom distribution of PTEs (As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U and Zn) in soil profiles of a metallurgical and industrial area in Kosovo with the following objectives: (i) assessing the local geochemical background and contamination threshold of PTEs in soil; (ii) defining the surface and vertical level and extent of soil contamination by PTEs using the values of their local geochemical background; (iii) identifying the primary and secondary soil contaminants and their relationships with the main sources of contamination in the study area.

The study was conducted in an area of northern Kosovo around the town of Kosovska Mitrovica affected by severe and widespread soil contamination by PTEs such as Cd, Pb, Sb and Zn, mainly due to deposition of particles emitted by the Zvečan smelter and the Trepça industrial complex, and blown by wind from the waste dumps near these plants (Borgna et al. 2009; Stafilov et al. 2010b; Gashi et al., 2011; Nannoni et al. 2011, 2016; Boisa et al. 2013; Šajin et al. 2013; Aliu et al. 2016, 2017, 2017; Brewer et al. 2016;

Prathumratana et al. 2020). Soil contamination by PTEs is very intense in a large area including the smelter and industrial site, as well as the towns of Kosovska Mitrovica and Zvečan, and extends up to about 20 km from this hotspot, north along the Ibar valley and south-east along the Sitnica valley.

The previous studies in the Kosovska Mitrovica area mostly determined concentrations of Pb and other PTEs in topsoil (normally up to a depth of 10 cm) to define their surface distribution in the entire Mitrovica region or in selected areas. Enrichment of PTEs in the soil was quantified using reference values from outside the Kosovska Mitrovica area such as the average concentration in European topsoil, Dutch target and intervention values and CLEA (Contaminated Land Exposure Assessment) soil guideline values (Boisa et al. 2013; Šajin et al. 2013; Aliu et al. 2016; Brewer et al. 2016). However, some data are available on the vertical distribution of PTEs in soil of this sector of northern Kosovo (Borgna et al. 2009), and a few attempts have been made to assess the local geochemical background of PTEs in soil. For this purpose, Borgna et al. (2009) used As, Cd, Cu, Pb, Sb and Zn concentrations in soil samples collected at depth of 90–100 cm, and Brewer et al. (2016) applied a statistical method to Pb concentrations in surface and subsurface soils.

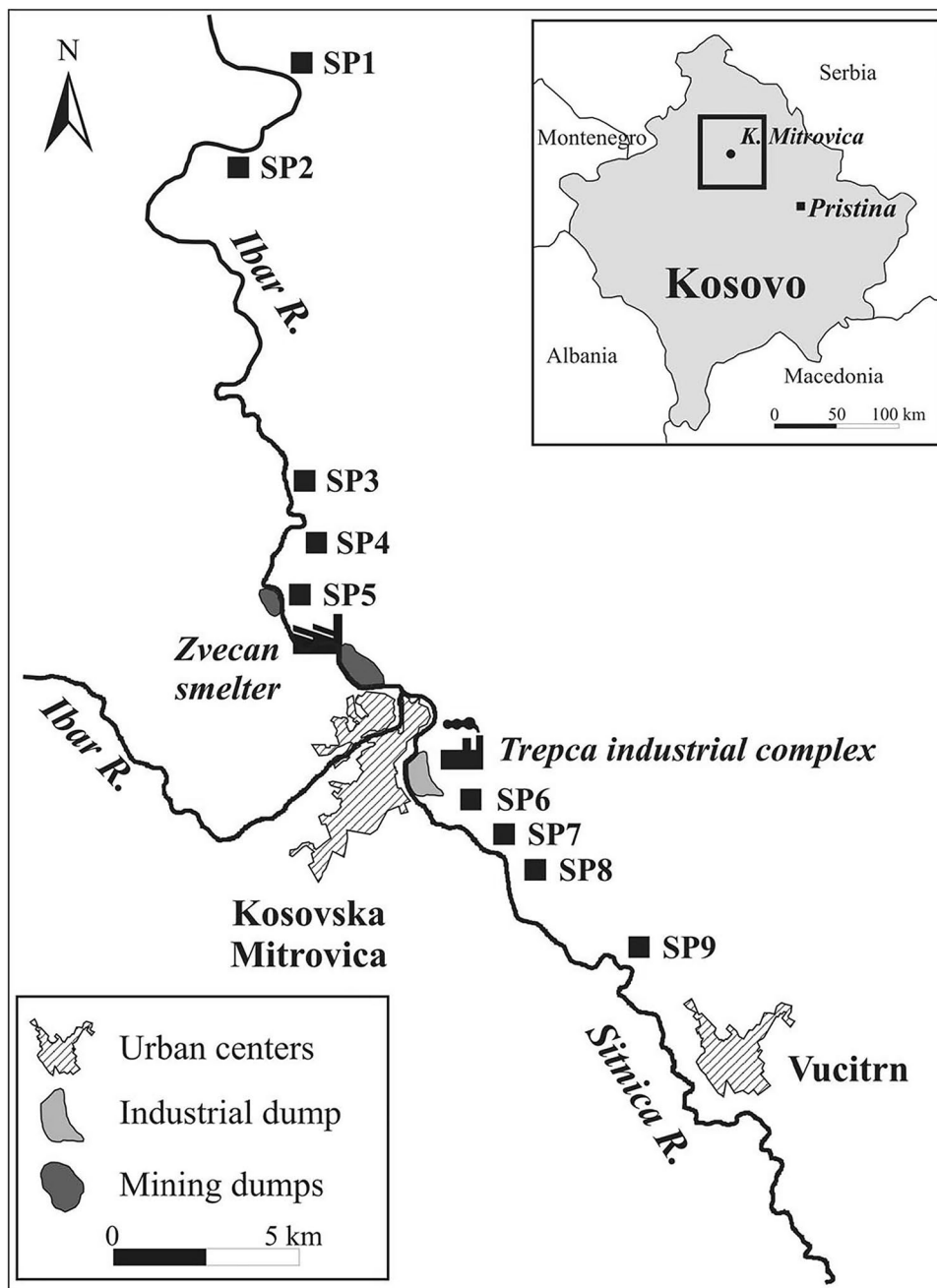
Materials and methods

Study area

The study area includes a former metallurgical and industrial area in northern Kosovo and extends to about 25 km north and south-east of the town of Kosovska Mitrovica along the valleys of the Ibar and Sitnica rivers (Fig. 1). The Sitnica river flows south-east to north-west in a large valley with asymmetrical slopes and meets the Ibar river in the town of Kosovska Mitrovica. The Ibar river flows west to east to Kosovska Mitrovica. Downstream of the confluence with the Sitnica river, it takes a northward direction in a narrow and engraved valley.

The geology of the Kosovska Mitrovica area is complex and consists of Palaeozoic to Quaternary magmatic, metamorphic and sedimentary rocks (Bogdanović et al. 1978). Triassic ultrabasic and basic magmatic rocks (serpentinites, diabases and basalts) crop out in the northern sector of the study area, and Cretaceous clayey-arenaceous-marly flysches in the western sector. Miocene sediments and intermediate volcanites (latites and quartzolites) are found east and north-east of Kosovska Mitrovica. Large outcrops of Pliocene clayey-sandy sediments and Pleistocene fluvio-lacustrine sediments characterize the geology of the southern sector of the study area.

Fig. 1 The study area with the location of soil profiles sampled



World-class Pb–Zn mineralizations of the Trepca mining district are found a few kilometres north-east of Kosovska Mitrovica. They are skarn mineralizations hosted by Upper Palaeozoic metalimestone as massive to sub-massive sulphide lenses. The ore assemblage consists mainly of coarse-grained sulphides such as Ag-bearing galena, sphalerite, pyrite and pyrrhotite.

The Trepca mining district is one of the largest ore districts in Europe consisting of about 40 mines, of which the Stari Trg and Trepca mines were the most important. In the study area metallurgical and industrial plants processed the ore of the Trepca mining district (Gashi et al.

2017). They included the Zvecan smelter, other secondary ore processing plants and the factories of the Trepca industrial complex. Sulphide ore was initially processed at the Tuneli Pare flotation plant and then mainly at the Zvecan smelter about 2 km north of Kosovska Mitrovica (Fig. 1). The Zvecan smelter opened in 1939 and was shut down by the United Nations in 2000 after the Kosovo war. During its operation, various contaminants (e.g. SO₂ and PTEs) were released to the atmosphere as gas and particles from the stacks of the metallurgical plant. Large quantities of waste from the flotation and smelting activities accumulated in the Gornie Polje, Zitkovac and Zarkov Potok

dumps close to the Zvečan smelter. The Trepça industrial complex in the eastern suburb of Kosovska Mitrovica included chemical and battery industries and a Zn electrolysis plant (Fig. 1). The waste from these industrial plants went to a large dump nearby. The Trepça industrial complex was closed in 1999 at the end of the Kosovo war.

Soil sampling

Ninety-five soil samples were collected in nine soil profiles (SP1 to SP9) at different distances from the Zvečan smelter along two transects, hereafter named transects N and SE (Fig. 1). Transect N extends north from the smelter for about 13 km along the Ibar valley; transect SE is about 11 km long and extends south-east from the smelter along the Sitnica valley. The transects N and SE were aligned with the prevailing winds.

The soil sampling sites along the transects N and SE were selected on the basis of the distribution of PTE concentrations in topsoil reported by Borgna et al. (2009). Soil samples were taken every 10 cm along the whole soil profile to a depth of 70 to 150 cm, in uncultivated sites within agricultural areas. The parent rock of soil samples consists of the alluvial sediments of the Ibar and Sitnica rivers. The soil sampling was performed using Edelman augers.

Soil treatment and analysis

In the laboratory, the soil samples were manually disaggregated, dried at +40 °C and then sieved using a 2-mm mesh sieve. Soil particles less than 2 mm were homogenized by quartering and pulverization. About 250 mg of pulverized soil sample was solubilized by acid digestion using a mixture of ultrapure reagents consisting of 2 mL HF, 2 mL HNO₃ and 1 mL H₂O₂ (US EPA 1996). Solubilization was performed in Teflon bombs using a Milestone ETHOS 900 microwave digester.

Concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U and Zn were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a Perkin Elmer NexION 350 spectrometer. Analytical accuracy was assessed by analysis of the standard reference materials SRM 2709 (San Joaquin Soil) and SRM 2710 (Montana Soil) from the National Institute of Standards and Technology (NIST). Recoveries ranged from 93% (Sb) to 106% (Zn) for SRM 2709, and from 90% (Tl) to 105% (Ni) for SRM 2710. Analytical precision was calculated by means of the percentage relative standard deviation (% RSD) of five replicate analyses of each soil sample. The values of % RSD were below 7.2%.

Geochemical index

The single pollution index (PI) is a geochemical index widely used for quantifying soil contamination by PTEs due to human contributions (Hu et al. 2013; Kowalska et al. 2018). A prerequisite for its calculation is knowledge of the geochemical background of PTEs in soil. In this study the single pollution index was calculated as the ratio of PTE concentration in the soil sample to its contamination threshold, namely the upper limit of its geochemical background in soil. The following scale of contamination was used: $PI < 1$ contamination absent; $1 < PI < 2$ low contamination; $2 < PI < 3$ moderate contamination; $3 < PI < 5$ strong contamination; $PI > 5$ very strong contamination.

Statistical analysis

The quantile–quantile (Q–Q) plot was used as the graphic technique of exploratory data analysis to identify populations in the whole dataset of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U and Zn concentrations in soil samples. The concentrations of PTEs (whole dataset and single populations) were processed to calculate the main statistical indices: min and max values, mean, median, standard deviation and coefficient of variation (CV).

Multivariate analysis was performed on data considered as compositional (Aitchison 1983). The R software (R Core Team 2021) and its library “compositions” (van den Boogaart et al. 2020) were used for the analysis. PCA analysis was performed through the “princomp” R function, which is aware of the “acomp” data class and processes it through a centered log-ratio transformation.

Results and discussion

Geochemical background of potentially toxic elements

As shown in Table 1, the concentrations of As, Cd, Co, Cr, Cu, Ni, Pb, Sb and Zn in soil samples collected from soil profiles in the Kosovska Mitrovica area were highly variable (CV from 0.54 to 2.06), while those of Tl and U were more uniform (CV ≈ 0.25). Exploratory data analysis suggested that concentrations of Cd, Pb, Sb and Zn in soil samples belonged to four main populations (A, B, C, D), As, Cu and Tl to three populations (A, B, C), Co, Cr and Ni to two populations (A, B) and U to one population (A; Table 1). This partitioning of PTE concentrations in population coupled with literature data on their contents in uncontaminated soils and in rocks similar to those cropping out in the Ibar

Table 1 Statistics of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U and Zn concentrations (in mg/kg) in all soil samples (all data) and populations A, B, C, D (SD=standard deviation; CV=coefficient of variation)

		Pb	Zn	Cd	Sb	As	Cu	Tl	Co	Cr	Ni	U
All data	N	95	95	95	95	95	95	95	95	95	95	95
	Min	18.3	70.6	0.35	0.84	14.2	22.5	0.32	10.9	42.8	36.7	1.26
	Max	4813	4321	29.4	54.9	399	134	1.33	94.5	668	1364	4.39
	Mean	391	379	2.49	5.66	45.8	43.8	0.74	24.7	170	232	2.46
	Median	133	171	0.87	3.03	28.7	35.7	0.73	18.6	113	109	2.28
	SD	806	653	4.57	8.53	63.3	23.7	0.18	18.3	151	323	0.63
	CV	2.06	1.72	1.83	1.51	1.38	0.54	0.24	0.74	0.88	1.40	0.25
Population A	N	16	34	41	19	46	72	38	81	81	81	95
	Min	18.3	70.6	0.35	0.84	14.2	22.5	0.32	10.9	42.8	36.7	1.26
	Max	59.0	132	0.77	1.43	26.5	45.2	0.69	29.0	201	203	4.39
	Mean	46.1	104	0.60	1.18	20.8	33.2	0.59	17.7	112	105	2.46
	Median	50.0	103	0.62	1.25	21.4	32.6	0.61	16.8	107	104	2.28
	SD	13.5	16.9	0.11	0.17	3.71	6.10	0.09	3.92	44.5	42.1	0.63
	CV	0.29	0.24	0.18	0.15	0.18	0.18	0.15	0.22	0.41	0.41	0.26
Population B	N	59	44	33	58	46	11	50	14	14	14	
	Min	62.5	139	0.80	1.59	28.2	47.5	0.71	47.1	325	602	
	Max	305	417	1.68	5.50	139	62.0	0.90	94.5	668	1364	
	Mean	143	218	1.09	3.19	49.6	54.3	0.80	65.4	508	963	
	Median	123	199	1.03	3.05	40.5	53.4	0.80	64.2	476	916	
	SD	63.1	70.7	0.24	1.06	23.8	4.52	0.06	15.2	92.0	262	
	CV	0.44	0.32	0.23	0.33	0.48	0.08	0.07	0.23	0.18	0.28	
Population C	N	17	14	18	15	3	12	7				
	Min	405	559	2.14	6.36	328	70.2	0.96				
	Max	2060	1317	10.7	20.8	399	134	1.33				
	Mean	875	864	5.79	13.0	372	98.1	1.18				
	Median	703	794	5.44	12.8	388	91.0	1.20				
	SD	454	241	2.65	5.33	38.1	22.2	0.13				
	CV	0.52	0.28	0.46	0.41	0.11	0.23	0.11				
Population D	N	3	3	3	3							
	Min	3728	2774	18.9	35.4							
	Max	4813	4321	29.4	54.9							
	Mean	4364	3590	23.9	45.0							
	Median	4550	3674	23.6	44.6							
	SD	566	777	5.26	9.78							

and Sitnica valleys was applied to assess the geochemical background of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U and Zn in the soils of the study area.

On this basis, the concentrations of As, Cd, Cu, Pb, Sb, Tl and Zn belonging to population A were taken as representative of their geochemical background in soils formed by the alluvial sediments of the Ibar and Sitnica rivers (Table 2). In other words, the minimum and maximum concentration values in population A identify the geogenic variability of these PTEs in soils of the study area due to natural factors and processes (e.g. mineralogical and geochemical characteristics of parent rocks, morphology, climate and weathering). Consequently, the upper limit of the geochemical background of As, Cd, Cu, Pb, Sb, Tl and Zn in soil corresponds to the respective contamination threshold, and concentrations of these PTEs in populations B, C, D identify variable levels of contamination.

Comparison with literature data suggests that the estimated geochemical background of As, Cd, Cu, Pb, Sb, Tl and Zn is within the range of their normal concentrations in uncontaminated soils (Reimann and de Caritat 1998; De Vos and Tarvainen 2006; Kabata-Pendias 2010). Moreover, the natural contents of As, Cd and Cu in soils formed by the alluvial sediments of the Ibar and Sitnica rivers include the corresponding average concentrations in sub-soils (90–100 cm) derived by this parent rock (As = 24 mg/kg; Cd = 0.5 mg/kg; Cu = 30 mg/kg), considered by Borgna et al. (2009) to be representative of their background values. Conversely, the geochemical background assessed for Pb, Sb and Zn was lower than their average concentrations in the 90–100 cm soil layer (Pb = 84 mg/kg; Sb = 2.4 mg/kg; Zn = 150 mg/kg). In addition, the contamination threshold of Pb (59 mg/kg) was found to be lower than the threshold of 80 mg/kg, as estimated by Brewer et al. (2016), using the

Table 2 Geochemical background and contamination threshold of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U and Zn in soils of the study area (data in mg/kg)

Element	Geochemical background	Contamination threshold
As	14.2–26.5	26.5
Cd	0.35–0.77	0.77
Co	10.9–29 ^a	29
	47.1–94.5 ^b	94.5
Cr	42.8–201 ^a	201
	325–668 ^b	668
Cu	22.5–45.2	45.2
Ni	36.7–203 ^a	203
	602–1364 ^b	1364
Pb	18.3–59	59
Sb	0.84–1.43	1.43
Tl	0.32–0.69	0.69
U	1.26–4.39	4.39
Zn	70.6–132	132

^aNormal geochemical background

^bAnomalous geochemical background

element concentrations in surface and subsurface soils (up to 50 cm) of the Kosovska Mitrovica area.

Despite the high variability, Co, Cr and Ni concentrations in the soil samples were geogenic, mainly determined by the mineralogical and geochemical characteristics of parent alluvial sediments, which are in turn related to the geolithological features of nearby outcropping rocks. In fact, the highest concentrations of Co, Cr and Ni in population B (Table 2) were measured in the soil samples of profiles SP1 and SP2 located in the northern sector of the study area where ultrabasic and basic magmatites (serpentinites, diabases and basalts) crop out. It is known that ultrabasic and basic magmatic rocks have high concentrations of Co, Cr and Ni (e.g. 110 mg/kg for Co, 2300 mg/kg for Cr, 2000 mg/kg for Ni in ultrabasic rocks; Reimann and de Caritat 1998) as these PTEs are vicariants of Fe and Mg in the femic minerals (mainly olivines and pyroxenes) of these magmatites. The high contents of Co, Cr and Ni in soil profiles SP1 and SP2 can, therefore, be considered anomalous natural concentrations that identify an anomalous geochemical background (Table 2), presumably due to the presence in the parental alluvial sediments of clasts of the ultrabasic and basic magmatites cropping out in the Ibar valley. In soil samples collected in the central and southern sectors of the Kosovska Mitrovica area where geology mainly consists of intermediate volcanites, clayey-arenaceous-marly flysch and clayey-sandy sediments, the concentrations of Co, Cr and Ni were significantly lower (population A in Table 1). They are normal natural concentrations that identify the normal

geochemical background of Co, Cr and Ni in soils of the study area (Table 2). These concentrations are comparable with the abundances of Co, Cr and Ni in intermediate and sialic magmatites as well as in sedimentary lithologies (Reimann and de Caritat 1998; Kabata-Pendias 2010).

Last, U concentrations in soil samples are consistent with the normal content of this element in uncontaminated soils (De Vos and Tarvainen 2006; Kabata-Pendias 2010) and, therefore, represent the geochemical background of U in the studied soils. However, it should be noted that the highest natural concentrations of U distinguished the soil of profile SP5 close to outcrops of intermediate volcanites. This finding agrees with U contents in sialic magmatic rocks (Gao et al. 1998; Reimann and de Caritat 1998).

Distribution of potentially toxic elements in soil profiles

To investigate the vertical distribution of As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U and Zn, these PTEs and soil profiles were categorized and grouped according to the contamination level of topsoil (0–10 cm) defined by the value of the single pollution index (PI).

The first category of PTEs included Cd, Pb, Sb and Zn: their concentrations in topsoil were always higher than the corresponding contamination threshold and indicated a prevalence of a strong to very strong contamination. Based on the contamination level of Cd, Pb, Sb and Zn in topsoil, two groups of soil profiles were distinguished: Group 1, soil profiles with low to moderate contamination ($1 < PI < 3$); Group 2, soil profiles with strong to very strong contamination ($PI > 3$).

In soil profiles of Group 1 concentrations decreased progressively up to a depth of 30 cm for Pb and Sb, 20–40 cm for Zn and 30–50 cm for Cd (Fig. 2). At greater depths, the contents of these PTEs were quite uniform and within the corresponding geochemical background.

Soil profiles of Group 2 showed a similar distribution of Cd, Pb, Sb and Zn characterized by a vertical decrease in concentrations that involved a wider thickness of profile or even the whole profile (Fig. 2).

Cadmium and Zn exhibited progressive and sharp declines in content down to depths of 50–90 cm and especially in the first 50 cm of soil profile (Fig. 2). Below, the concentrations of these PTEs were homogeneous and geogenic. Only in soil profile SP6, located close to the Trepca industrial complex, Zn contents were higher than the respective contamination threshold down to the bottom of the profile.

Concentrations of Pb and Sb decreased progressively down to the bottom of the soil profiles SP2, SP3, SP4, SP5 and SP6, although the decline was particularly marked in the upper 50 cm (Fig. 2). In these soil profiles contamination by

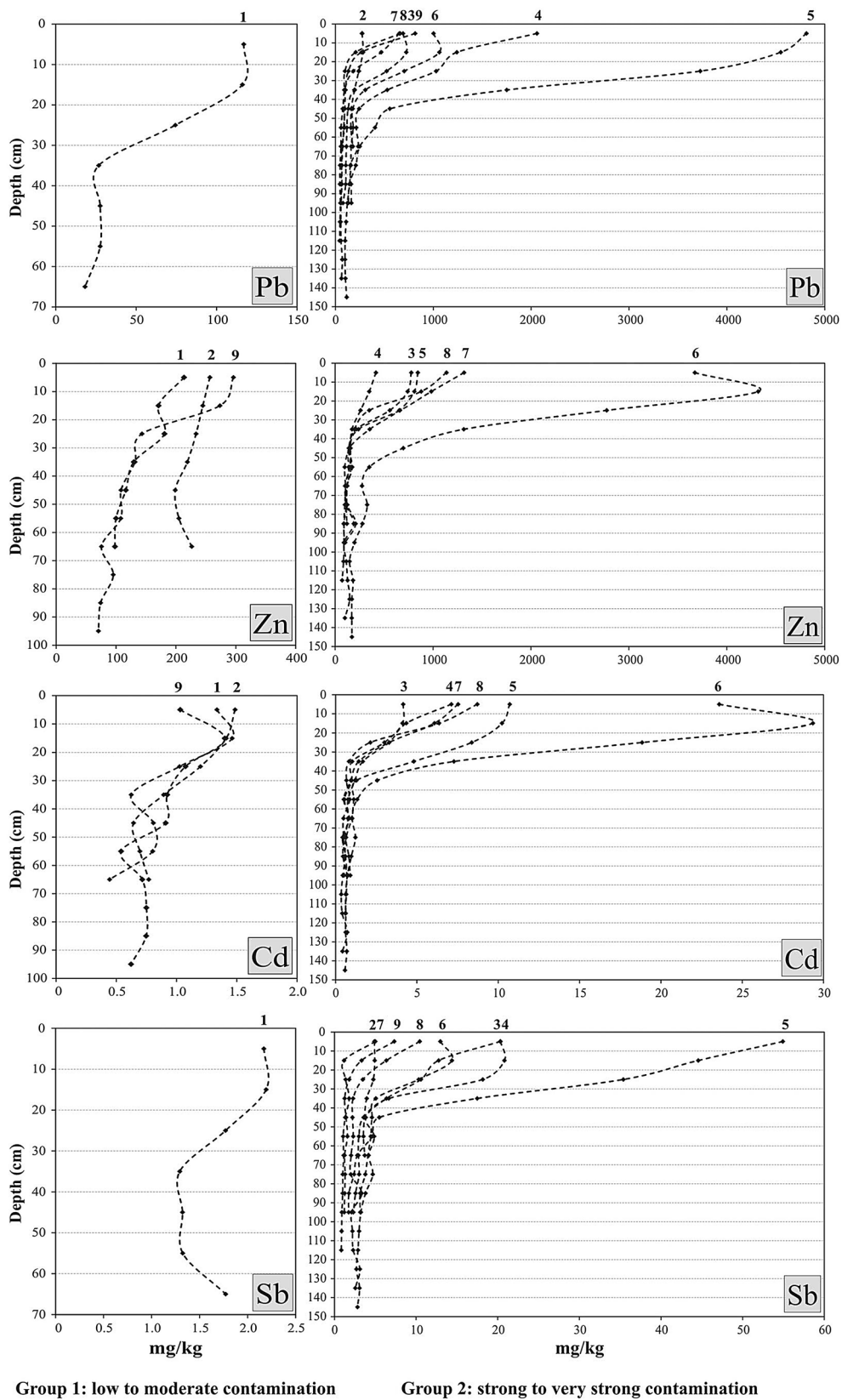


Fig. 2 Vertical distribution of Cd, Pb, Sb and Zn concentrations in soil profiles (soil profile identification is at the top of each graph)

Pb and Sb affected the whole soil thickness. In soil profiles SP7, SP8 and SP9 from the southern sector of the study area, Pb and Sb concentrations decreased down to depths of 50–70 cm and 30–40 cm, respectively. At greater depths they were quite uniform and within the corresponding geochemical background.

Enrichment of Cd, Pb, Sb and Zn in the upper layer and progressive decline in their concentrations with depth were also found in the Kosovska Mitrovica area by Borgna et al. (2009) in two soil profiles sampled down to the bottom, and by Brewer et al. (2016) who investigated the distribution of Cd, Pb and Zn in soils down to a depth of 50 cm.

The results of this study recall the vertical distribution of Cd, Pb, Sb and Zn in soils contaminated by metallurgical activities. Steckerman et al. (2000) found that Cd, Pb and Zn concentrations decreased abruptly in the upper part of soil profiles and contamination was mostly in the first 20–30 cm. They also found that migration of these PTEs increased with their concentrations in topsoil. Similarly, Cd, Pb, Sb and Zn were significantly enriched in the upper 20 cm of soils near a Pb-Sb smelter in southwest China (Yuan et al. 2017). Moreover, the distribution of Pb concentrations in the strongly to very strongly contaminated soil profiles of the present study is consistent with the results of Gelly et al. (2019), who found that Pb contamination involved the whole thickness of soil profiles close to a Pb-Ag smelter. These authors estimated the human contribution to be more than 90% of the total element content in topsoil and 65–78% in subsoil.

In metallurgical sites accumulation of Cd, Pb, Sb and Zn in the upper layer of soil profiles is mainly the result of the following: (i) deposition of PTE-bearing airborne particles emitted by smelters or blown by wind from mining dumps; (ii) adsorption and precipitation/coprecipitation of the PTE aliquot mobilized in soil by chemical alteration of the smelter-derived particles. Adsorption of PTEs mainly occurs on the surface of organic matter (e.g. humic substances), Fe–Mn oxyhydroxides and clay minerals, precipitation as own minerals such as carbonates, oxides/hydroxides, sulphates and phosphates, and coprecipitation with Fe–Mn oxyhydroxide colloids (Wilson et al. 2010; Yuan et al. 2017; Lee et al. 2020). These redistribution processes mainly depend on the alteration of particles emitted by smelters, soil physico-chemical properties (e.g. pH and cation exchange capacity), content and characteristics of reactive soil constituents (e.g. clay minerals, Fe–Mn oxyhydroxides and organic matter) as well as element behaviour in adsorption and precipitation/coprecipitation.

Soil enrichment of Pb and Zn in surface soils due to precipitation of own minerals, such as carbonates, sulphates and phosphates and/or coprecipitation in minerals such as calcite, was mainly found in contaminated neutral to alkaline calcareous soils (Jacquat et al. 2008; Liang et al. 2014). In this regard, Nannoni et al. (2011) detected

cerussite (PbCO_3), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) and minor anglesite (PbSO_4) in highly Pb-contaminated topsoils formed by the alluvial sediments of the Ibar and Sitnica rivers. These soils had neutral to sub-alkaline pH (6.7–7.6) and a variable carbonate content from < 1 to 14.8%.

The downward migration of Cd, Pb, Sb, Zn and other chemical elements in soils contaminated by smelters is ruled by several factors including level of contamination, physical characteristics and composition of smelter-derived particles, soil properties, surface reactivity of soil constituents, element speciation and transport in soil solution, behaviour in adsorption and precipitation/coprecipitation reactions, land use and climate (Fernandez et al. 2008; Tyszka et al. 2016; Lee et al. 2020). Cadmium, Pb, Sb and Zn move down through soil solution both in dissolved forms as free ions and ionic and non-ionic complexes, and in particulate forms adsorbed by colloids (e.g. humic substances, Fe–Mn oxyhydroxides and clay minerals), as well as included as main or trace constituents in smelter-derived fine and ultrafine mineral particles (Citeau et al. 2003; van Oort et al. 2006; Gelly et al. 2019). Studies on vertical movement in soil profiles showed that Pb and Sb were less mobile than Cd and Zn, which were predominantly in dissolved forms in soil solution (Denaix et al. 2001; Clemente et al. 2008). Nevertheless, the downward migration of Pb in soil may be quite fast from 0.3 to 1.36 cm/year (Ettler et al. 2004, 2011; Prapaipong et al. 2008; Lee et al. 2020). Since the Zvečan smelter started working in 1939, these vertical movement rates sustain the depth of Pb contamination in soils of this study, which normally extended down to 100 cm.

The second category of PTEs included As, Cu and Tl: their concentrations in topsoil indicated that the upper part of soil profiles was uncontaminated to moderately contaminated (Fig. 3). Soil profiles SP3, SP4 and SP5 were the only exception as they showed strong to very strong As contamination in topsoil. Based on the contamination level of these PTEs in topsoil, two groups of soil profiles were distinguished: Group 1, soil profiles with topsoil uncontaminated by As, Cu and Tl ($\text{PI} < 1$); Group 2, soil profiles with topsoil affected by low to moderate contamination by Cu and Tl ($1 < \text{PI} < 3$) and low to very strong contamination by As ($1 > \text{PI} > 5$).

In soil profiles of Group 1, the natural concentrations of As, Cu and Tl decreased slightly in the upper 40 cm or had a uniform distribution with depth (Fig. 3). In contaminated soil profiles of Group 2, As and Cu showed a decrease in concentration with depth and reached geogenic contents at depths between 30 and 90 cm and 20 and 60 cm, respectively (Fig. 3). A rapid decrease in As concentrations occurred in the upper 50 cm of strongly to very strongly contaminated soil profiles SP3, SP4 and SP5. Below 50 cm, As concentrations were uniform and slightly higher than the contamination threshold or within the geochemical background. As a

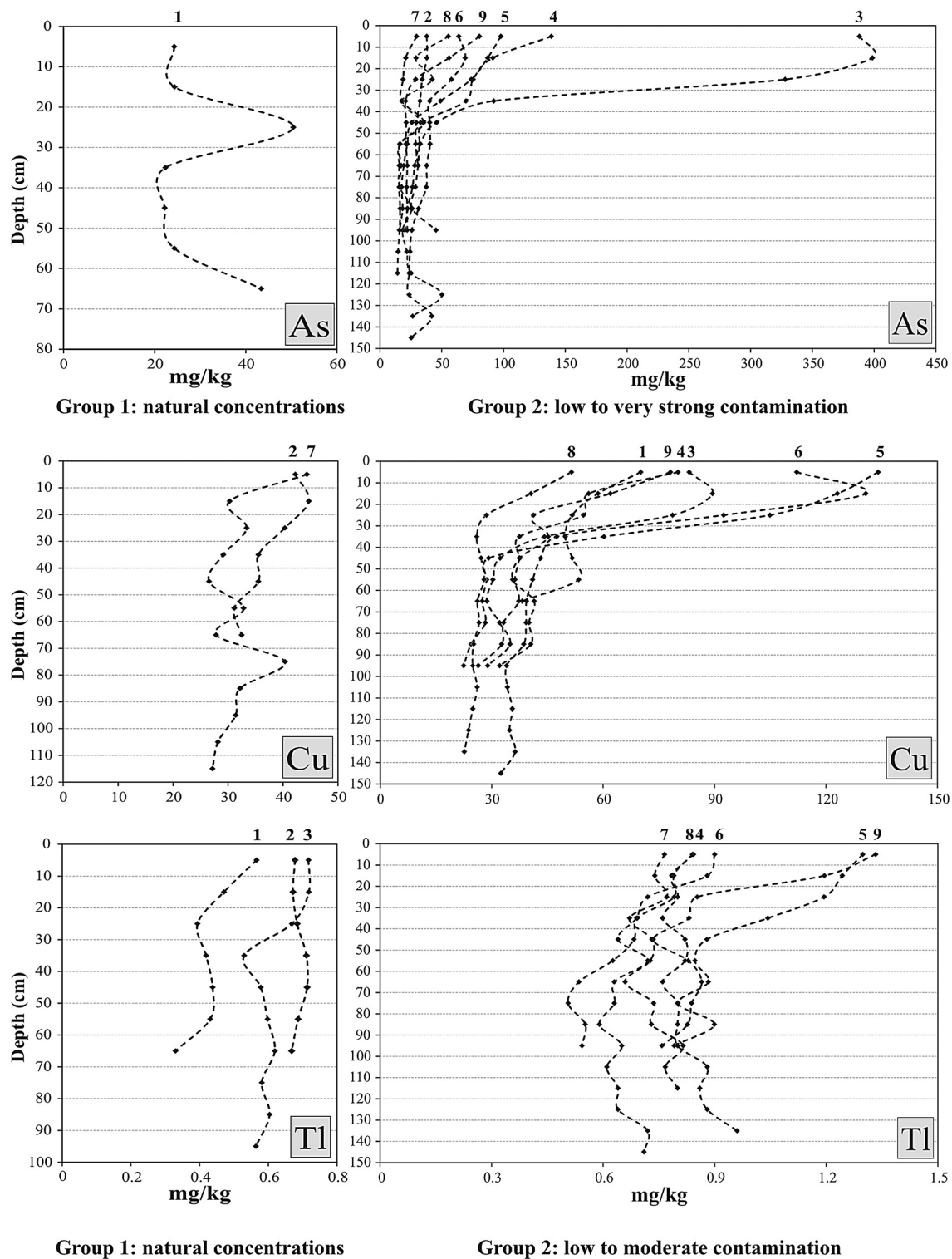


Fig. 3 Vertical distribution of As, Cu and Tl concentrations in soil profiles (soil profile identification is at the top of each graph)

rule, Tl concentrations declined in the upper 20–40 cm of soil profiles of Group 2 and were slightly above the contamination threshold in the whole thickness of soil profiles SP5, SP7, SP8 and SP9.

The vertical distribution of As, Cu and Tl in soils of this study was similar to that found in soil profiles of areas contaminated by smelter emissions. In particular, the pattern of Cu concentrations in the soil profiles was comparable with

the results of Brewer et al. (2016) in soils of the Kosovska Mitrovica area down to a depth of 50 cm. Ettler et al. (2014) showed that Cu accumulated, mostly bound to organic matter, in the upper part of soil profiles near a Cu smelter in the northern sector of the Zambian Copperbelt. Similarly, Tl was enriched in the upper layer, especially in the organic horizon, of soil profiles from a Zn smelting site in southern Poland and its concentrations declined with depth (Vaněk et al. 2013). These findings suggest a role of insoluble organic matter in the retention and accumulation of Cu and Tl in surface soils. Nevertheless, migration of Tl down to the bottom of soil profiles was recognized by Vaněk et al. (2013), probably due also to element transport in particulate form adsorbed by colloids of clay minerals and Mn oxides.

The third category included the geogenic PTEs (Co, Cr, Ni and U): their concentrations in soils from profiles were constantly within the corresponding geochemical background.

In soil profiles SP1 and SP2 the anomalous natural concentrations of Co, Cr and Ni showed no significant variation with depth, while in the other profiles the vertical distribution pattern was variable. In fact, the normal natural concentrations of Co, Cr and Ni had both a homogenous distribution and an irregular variation in depth, as well as a slight increase down to depths of 40–70 cm. In soil profiles natural concentrations of U decreased down to 30–40 cm or were rather homogeneous with depth.

The surface and vertical distribution of PTEs considered to be soil contaminants in the Kosovska Mitrovica area (As, Cd, Cu, Pb, Sb, Tl and Zn) was also investigated in relation to the distance from the Zvečan smelter along the transects N and SE, focusing on topsoil (0–10 cm), the 50–60 cm layer and the bottom of the soil profile.

The highest concentrations of Pb (1003–4813 mg/kg) and Sb (13–54.9 mg/kg) were found in topsoil of profiles SP3, SP4, SP5 and SP6 up to about 5 km from the Zvečan smelter (Fig. 4). At greater distances from the metallurgical plant, Pb and Sb concentrations in topsoil progressively decreased toward north along the Ibar valley, whereas they were quite uniform toward south-east along the Sitnica valley. This distribution pattern of Pb and Sb in topsoil was the same at the 50–60 cm layer, whereas it was slight for Pb and absent for Sb in the bottom of soil profiles.

As shown in Fig. 4, the peak of Cd and Zn concentrations (23.6 and 3674 mg/kg, respectively) was recorded in the topsoil of profile SP6 near the Trepca industrial complex. This finding indicates that the industrial activities at the Trepca complex influenced the distribution of these PTEs in soils of the Kosovska Mitrovica area. Furthermore, the very high concentrations of Cd and Zn measured by Brewer et al. (2016) in the waste piles of the Trepca industrial complex (especially waste of the Zn electrolysis plant) suggest that dispersal of these materials by wind was likely the main

source of contamination. A marked decrease in Cd and Zn concentrations was found in topsoil of profiles SP7 and SP5, located about 2 km south-east and 5 km north-west of the Trepca industrial complex (7.5 and 10.7 mg/kg for Cd; 1317 and 846 mg/kg for Zn). At greater distances from the industrial plants, the contents of these PTEs declined further, reaching concentrations below 1.5 mg/kg for Cd and 300 mg/kg for Zn in topsoil of profiles at the limit of the transects N and SE. Conversely, Cd and Zn contents were rather uniform at the 50–60 cm layer and the bottom of all soil profiles, though slightly higher concentrations were measured in soil profile SP6.

Similarly to Pb and Sb, the highest concentrations of Cu and Tl (80.2–134 mg/kg and 0.84–1.3 mg/kg, respectively) were recorded in topsoil of profiles within 5 km of the Zvečan smelter (Fig. 4). At the 50–60 cm layer and the bottom of the soil profiles, Cu and Tl did not show any variation trend in relation to distance from the contamination sources.

In line with the spatial distribution in surface soils (0–5 cm) of the Kosovska Mitrovica area (Stafilov et al. 2010b), As showed the highest concentration (388 mg/kg) in topsoil of profile SP3 from the Ibar valley, about 4 km north of the Zvečan smelter (Fig. 4). Arsenic concentrations decreased sharply north and south of this site and were higher in topsoil of profiles from the Sitnica valley (29.6–80.6 mg/kg). Unlike in topsoil, As contents were quite uniform in the 50–60 cm layer (16.4–40.6 mg/kg) and at the bottom (14.2–45.4 mg/kg) of soil profiles along the transects N and SE.

Level and extent of contamination by potentially toxic elements

The upper part of soil profiles showed very strong contamination by Pb and Sb, except profiles SP1 and SP2 located 13 and 11.5 km north of the Zvečan smelter. The soil thickness most contaminated by Pb (PIs = 5.2–81.6) and Sb (PIs = 5.1–38.4) was found up to depths between 30 and 60 cm in soil profiles within 5 km north and south-east of the metallurgical plant (SP3, SP4, SP5, SP6), and between 10 and 20 cm in soil profiles 6 to 11 km south-east of this contamination source (SP7, SP8, SP9). Moreover, PI values suggest that Pb and Sb contamination: i) decreased progressively with depth in all soil profiles; ii) involved the whole thickness of soil profiles closer to the Zvečan smelter (SP2, SP3, SP4, SP5, SP6), where the bottom soil showed low to moderate contamination; iii) reached its highest level in soil profile SP5 about 1 km from the metallurgical plant.

Most soil profiles showed very strong contamination by Cd (PIs = 5.3–38.1) and Zn (PIs = 5.4–32.8) down to depths of 20–40 cm and 10–50 cm, respectively. Cd and Zn contamination peaked in the soil profile closest the Trepca industrial complex (SP6) and decreased with distance from

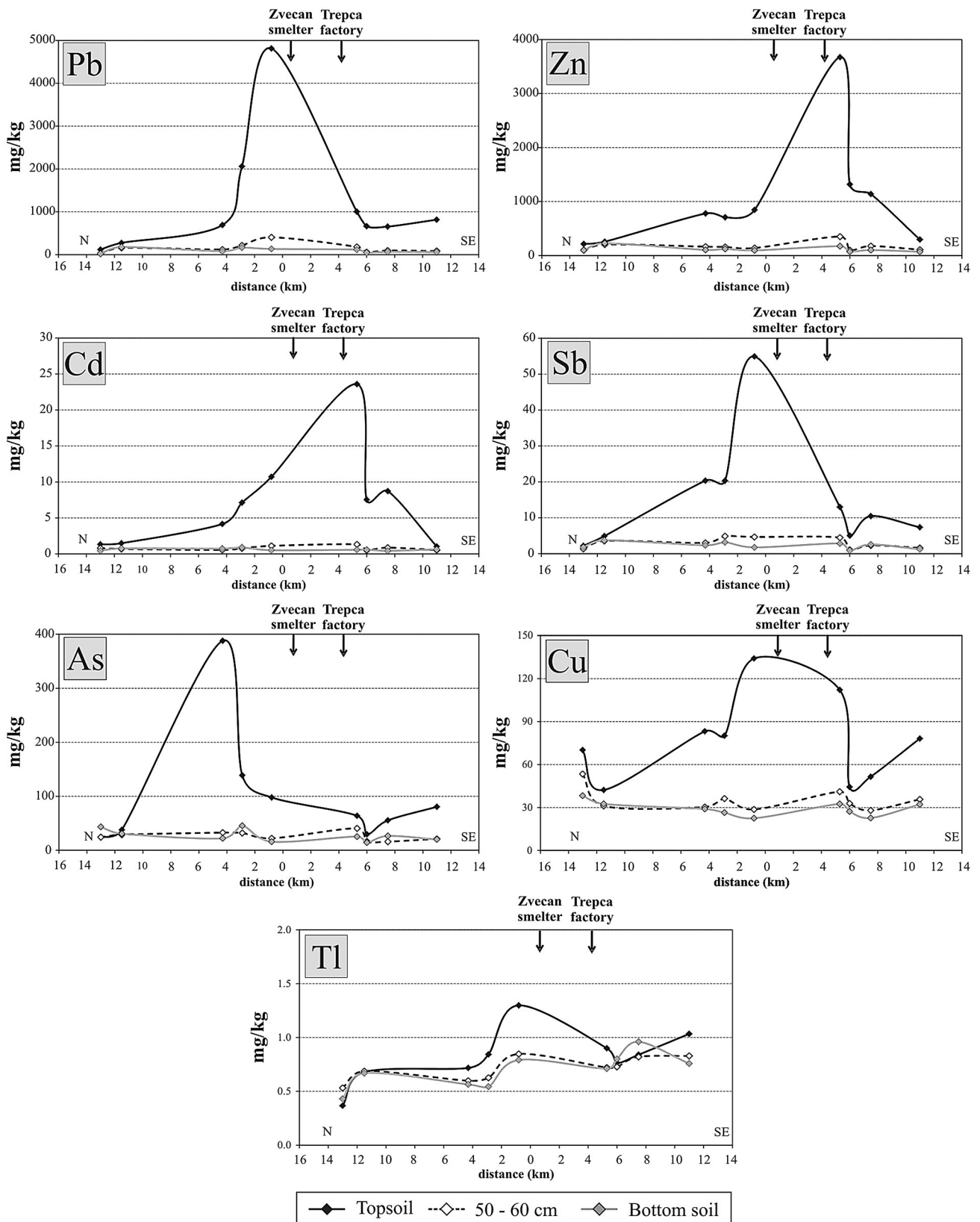


Fig. 4 Surface and vertical distribution of As, Cd, Cu, Pb, Sb, Tl and Zn concentrations in relation to distance from the Zvecan smelter along the transects N and SE

this site. Low to moderate contamination characterized the upper part of soil profiles most distant from the metallurgical and industrial plants (SP1, SP2, SP9). In all soil profiles Cd and Zn contamination declined with depth, usually reaching depths of 40–90 cm and 30–70 cm, respectively.

Arsenic contamination was found in soil profiles down to a depth of 90 cm and was low to moderate ($PI < 3$), except in profiles SP3, SP4 and SP5 in which strong to very strong enrichments ($PIs = 3.3–15$) were found up to depths between 20 and 40 cm.

Low to moderate Cu contamination was recorded in the first 40 cm of soil profiles within 5 km of the Zvečan smelter. Low Tl enrichment was detected in soil profiles near the metallurgical plant (SP4, SP5) and industrial site (SP6, SP7, SP8) as well as close to the town of Vucitrn (SP9).

Level and extent of contamination by PTEs in the study area suggest that Cd, Pb, Sb and Zn were the primary soil contaminants, while As, Cu and Tl were secondary contaminants. The main sources of contamination were the Zvečan smelter for Pb, Sb, As, Cu and Tl, and the Trepça industrial complex for Cd and Zn.

The above-mentioned relationships between PTEs were confirmed by the results of compositional principal component analysis (PCA) and Q-mode cluster analysis (CA). As shown in Fig. 5, PCA biplot and CA dendrogram split PTEs in three groups matching the subdivision in primary (Cd, Pb, Sb, Zn) and secondary (As, Cu, Tl) soil contaminants and geogenic elements (Co, Cr, Ni). Furthermore, the associations between the primary soil contaminants in the CA

dendrogram support that the prevalent source of contamination is different for Pb–Sb (Zvečan smelter) and Cd–Zn (Trepça industrial complex).

Conclusions

The geochemical background and contamination threshold of potentially toxic elements (PTEs) such as As, Cd, Co, Cr, Cu, Ni, Pb, Sb, Tl, U and Zn in soils of a metallurgical and industrial area in Kosovo were determined by exploratory data analysis of their concentrations in top-to-bottom soil samples from profiles. The contamination threshold was used as reference value to quantify the anthropogenic enrichment of PTEs in soil and to define the surface and vertical level and extent of soil contamination.

Cadmium, Pb, Sb and Zn were the primary soil contaminants as these PTEs showed the highest levels and widest extent of contamination, while As, Cu and Tl were secondary contaminants as their contamination levels were generally low to moderate. The main sources of soil contaminants were the Zvečan smelter for Pb, Sb, As, Cu and Tl, and the Trepça industrial complex for Cd and Zn.

Lead and Sb showed the highest levels of contamination in the upper part (between 30 and 60 cm) of soil profiles within 5 km north and south-east of the Zvečan smelter. Contamination by these PTEs decreased with depth in all soil profiles and affected the whole thickness of soils closer to the metallurgical plant.

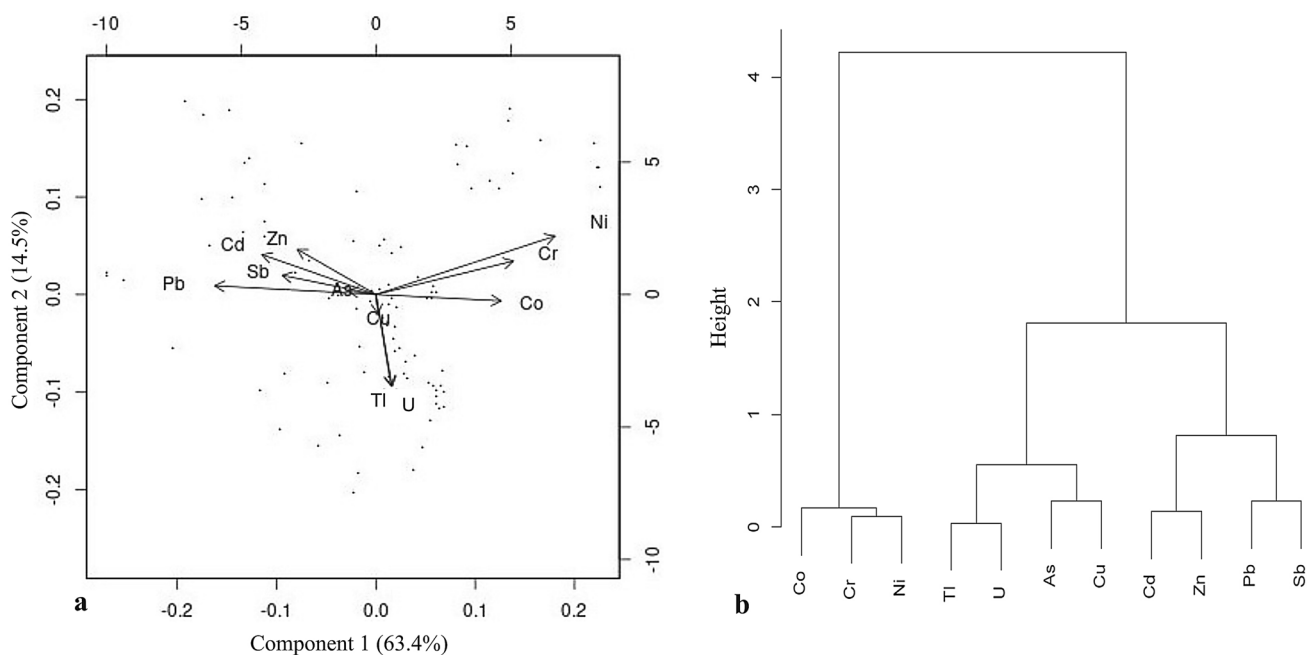


Fig. 5 Grouping of the potentially toxic elements (PTEs) by compositional multivariate statistical analysis: **a** principal component analysis (PCA) biplot; **b** Q-mode cluster analysis (CA) dendrogram

Contamination by Cd and Zn declined with distance from the Trepca industrial complex and decreased with depth, usually extending down to depths of 40–90 cm and 30–70 cm, respectively.

Among the PTEs analysed, Co, Cr, Ni and U were geogenic as their concentrations in soil were constantly within the corresponding local geochemical background. Anomalous natural concentrations of Co, Cr and Ni were found in soils from the northern part of the study area, where the geology consists mainly of ultrabasic and basic magmatic rocks.

The results of this study highlight that exploration of the top-to-bottom distribution of PTEs in soil profiles is an effective geochemical approach to assess their geochemical background in soil of contaminated areas.

Authors' contributions GP: conceptualization, formal analysis, supervision, writing—original draft, writing—review & editing. LADL: investigation, formal analysis, writing—original draft. FN: investigation, formal analysis, writing—original draft. All authors read and approved the final manuscript.

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Code availability Not applicable.

Availability of data and materials The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest The authors declare that they have no conflicts of interest and competing interests.

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