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Contents of potentially toxic elements in residual soils of a long-term mining region: a key study from Central and Western Serbia

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ABSTRACT

Regional geochemical research of residual soil was conducted in an area of about 20,000 km^2 in the region of Central and Western Serbia. This region has six metallogenetic zones where mining has been documented since ancient times. We study the contents, spatial pattern and natural background of potentially toxic elements (PTEs) of this mining province, to establish the geochemical background variation in the residual soil. The natural (geogenic) contents of PTEs were investigated in the top and bottom residual soil samples. Based on 108 geochemical data, the limits of natural background values (mg·kg-1) were determined by the integral method: As (38.5), Cd (0.5), Co (36.3), Cu (51.9), Cr (170.1), Hg (0.21), Mn (1974), Mo (0.9), Ni (215.2), Pb (61.7), Sb (2.4), V (84.4) and Zn (116.6). In the horizontal concentration patterns, four groups of PTEs with similar spatial distributions were identified: (As, Pb, Zn); (Cd, Hg, Mo, Sb); (Co, Cr, Ni) and (Cu, Mn, V). Correlation analysis (CA) distinguishes correlations between As-Sb, Co-Cr-Ni, and Cr-Ni. Principle component analysis indicates five different element groups: (Ni, Co, Cr, Mn); (As, Sb, Mo); (Pb, Zn); (Cu, Cd) and (Hg). Our data show that anomalous concentrations of As, Cr, Hg, Ni, Pb, Sb and Mn are geogenic, whereas higher contents of As, Hg, Pb, Sb and Zn in several locations are of a mixed geogenic and anthropogenic origin. Finally, anomalous concentrations of Pb and Zn, when detected outside the area where the ore deposits occur, are purely anthropogenic.

Keywords: spatial pattern; potentially toxic elements; residual soil; natural background; cross-correlation; risk assessment.

INTRODUCTION

By definition, residual soil is formed *in situ* above the geological substrate, as a result of its weathering (Darnley, 1995; Hillel, 2008). The geochemistry of residual soil is close to the parent material and may correspond to the geochemical baseline that defines the natural composition and the present state of the surface environment, providing a base data against which any changes can be measured (Darnley, 1997). From a geochemical and geoecological point of view, inorganic components of residual soil are the essential factor in determining the extent to which natural processes affect its chemical composition, especially in terms of potentially toxic elements (PTEs) such as As, Hg, Cd, Co, Cu, Cr, Mn, Mo, Ni, Pb, Sb, V and Zn. Therefore, the knowledge of local geology and the natural background of PTEs are of paramount significance when we aim to identify sources of human pollution in urban and rural areas, control PTEs distribution and assess human health risks (Argyraki et al., 2014; Urrutia-Goyes et al., 2017).

Residual soil predominantly consists of particles of decayed rocks and their minerals and therefore it is chemically most similar to lithologies on which it is formed. Its origin represents a complex interplay between lithosphere, hydrosphere, atmosphere and biosphere, aided by solar energy (e.g. Kabata-Pendias and Pendias, 1984). Among numerous soil pollutants of special importance is the status of As, Hg, Cd, Co, Cu, Cr, Mn, Mo, Ni, Pb, Sb, V and Zn in the soil, which are potentially toxic but also some of them are also bio-essential. They can be transferred to other ecosystems, such as groundwater or crops, and consequently, affect human health. Their variation is a net effect of the natural processes related to the weathering of the underlying basement rocks and the accumulations resulting from anthropogenic factors including industry and agriculture activities.

As a result of its specific geological setting, Balkans has a complex geological composition and a tremendous metal endowment being situated in a major suture zone of the Alpine- Himalayan orogenic belt. The Serbo-Macedonian Metallogenetic Province (SMMP) of the central Balkan Peninsula represents a main Pb-Zn-dominated belt of the large-scale Alpine-Balkan-Carpathian-Dinaride geodynamic-metallogenetic system (e.g., Janković, 1997; Heinrich and Neubauer, 2002) and may be interpreted as the northwestern part of the Oligocene to Miocene Serbo-Macedonian-Rhodope metallogenetic system (e.g., Neubauer, 2002). The SMMP is neighbored to the east by a Cu-dominated Carpatho-Balkan Metallogenetic Province (CBMP) (Antonijević and Mijatović, 2014). Both belts differ not only regarding the dominant metal inventory (Berza et al., 1998; Serban, 2020) but also in terms of the petrogenetic, geochronological and geodynamic character of spatially related magmatism. Given such geological and metallogenic variability, the raw-material industry has traditionally produced Pb, Zn, Fe, Cu, Ag, Au, Sb, Sn and Al, whereas, in the last decade, several new ground-breaking discoveries occurred and some of them are the ores that represent the strategic resources of the twenty-first century, like boron, lithium and rare earth elements, promoting this region a Europe-wide hotspot in raw materials. However, in Serbia geochemical mapping of soils are scarce, and only recently the Geological Survey of Serbia has executed a few projects (Cvetković et al., 2019) mostly in the central and western parts of the country.

The present study is based on a dataset obtained during a soil geochemical survey of a large area of Central and Western Serbia carried out by the Geological Survey of Serbia (Figure 1). This is the area of choice because it covers parts of two continental terrains (Dinaridic Belt and its metamorphic margin, and the Serbian-Macedonian Mass that represents the margin of the European continent) and the Vardar Zone suture in-between (Cvetković et al., 2016; Spahić and Gaudenyi, 2019). Moreover, it encompasses the Serbo-Macedonian Metallogenetic Province (SMMP) of the central Balkan Peninsula (Janković, 1990) and the area that has experienced an accelerated expansion of human occupation with profound effects on land use and the environment. This study represents the first comprehensive geochemical research on the residual soil in the Balkans. Our idea is that the knowledge of the natural and current background levels of the studied PTEs in the geologically complex area characterized by ancient and modern mining activities is vital for any new research in similar areas. These fundamental findings on the residual soil's geochemical composition will facilitate a more accurate estimation of anthropogenic environmental impact and the degree of pollution in the future.

The objectives of this study are, as follows:

1) to determine concentrations and regional natural backgrounds of the following PTEs: As, Cd, Co, Cu, Cr, Hg, Mn, Mo, Ni, Pb, Sb, V, and Zn in the residual soil in Central and Western Serbia;

2) to define their interrelationships and the spatial horizontal pattern in the top residual soil;

3) to assess the level and origin of contamination, as well as the degree of environmental impact, and identify areas with geochemical anomalies.

DESCRIPTION OF THE STUDY AREA
Location and general aspects of the study area

The studied area comprises parts of Central and Western Serbia and is also the central part of the Balkan Peninsula (Figure 1). Undulating terrain with flat 300-2,000 m a.s.l. plateaus is characterised by developed residual soil profiles. It comprises of many protected areas (Amidžić et al., 2007) with numerous protected plant and animal species. Geomorphologically speaking, this is predominantly a highland terrain, with several distinct landscapes located in the central and western parts of the studied region. The central part is dominated by landscapes around Rudnik Mtn., the Gledić Mtns, Jastrebac Mtn., Goč Mtn., Željin Mtn. and Kopaonik Mtn. The western part of the studied area is made up of the Radovljica-Raška Mtns. and the Podrinje-Valjevo Mtns. (Jovičić, 2009). The area is characterised by a temperate continental climate, with more or less pronounced local characteristics. Airflow is largely due to orography. Northwest and southeast winds prevail (Figure 1). In the mountainous regions, the most frequent are southwestern winds (Ducić and Radovanović, 2005). Regional industrial centres in the study area are Loznica, Valjevo, Lazarevac, Kragujevac, Jagodina, Užice, Čačak, Kraljevo, Novi Pazar, etc. The population in these cities is continually on the rise, with an average of around 100,000 people (Figure 1).
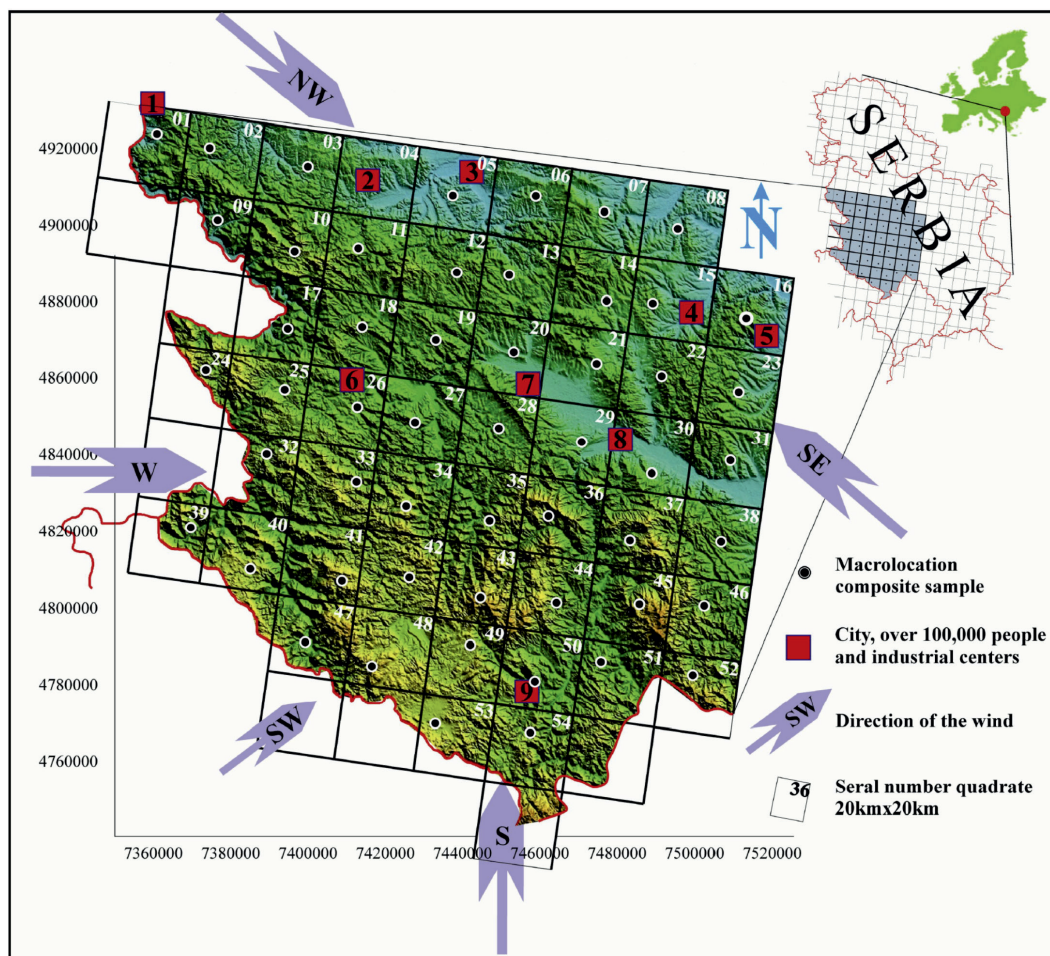
Figure 1. Geographical position of the study area; referential geochemical network (20x20 km^2); macro location composite samples; Wind directions; and industrial centres (1. Loznica 2. Valjevo Lazarevac 4. Kragujevac 5. Jagodina 6. Užice 7. Čačak 8. Kraljevo 9. Novi Pazar). Geographic base: Republic Geodetic Authority.

Geological setting and soil classification

In terms of geology, the territory of Serbia is one of the most complex parts of the Balkan Peninsula. The region occupies a major part of the Alpine-Himalayan collisional orogenic belt consisting of several juxtaposed Phanerozoic orogens. The geology of its central axis is dominated by the main mega-suture zone named the Vardar-Sava Zone (Cvetković et al., 2016; Karamata et al., 1997; Karamata et al., 2000; Pamić, 1983, 2002; Schmid et al., 2008), which mirrors the evolution of the Vardar branch(es) of the Neotethyan ocean, including its late Permian-Triassic opening, Jurassic intra-oceanic arc systems and ophiolite obduction and finally its closure in Cretaceous (for further discussion see Schmid et al., 2008 and Cvetković et al., 2016). During these geological events, several large and complex regional geological units were formed. They differ in terms of both the geological structure and geotectonic position. The inset of

Figure 2 shows all major geotectonic units of the Balkan Peninsula according to Karamata et al. (1997, 2000), comprising the Pannonian Basin (a) in the north, the Internal Dinarides (b) in the west, the Vardar Zone (c) in central Serbia, the Serbian-Macedonian Mass (d), and the western Carpatho-Balkanides Belt (e). The studied area covers to a large extent the Dinaridic Belt and the Vardar Zone, which are dominated by dismembered ophiolitic sequences considered to be derived from one (Schmid et al., 2008) or two (Karamata et al., 1997, 2000) Mesozoic oceanic domains.

Lithologicaly, the studied area consists of marine and freshwater sediments, deep and volcanic igneous rocks, as well as regional and contact metamorphic rocks. An intensely tectonized Paleozoic substrate is immediately noticeable, followed by a Triassic limestone platform and Jurassic ophiolite belt. Flysch sediment deposits occur in the upper Cretaceous. The youngest geological elements
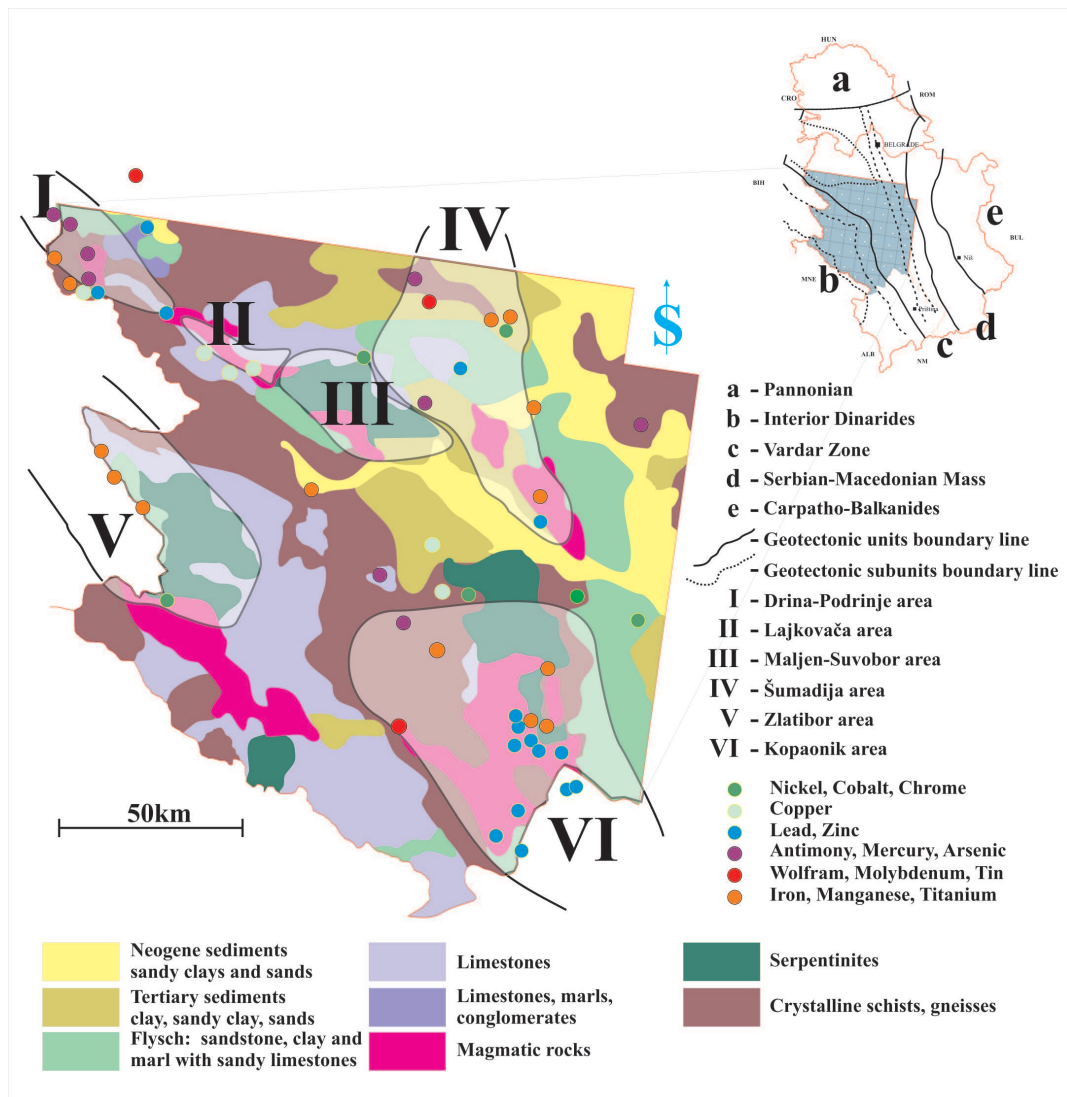
Figure 2. Geotectonic sketch with the geological composition (a- Pannonian basin, b- Interior Dinarides, c- Vardar zone, d- Serbian-Macedonian Mass, e- Carpato-Balcanides); metallogenic zones, with ore deposits and PTEs occurrence, in the study area (I- the Drina-Podrinje area, II- Lajkovac area, III- Maljen Mtn.-Suvobor Mtn. area, IV- Šumadija area, V- Zlatibor Mtn. area, VI- Kopaonik Mtn. area), (modified from Serbian geological map, scale 1:1,000,000).

were formed in continental "intramontane" lacustrine basins and the Tertiary and Quaternary Pannonian Sea sediments (Figure 2).

In terms of ore deposits and mineralization, there are six metallogenic regions in Central and Western Serbia (Figure 2): the Drina - Podrinje (I), Lajkovac (II), Maljen-Suvobor (III), Šumadija (IV), Zlatibor (V), and Kopaonik (VI) (Janković, 1990), with several metallic mineral deposits (Figure 2). The position of the largest mineral deposits and their tailings occurring in the studied area is also given together with the sampling position in Supplementary Dataset 1 (Google Earth).

PTEs are predominantly related to lead, zinc, antimony and copper deposits (Figure 2; Supplementary Dataset 1). Exploitation is mostly by underground mining, with large tailings ponds in the immediate vicinity, usually lacking proper conservation and ecological remediation measures.

According to the World Reference Base (WRB) classification, there are eighteen soil types in Serbia (Figure 3). Five classes of soils in the study area predominate: Dystic Cambisol-Dystic Leptosol; Vertisol; Eutric Cambisol (on limestone), Eutric Cambisol (on loess) and Planosols- Luvisols. Also, three more classes occur subordinately: Lithic Leptosol-Dystric Camboisol;
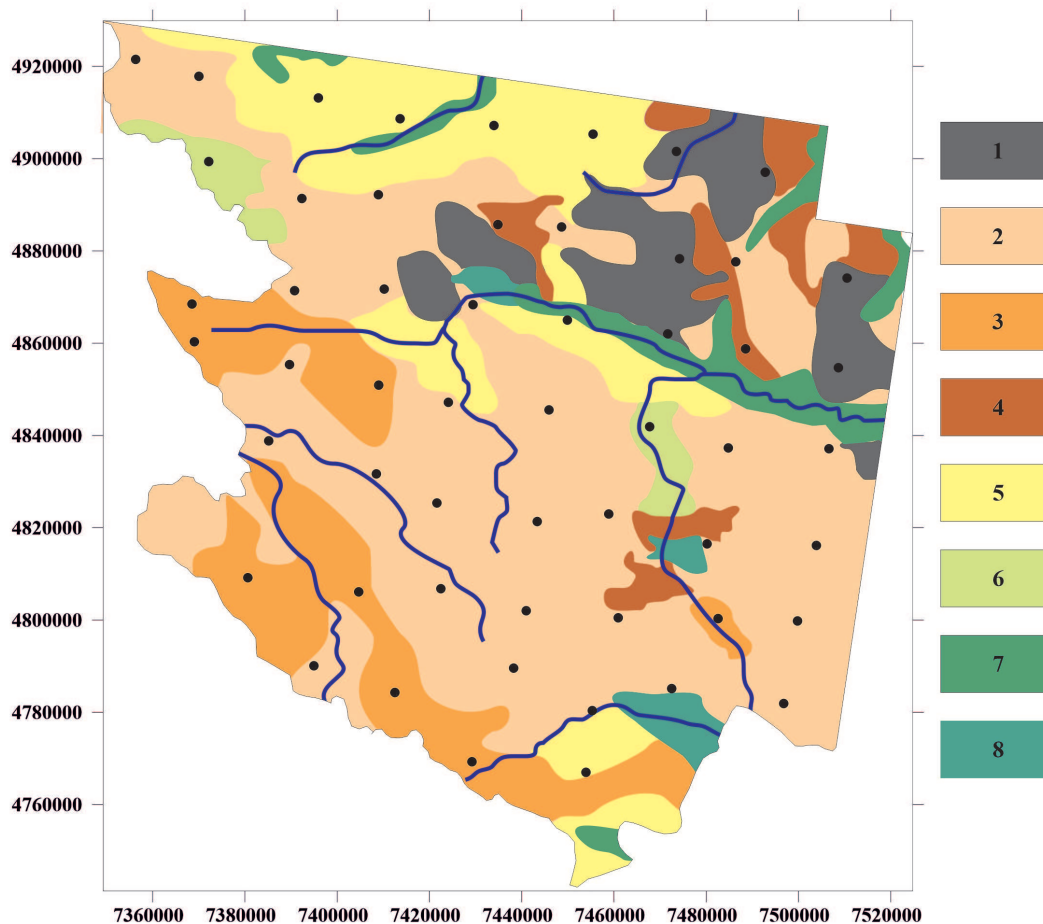
Figure 3. Soil map of the study area; 1. Vertisol; 2. Dystic Cambisol-Dystic Leptosol; 3. Eutric Cambisol (on limestone); 4. Eutric Cambisol (on loess); 5. Planosols - Luvisols; 6. Lithic Leptosol - Dystric Camboisol; 7. Arenosol and 8. Fluvisols, (modified from Serbian soil map, scale of 1:1,000,000, Protić et al., 2005).

Arenosol and Fluvisols (Protić et al., 2005). The reference group Cambisol occupies the largest part of the study area. These are soils with little or no visual differentiation of the profile. Under the surface, the horizon is usually brown to grey. It is strongly influenced by the mineralogy of the parent rock, the altitude and the content and type of organic matter.

MATERIAL AND METHODS
Sampling strategy and sample preparation

The bedrock of the studied area comprises 63% sedimentary, 22% magmatic and 15% metamorphic rocks. According to the age, Palaeozoic rocks prevail with 28%, followed by 22% of Triassic rocks, 11% of Jurassic formations, 15% of Cretaceous and 24% of Neogene rocks. The largest number of samples (43%) were taken from the elevations 500-1,000 m a.s.l., 33% come from

the elevations of up to 500 m a.s.l. and 24% from the elevation of 1,000-1,500 m a.s.l.

The most important segment of the sampling strategy was to collect the samples from the residual profiles that demonstrate *in-situ* development and no signs typical for the transported and/or contaminated soils. Moreover, the selected profiles are the least exposed to anthropogenic pollution. Particular care was taken to recognize well-developed residual soil profiles in the hills and the flat undisturbed plateaus (300-1,500 m a.s.l.) that were our preferred sampling sites. Inclined and steep surfaces were avoided due to the transport of particles by gravity. One of the decisive criteria for the residual character of the selected soil was finding a solid rock or partially decomposed rock material in the substrate, that belongs to the basement lithology. The sampling sites were far from populated and industrial areas, road and electric power

networks, as well as toxic waste dumps.

The position of the sampling points is presented in Supplementary Dataset 1 (Google Earth). The network, disposition and location of the sampling sites comply with international recommendations, the IGCP 259 and IGCP 360 international projects sampling instructions, and the FOREGS standards (Reimann et al., 2003, 2005; Salminen et al., 2005; De Vos et al., 2006). Systematic sampling is also in line with defined ISO 10381-1 and ISO 1038-2 protocols. For this study, the total area of Central and Western Serbia is approximately 20,000 km^2. A total of 108 samples were analyzed, 54 of which were composite top layer samples and 54 composite subsoil layer samples.

The basic geochemical reference network is analogous to the Lambert Equal Area geodetic coordinate network (Supplementary Dataset 2) and is based on the networks of geochemical atlases of Europe and Serbia (currently under preparation). The sampling methodology is presented in detail in the internal document of the Geological Institute of Serbia (Jovanović, 2010). Samples were taken by inert tools predominantly in the central part of the projected network square. The deviation tolerance due to the absence of a representative location does not exceed 20%. The resolution of the 20x20 km unit cell is 400 km^2 (Figure 1). Topsoil samples were taken from the top 25 cm, while subsoil soil samples came from 50-75 cm depth. After taking five separate samples, one from each angle of the 10×10m square and one from its centre (Subsite 1-5; Figure 4), two composite samples of 3 kg each are made on the spot (Figure 4; Supplementary Dataset 1).

Composite samples of the top and subsoil residual soils were sieved at 2 cm to remove the coarse fraction and were later homogenized in the laboratory, air-dried, quartered,

powdered, packed and archived (Jovanović et al., 2013). All tools were thoroughly cleaned between the samples to avoid cross-contamination. The samples prepared in this way were further analyzed. The quantities of samples were determined and their preparation was done according to ISO protocols and the European recommendations given by Darnley (1995), the FOREGS (Salminen et al., 2005) and GEMAS (Reimann, 2009) instructions.

Granulometry (Particle Size analyses)

Particle size analyses were performed either by sieving or the pipette method. Sieving was performed using 2, 1, 0.5, 0.25, 0.125, and 0.063 mm sieves; for the pipette method, a fraction finer than 0.063 mm size (at a temperature of 20 °C) was taken. For analysis of samples, defined pipetting time intervals were used to divide particles of 0.02, 0.01, 0.005, and 0.002 mm size; samples were classified according to Konta (1973). Percentual representation of grain size, average frequency, sorting and asymmetry is calculated (Supplementary Dataset 2), and the soil was classified using a three-component diagram (Figure 5).

Instruments and analyses

The soil samples were analyzed in 2013 for pH, electrical conductivity (EC), organic matter content (OM) and PTEs.

The pH was measured in a solution of soil and water with a ratio of 1:5, using a Lutron YK-2001 pH meter device. EC (electrical conductivity) was measured in a solution of soil and water with a ratio of 1:5 by a Hanna EC 214 conductivity meter. For each analysis, 10 g of each sample and 50 ml of distilled water were used. The results were determined 2 h after the preparation of the
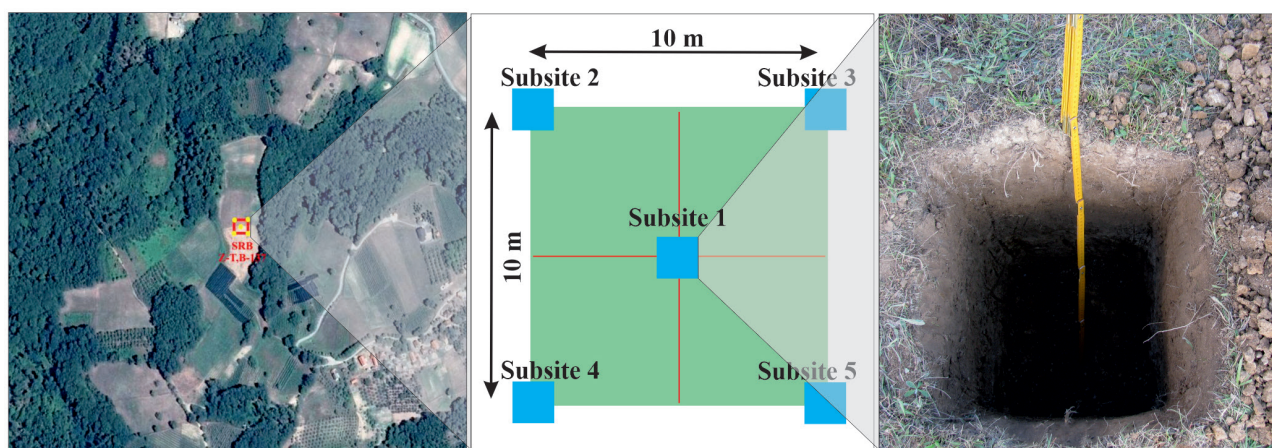

Figure 4. Selected representative location on the highest flat plateau, scheme by which a composite sample was formed and shape and profile of the individual sample (50x50x75cm).
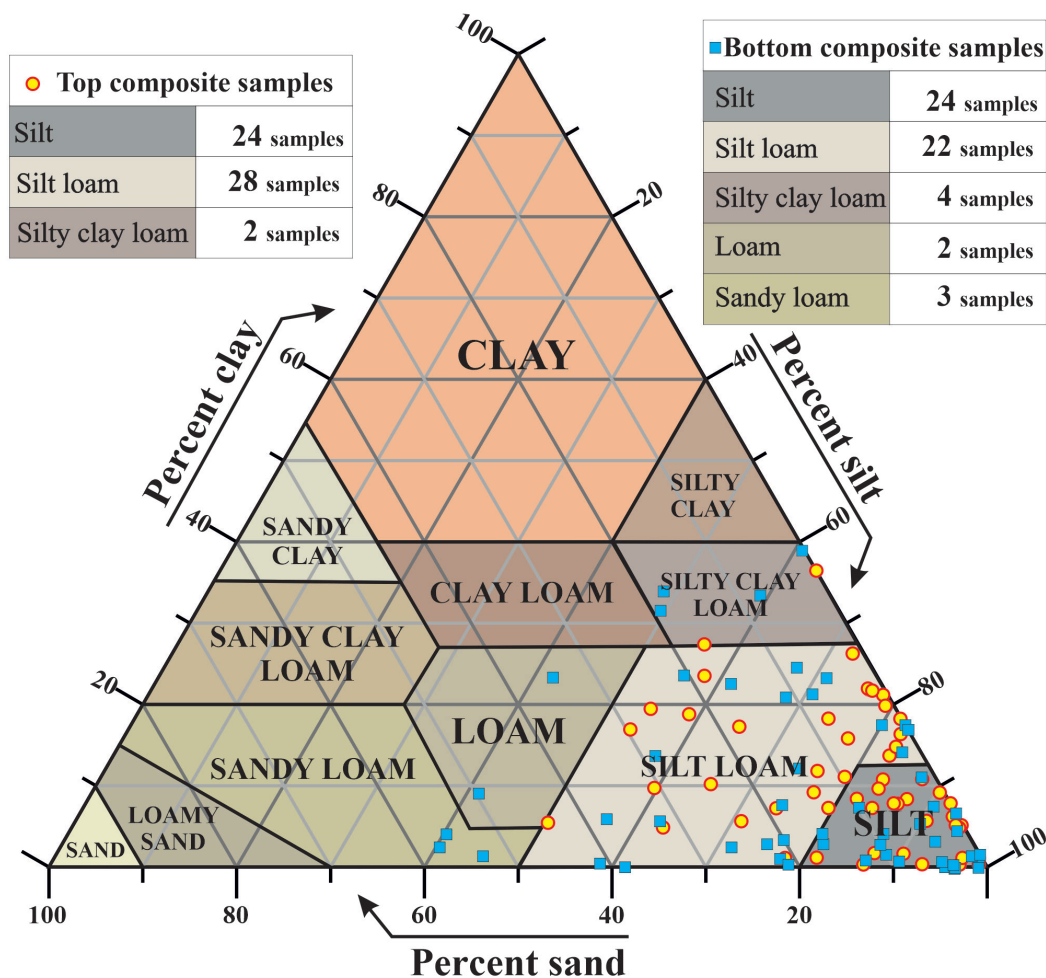
Figure 5. Classification of top and sub composite samples of residual soil; Soil Classification Plotted on USDA texture triangle.

suspension, and the mixture was intermittently stirred with a glass rod for homogenization. Calibration of the pH meter was carried out with buffer solutions of pH 4, 7, and 10 at the beginning of each set of analyses. The content of OM was determined by the Kotzmann method (Colombo et al., 1998) involving the oxidation of potassium-permanganate followed by titration with oxalic acid. The aforementioned analyses were performed in the laboratory of the Geological Survey of Serbia.

Concentrations of PTEs were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), at ACME (integrated by Bureau Veritas) Analytical Laboratories in Vancouver (Canada), accredited under ISO 9002. After the total dissolution (a mixture of $HClO_4$, HNO_3, HCl and HF concentrated acids), simultaneous multi-element analyses were performed. The solutions were analysed by mass spectrometry using a Perkin Elmer Elan 6000 or 9000 ICP-MS. The accuracy and analytical precision were determined using analyses of reference materials (ACME Analytical Laboratories Ltd Methods and Specifications for Analysis - STD SO-17, STD SO-18, STD DS8, STD DS9, certified in-house against 38 Certified Reference Materials, including USGS AGV-1, G-2, GSP-2 and W-2, all confirmed by correspondence with the laboratory personal) and duplicate samples in each analytical set. The results were within the 95% confidence limits of the recommended values given for this certified material. The relative standard deviation (RSD) was between 5 and 10%.

The results of the analyses of pH, EC, OM and PTEs in residual soils are given in Supplementary Dataset 2.

Data analysis and the applied software

The geostatistic analysis included the processing of the database of 108 representative samples of the residual soil. Each tested location was georeferenced using Garmin GPSMAP 64 manual GPS navigation. The

collected field data and laboratory results were entered in Ms Excel tables, forming a unique geochemical database of all individual locations (Supplementary Dataset 2 and 3). If the measured concentrations were below the detection limit, they were recorded in half the value of their detection limits, following the FOREGS-EGS Geochemical Baseline Mapping recommendations (Darnley, 1995; Salminen et al., 2005; De Vos et al., 2006). All the relevant parameters were statistically processed by specialized software (Grapher 13 and SPSS 23). The main parameters of descriptive statistics are shown in Table 2. The percentile calculation (5, 10, 25, 50, 75, 90, 95, 95%) is shown on the scale, with the spatial distribution pattern for each PTE (Figure 6). The correlation connectivity of PTEs was also verified through principle component analysis (PCA) and Cluster analysis (CA). PCA was used to reduce the size of the basic matrix of test results, and to account for the relationship between PTEs studied.

The spatial distribution has recently proved crucial for the geochemical interpretation of statistical parameters, as well as for the identification of polluted areas (Vong et al., 2006; Guo et al., 2012; Li et al., 2004; Chen et al., 2010; Lee et al., 2006). To show the most precise concentrations of PTEs at sampling points, a deterministic spatial interpolation technique was applied to each geochemical

map. The spatial component was recorded in the Gauss-Kruger projection and finalized in the Surfer 15 software. The spatial continuity of the data has been modelled using different variogram calculations by manually selecting the suitable variogram models and producing a predictive analysis using kriging. This approach is combined with varying the smoothing value of the georeferenced Grid Data framework and with setting the micro variance to zero and trying several values for the error variance to judge the effect, which altogether eliminated the bull's eye effect. Final graphic processing was done in CorelDRAW X3 and presented in a raster JPG format.

Environmental risk assessment geoaccumulation index (Igeo) and metal pollution index (MPI)

The analysis of the present concentrations of PTEs, their origin and the pollution of the residual soil of Central and Western Serbia was performed utilizing the geoaccumulation index (Igeo) (Müller, 1969) and the metal pollution index (MPI) (Usero et al., 1997).

Igeo was introduced by Müller (1969) and since then it has been widely applied to quantify the enrichment of PTEs in the soil and sediments (Gowd et al., 2010; Sengupta et al., 2010; Iqbal and Shah, 2011), and ultimately for the assessment of anthropogenic heavy
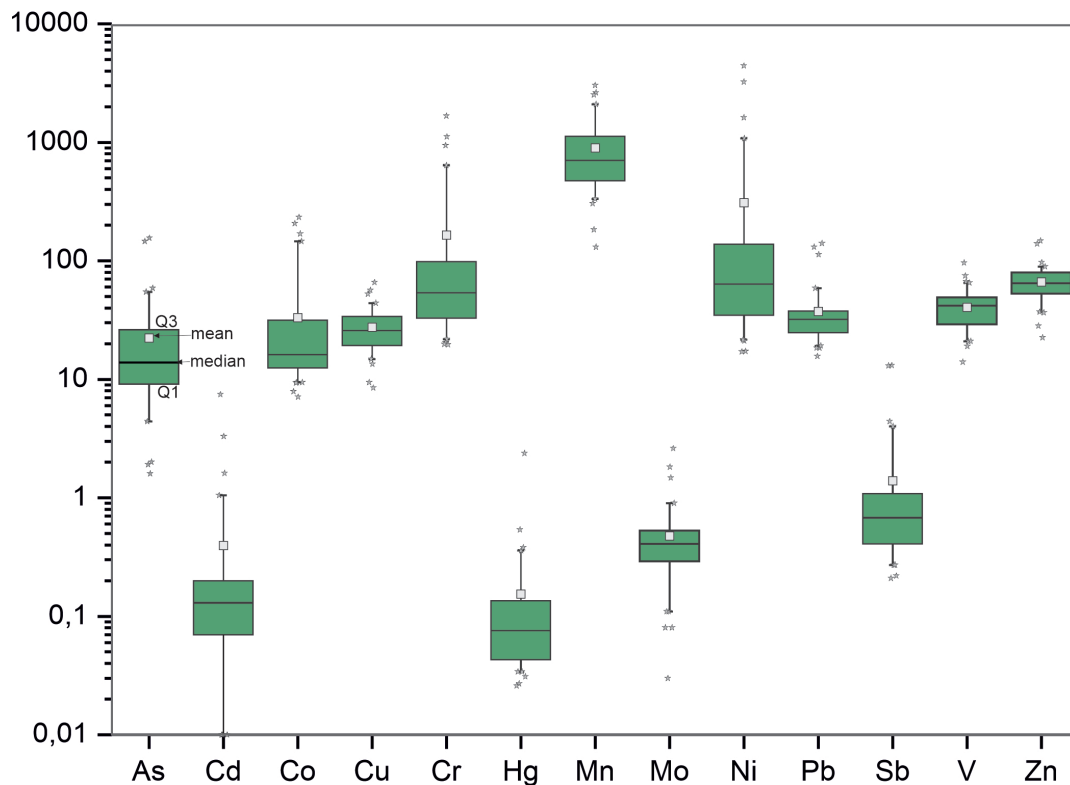

Figure 6. Grafik box plot of PTEs in the residual soil of Central and Western Serbia.

metal pollution. The geoaccumulation index is defined by the equation: $Igeo = log_2 C_n/1.5B_n$, where C_n denotes the concentration of PTEs in the composite sample at the sample-taking spot in the top residual soil. Constant 1.5 allows the correction of the background matrix, and analyse the natural content fluctuation of analysed chemical elements in the environment in general (Muller, 1969). In the original study, the parameter B_n denotes the heavy metal concentration used as a reference ("zero value") in uncontaminated (clay-rich) sediments (Müller, 1969). In our study, we calculated the parameter B_n, that is, the natural regional background distribution of the PTEs as the geochemical threshold values proposed by Reimann et al. (2018) (see below).

The geoaccumulation index for each metal defines seven different levels of soil contamination (Müller, 1969; Huu et al., 2010):

1) Igeo<0 unpolluted environments;
2) 0≤Igeo<1 unpolluted to moderately contaminated;
3) 1≤Igeo<2 moderately contaminated;
4) 2≤Igeo<3 moderately to highly contaminated;
5) 3≤Igoo<4 highly contaminated;
6) 4≤Igeo<5 highly to extremely contaminated, and
7) Igeo≥5 extremely contaminated environment.

Igeo values greater than 1 indicate the potential impact of anthropological pollution.

The metal pollution index (MPI) was calculated to estimate the total load of PTEs in individual locations, following the examples of Usero et al. (2000) and Adeniyi et al. (2008). MPI is expressed as the geometric mean value of all the studied elements (the formula: $MPI = (Cf_1 x Cf_2 x Cf_3 ... Cf_n) x 1/n$, where Cf equals the concentration of metal in a sample) and this index may signalize extremely high PTEs load of residual topsoil. The total heavy metal load of each location, after statistical processing and percentile calculation, was aimed at determining anomalous areas of possible ecological risks by the interpolation method.

RESULTS AND DISCUSSION
Characterization of residual soil (particle size, pH, EC and OM)

Particle size distribution of the soil is critical for its classification, but also for anticipation of its potential affinity for PTEs. For example, silt and clay fractions are the main carriers of natural and anthropogenic heavy metals (Banat et al., 2005). Our particle size analysis shows that the average grain size, characteristic of the entire test area, amounts to a minimum of 0.01 mm to a maximum of 0.24 mm, the mean value being 0.068 mm. The most frequent fraction of the tested particles is 0.014 mm and belongs to silt particles (Supplementary Dataset

2). We characterized the percentage values of fractions (Konta 1973) with the following grain components: sandy fraction: of 0.2-45.1% (mean value 9.6% for top soil), of 0.1-63.5% (mean value 10% for subsoil soil); silty fraction of 48.9-99% (mean value 80.1% for top soil), of 35.9-98.8% (mean value 74.9% for subsoil soil) and clayey fraction: of 0-36% (mean value 10.3% for top soil), of 0-57% (mean value 15.1% for subsoil soil) (Table 1). Using the fraction percentages of each sample, we classified the investigated top residual soil into three groups: silty loam soil (28 samples); silty soil (24 samples) silty clay loam soil (2 samples) (Figure 5). Similarly, subsoil residual soil samples clasify into five groups: loam soil (24 samples); silty loam soil (22 samples) silty clay loam soil (4 samples); sandy loam soil (3 samples) and loam soil (2 samples) (Figure 5).

Generally, there are no significant texture differences between the top and subsoil layers. The sand and clay content is slightly higher in the subsoil layer due to the proximity of the parent rock. As shown in Supplementary Dataset 2, most of the studied soils lie on the sedimentary bedrock. The predominantly low occurrence of clay fractions represents independent evidence for the residual character of the sampled soil profiles. At the first glance, all samples found in the silt field (about 44%), the loam field (about 46%) and the silty clay loam field (about 5%) have the highest affinity for PTEs (Figure 5). Still, our results of the particle size analyses do not correlate with PTEs concentrations. The grouping of the granulometric composition indicates a uniform degree of physicochemical weathering of the heterogeneous geological substrate.

For the studied samples of the topsoil, the pH ranges between 4.01 to 7.86 (Table 1). According to the classification recommended by the United States Department of Agriculture, the most common pH values of the studied soil samples belong to slightly acidic soils. Extremely acid soil has 7%, neutral soil about 6% and slightly alkaline soil about 4%. Subsoil in the studied area indicates a more alkaline composition. The moderately acid type (about 28%) is the most prevalent, followed by strongly acid, slightly acid and neutral soil types with 15% each.

Generally, pH is known to play a very important role in the accumulation, availability and mobility of individual PTEs (e.g. Adriano, 2001; Krishna and Govil, 2007; Cachada et al., 2013). It is a key factor in the dynamics of chemical reactions and governs the surface charges in soil minerals (Adams, 1984; Sato, 2003; Violante et al., 2010). Contamination of the soil with heavy metals results in its acidification and subsequently affects other soil properties (Yu et al., 2006). Our results demonstrate that only a very small proportion of the studied samples were in the group of strongly acidic and extremely alkaline soils. This fact,

PM

Table 1. Basic statistical parameters for particle size, pH, EC and OM in the upper residual soil (n=54) and the subsoil residual soil (n=54).

		Sand (%)	Silt (%)	Clay (%)	pH (H⁺)	EC (mS/m)	OM (%)
Top soil	Min	0.2	48.9	0.0	4.01	149	3.3
	Mean	9.6	80.1	10.3	5.55	273	7.8
	Median	6.2	82.5	8.5	5.48	282	7.2
	Max	45.1	99.0	36.0	7.86	363	11.8
	Sand.dev.	10.3	12.5	7.9	0.83	44	2.0
	Kurtosis	1.6	-0.1	0.9	0.76	0	-0.6
	Skewnes	1.4	-0.7	0.9	0.79	0	0.4
	25th percentile	1.4	74.0	5.0	4.99	241	6.1
	50th percentile	6.2	82.5	8.5	5.48	282	7.2
	75th percentile	14.7	88.6	16.1	6.13	306	9.8
Bottom soil	Min	0.1	35.9	0.0	4.36	167	3.8
	Mean	10.0	74.9	15.1	6.18	256	5.6
	Median	4.6	79.1	10.0	5.99	262	5.2
	Max	63.5	98.8	57.0	7.99	343	9.1
	Sand.dev.	12.2	18.3	15.6	0.95	40	1.4
	Kurtosis	6.0	-0.8	0.9	-0.80	0	1.0
	Skewnes	2.1	-0.6	1.3	0.32	0	1.4
	25th percentile	1.5	60.6	3.3	5.45	228	4.6
	50th percentile	4.6	79.1	10.0	5.99	262	5.2
	75th percentile	17.3	90.1	21.1	6.94	280	5.9
	Mean total	9.8	77.5	12.7	5.87	264	6.7
	Median total	5.9	81.1	9.0	5.71	269	6.0

together with the absence of the correlation between the pH values and the PTEs concentrations, implies that there is no measurable contamination of the studied soil samples, and indirectly confirms their residual nature.

The EC (electric conductivity) values are shown in Table 1 and range from min. 149 mS/cm to max. 363 mS/cm, medium 273 mS/cm for top residual soils, and for subsoil residual soils are min. 167 mS/cm to max. 343 mS/cm, medium 256 mS/m.

Soil OM (organic matter) is the organic component of the soil. OM affects the increased adsorption of PTEs in soil. During OM decomposition, individual PTEs can be effectively bound to the organic fraction. The aqueous phase of PTEs provides a mobile medium for chemical reactions and circulation through the soils (Yu et al., 2006; Violante et al., 2010). OM content in the studied top and subsoil residual soil samples ranges from 3.3 to 11.8% (mean 7.8%) and from 3.8 to 9.1%

(mean 5.6%), respectively (Table 1). According to the land-based classification of OM content (Blume et al., 2016), the residual soils of Central and Western Serbia belong to very humus soils. OM content is much lower in subsoil residual soil. OM does not correlate with the concentrations of PTEs. Considering that the OM content of the residual soil tested has a low value (about 7%), it is concluded that most PTEs are related to the inorganic soil fraction. The correlation coefficients between pH and OM indicate a negligible correlation (low value of the coefficient R) between pH and OM in the sampled horizons. A set of factors (other than OM and pH content), such as the presence of carbonate (as a buffer system), clay (type and quantity), ionic constituents in soil solution (Al^{3+}, Fe^{3+}) and vegetation (Tančić, 1994) could be the reason for such poor correlation, which we did not further discuss.

Descriptive statistical data and concentration comparison

Descriptive statistics on the concentration of heavy metals in the residual soil of the study area are given in Table 2, together with percentile contents for top residual soil. Based on the percentile values (5, 10, 25, 50, 75, 90, 95 and 98), a distribution map was made for each element (Figure 7). In addition, for comparison, Table 2 shows the mean and median values of PTEs on UCC, world, European and Croatian soils formed on a similar geological basement and geographically located relatively close to the study area.

The concentration ranges (mg·kg^{-1}) in topsoil were, as follows: As of 1.6 to 155 (average 22.3), Cd 0.02-7.5 (0.39), Co 7.1-234 (33.1), Cu 8.5-65.7 (27.5), Cr 19.6-

Table 2. Basic statistical parameters and comparative values of PTEs concentration (mg·kg^{-1}) in the top residual soil (n=54) and the sub residual soil (n=54) and regional natural background (n=108)

THIS STUDY		As	Cd	Co	Cu	Cr	Hg	Mn	Mo	Ni	Pb	Sb	V	Zn
Top oil	DL	0.1	0.01	0.1	0.01	0.5	0.005	1	0.01	0.1	0.01	0.02	2	0.1
	Min	1.6	0.01	7.1	8.49	19.6	0.03	131	0.03	17.1	1.39	0.06	12	27
	Mean	22.3	0.39	33.1	27.49	164.9	0.154	898	0.48	308.9	30.14	1.5	43	69.8
	Median	13.8	0.13	16.1	25.84	52.3	0.08	678	0.4	59.4	24.28	0.68	43	68.7
	Max	155.4	7.45	233.8	65.74	1674.8	2.36	3036	2.62	4411.8	143.5	17.2	80	182.6
5th percentile		2.48	0.01	9.31	13.71	20.66	0.03	309.80	0.09	21.20	9.33	0.18	15.80	38.84
10th percentile		4.76	0.02	10.43	15.99	23.89	0.03	405.60	0.14	25.70	12.15	0.21	21.90	42.49
25th percentile		9.10	0.06	12.53	19.35	32.90	0.04	476.00	0.29	34.80	16.50	0.45	33.00	54.70
50th percentile		13.75	0.12	16.05	25.84	52.30	0.08	678.00	0.41	59.35	24.28	0.68	43.00	68.70
75th percentile		26.30	0.21	31.50	34.03	98.10	0.14	1122.0	0.53	138.30	34.17	1.40	54.00	76.60
90th percentile		46.64	0.90	59.26	43.00	525.79	0.33	1660.6	0.65	698.98	45.96	2.38	65.10	92.31
95th percentile		57.84	1.50	164.22	50.86	881.68	0.38	2442.0	1.36	1512.9	98.41	4.45	75.00	99.50
98th percentile		150.01	5.04	217.85	60.24	1352.26	1.30	2798.8	2.16	3733.0	136.08	15.26	79.42	162.0
Bottom oil	Min	2.48	0.01	9.31	13.71	20.66	0.03	309.80	0.09	21.20	9.33	0.18	15.80	38.84
	Mean	4.76	0.02	10.43	15.99	23.89	0.03	405.60	0.14	25.70	12.15	0.21	21.90	42.49
	Median	9.10	0.06	12.53	19.35	32.90	0.04	476.00	0.29	34.80	16.50	0.45	33.00	54.70
	Max	13.75	0.12	16.05	25.84	52.30	0.08	678.00	0.41	59.35	24.28	0.68	43.00	68.70
BACKGROUND (Top soil + Bottom soil)														
25th percentile		8.9	0.1	12.5	17.5	31.0	0.0	552.3	0.3	31.5	20.5	0.4	30.0	53.8
50th percentile		12.9	0.2	15.6	24.3	47.0	0.1	752.0	0.4	42.1	28.2	0.7	42.0	66.9
75th percentile		20.8	0.3	22.0	31.3	86.6	0.1	1121.0	0.5	105.0	37.0	1.2	51.8	78.9
Q3+1.5(Q3-Q1)		38.5	0.5	36.3	51.9	170.1	0.209	1974.1	0.9	215.2	61.7	2.4	84.4	116.6
UCC*														
Mean		1.50	98	17	25	85	0.056	600	1.5	50	16	0.2	110	71
WORLD SOILS**														
Mean		4.7	1.1	6.9	14	42	0.1	418	1.8	18	25	0.62	60	62
EUROPEN SOILS***														
Median		7.03	0.145	7.78	13	60	0.037	650	0.62	18	22.6	0.60	60.4	52
CROATIA SOILS****														
Median		12	0.4	13	25.4	88.2	0.06	722	-	47.5	33	-	108	88

DL: detection limit

* Upper continental crust, from Taylor, S. R., and McLennan, S. M. (2001)

** World soil, from Kabata-Pendias and Pendias, (1999, 2001)

*** Europen soils, from Salminen, R., et al. (2005)

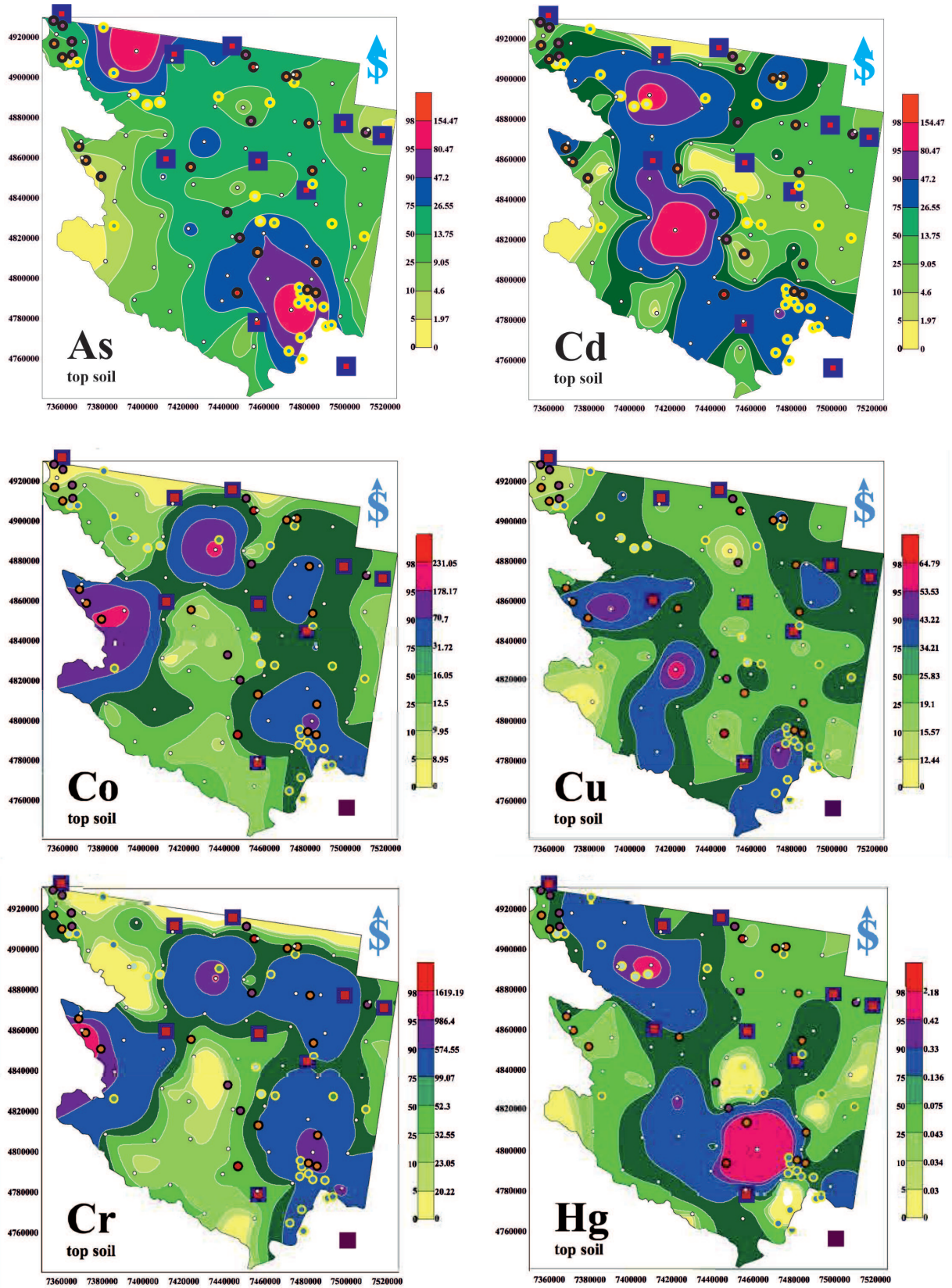**** Croatia soils, from Halamić, J., Miko, S., (2009)

Figure 7. Spatial pattern of PTEs (mg·kg^{-1}) in the top residual soil of Central and Western Serbia.
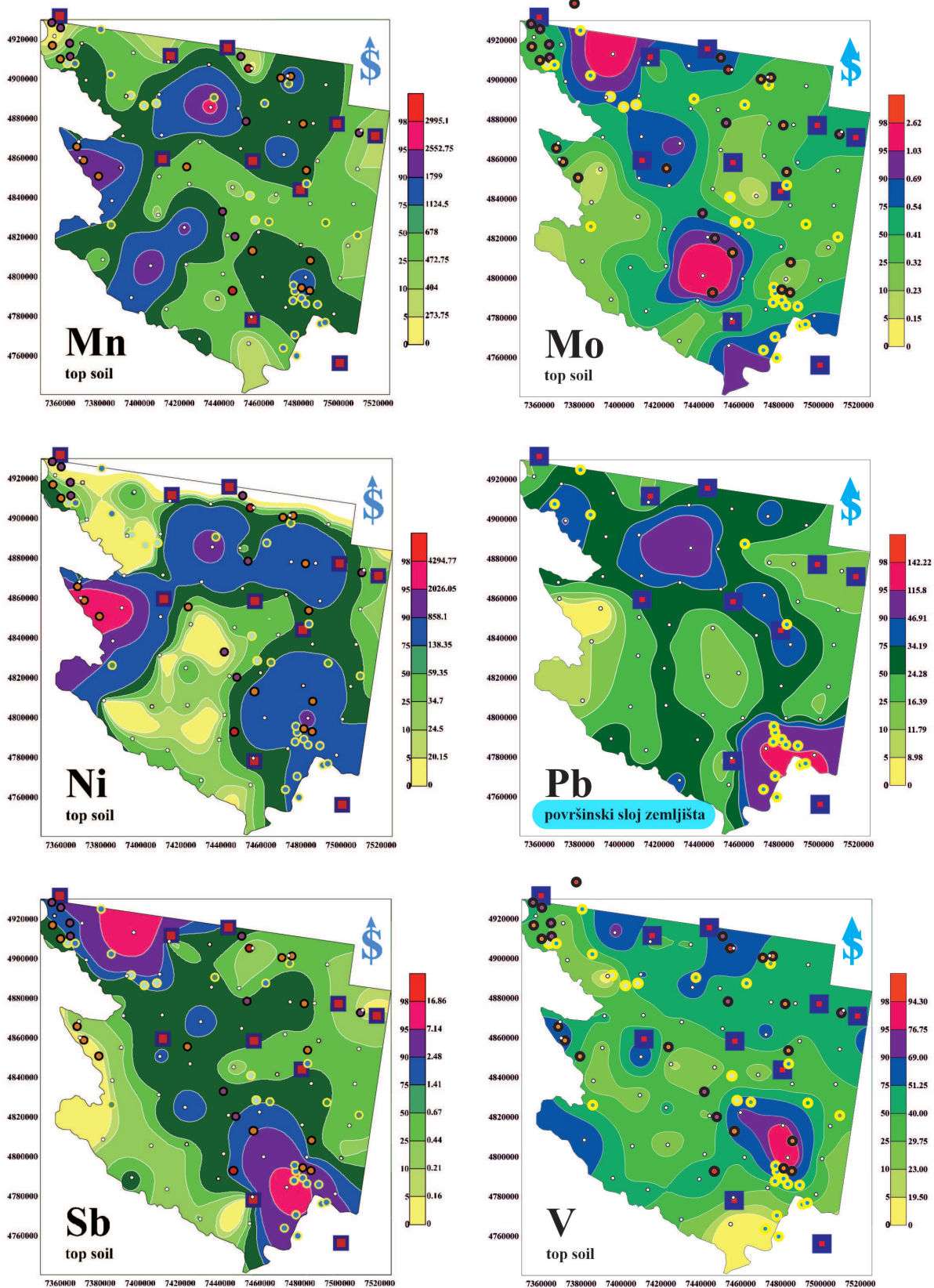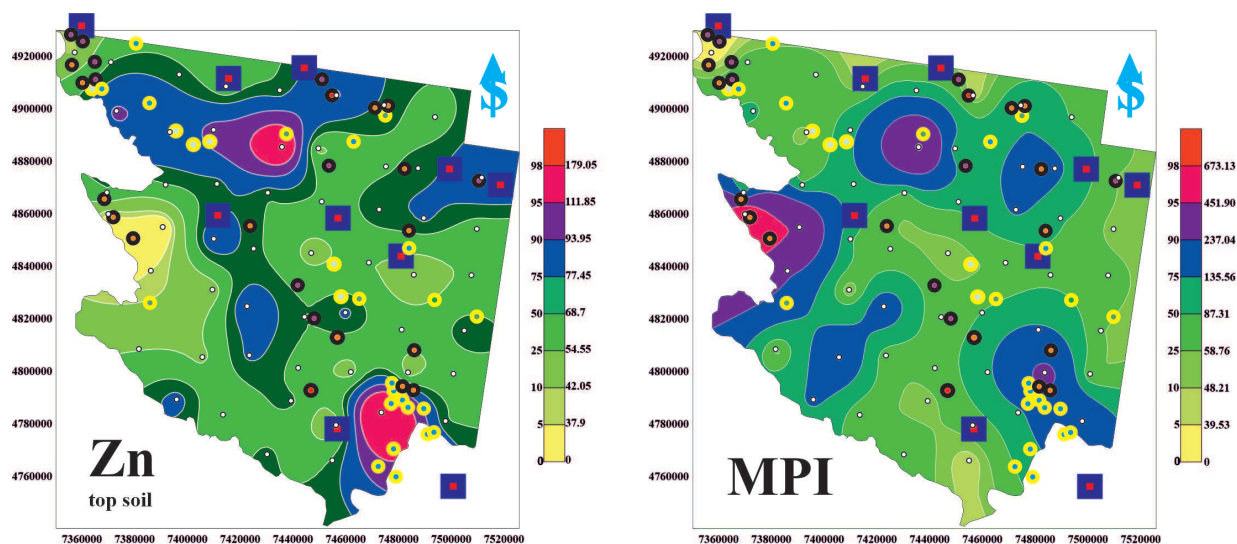
Figure 7. ... Continued

Figure 7. ... Continued

1675 (164.9), Hg 0.03-2.36
(0.15), Mn 131-3036 (898), Mo 0.16-2.6 (0.48), Ni 17.1-4412 (308.9), Pb 1.4-144 (30.1), Sb 0.06-17.2 (1.5), V 12.0-80 (69.8) and Zn 27-183 (43). For the subsoil residual layer, the concentration ranges were, as follows: As 1.7-114 (17.9), Cd 0.04-2.7 (0.35), Co 4.8-236 (25.3), Cu 5.5-167.1 (25.04), Cr 16.5-1735 (132.6), Hg 0.03-3.69 (0.17), Mn 1117-3129 (926), Mo 0.16-2.7 (0.51), Ni 13.2-2497 (188.8), Pb 15.6-141 (37.4), Sb 0.21-13.1 (1.4), V 14.0-96 (41) and Zn 23-147 (66.5) mg·kg^{-1}.

When looking at the average concentrations of PTEs in the top residual soil of Central and Western Serbia, the order from highest to lowest concentration is, as follows: Mn>Zn>Ni>Cr>V>Cu>Pb>Co>As>Sb>Mo>Cd>Hg.

The values of the coefficient of variation (CV=100SD/mean) have the sequence of Cd>Ni>Hg>Sb>Cr>Co>As>Pb>Mo>Mn>Cu>V>Zn. Median values of PTEs in the subsoil residual soil can be listed as follows: Mn>Zn>Cr>V>Ni>Pb>Cu>Co>As>Sb>Mo>Cd>Hg. The values of the variation coefficients have the following sequence: Hg>Ni>Cr>Sb>Co>Cd>As>Mo>Cu>Pb>Mn>V>Zn.

The mean and median values of particular elements are quite different (As, Co, Cr, Hg, Ni, Pb and Sb). The same can be said for Kurtosis and Skewness. The skewness coefficients of most PTE (e.g., As, Cd, Co, Cr, Hg, Ni, Sb) are well above zero, indicating the presence of the samples with high concentrations. These outliers can easily be identified in the Box-Plots reported in Figure 6. This high data heterogeneity can indicate the potential presence of pollution or proximity to mineralization.

Compared to the upper continental crust (Taylor and McLennan, 2001) (Table 2), Serbian soils are rich in As,

Sb, Ni, and Hg, while Cd, Mo and V are depleted. When compared to the world soil (Kabata-Pendias and Pendias, 2001), high contents of Ni, Co, As, and Sb are observed, while Mo, Cd and V are depleted. The increased contents of Ni, Co, Hg and As are observed as compared to residual soils in Europe as well (Salminen et al., 2005), while the European residual soils have lower concentrations of V, Cr, Mo and Cd when compared to the Serbian ones. Similarly, elevated median concentrations of Hg, Ni, As, and Cu can also be observed in the Croatian soils (Halamić and Miko, 2009), while they have lower concentrations of Cd and V. On the other hand, Serbian and Croatian soils show similar concentrations of Cr, Pb and Zn.

Natural regional background PTEs

In this section, it is explained how we define appropriate reference values for natural regional background PTEs. Our underlying assumption is that our samples represent uncontaminated soils, that is, weathering products with natural trace metal contents of geogenic origin. In principle, our approach is to integrate geochemical and statistical methods, similar to one applied in seminal environmental studies (Müller, 1969) and further developed in several more recent publications (Matschullat et al., 2000; Reimann and Garrett, 2005; Gałuszka, 2007; Gałuszka and Migaszewski, 2011; Desaules, 2012). Finally, our ultimate choice was to estimate the geochemical threshold values proposed by Reimann et al. (2018) as the natural regional background distribution of the PTEs (see below).

For the calculation of the ambient natural background of PTE distribution in the residual soil of Serbia, chemical analysis of the representative samples of residual soil was geostatistically processed using the boxplot method

(Figure 6). The boxplot diagram as originally proposed by Tukey (1977), typically divides geochemical data into four equal ranges of values based on the median, quartile 1, and quartile 3, also showing the anomalous values (outliers). Inside the boxplots of individual elements, the upper inner fence is calculated, which represents the limit above which individual isolated points (outliers) appear, according to the formula Q3+1,5*(Q3-Q1), where Q3 and Q1 represent the third and the first quarter (75th to 25th percentiles). This parameter is used as a threshold value in geochemical mapping to detect anomalous values of trace elements in a soil geochemical composition. The main advantage of this approach is to solely depends on the data distribution. As being considered one of the most reliable and powerful tools to calculate meaningful threshold values for any given data set (Reimann and Caritat, 2017), we choose it to estimate the natural background distribution of the PTEs in Western and Central Serbia.

In our calculation, a set of all 108 samples was treated including both the topsoils and the subsoils, and Figure 6 shows the boxplot of the top residual soil horizons for each element. The reasoning for the inclusion of both groups of samples is their general concordance in both in the variation and content of the PTE distribution (see descriptive statistics in Table 2), as also demonstrated in Supplementary Dataset 3. Outliers in the statistical calculation are not excluded from the total dataset. Figure 7 graphically shows the horizontal distribution in the top residual soil horizon for each element.

Large ranges of values of individual PTEs are primarily conditioned by the heterogeneity of the geological substrate (Figures 6 and 7). This assumption should be confirmed by future studies, where higher sampling resolution will be applied, especially in anomalous zones where the values are much higher than the natural background. The natural background values of PTEs in the residual soils from Central and Western Serbia are, as follows (mg·kg⁻¹): As (38.5), Cd (0.5), Co (36.3), Cu (51.9), Cr (170.1), Hg (0.21), Mn (1974), Mo (0.9), Ni (215.2), Pb (61.7), Sb (2.4), V (84.4), Zn (116.6) (Table 2).

Visualization of the spatial distribution of the PTE in the top residual soil of Central and Western Serbia

To visualize the geochemical distribution, the results of the chemical analysis were divided into eight percentile classes: 5th, 10th, and 25th (lower quartile), 50th (median), 75th (upper quartile), 90th, 95th and 98th. The interpolated maps of As, Cd, Co, Cu, Cr, Hg, Mn, Mo, Ni, Pb, Sb, V and Zn concentrations are shown in Figure 7. Each individually selected class of the map is displayed as a polygon of the appropriate colour.

Visualization of the spatial distribution of the analysed element concentrations and their comparison with the geological substrate and ore mineralization (Figure 2), facilitated the geochemical interpretation of statistical parameters. In general, possible anthropogenic influence from largely populated cities was also considered, primarily through the presence of particles transported by wind and rain (Figure 1). By visualization of geochemical maps, four element groups with similar spatial distribution were isolated: (Co, Cr, Ni), (Cd, Hg, Mo, Sb), (As, Pb, Zn) and (Cu, Mn, V).

i) Co, Cr and Ni show the most similar spatial distribution. The third quartile areas of these elements are almost identical. Concentrations within the limits of the percentile values of 75% to 90% are also very similar, with a slight deviation in Co concentration. The anomalous values of these elements are mostly observed in the metallogenic zones of Zlatibor Mtn., Šumadija and Kopaonik Mtn. The predominant geological substrate of residual soil in these anomalous areas is ultrabasic in composition (Figure 7 and Figure 2). The presence of Cr, Co and Ni in the residual soil can certainly be attributed to the bedrock disintegration. No elevated concentrations were apparently close to densely populated cities.

ii) A great similarity in the spatial distribution was observed for Cd, Hg, Mo and Sb. The maps of their spatial distribution in residual soil show the maximum concentrations in Kopaonik Mtn., Lajkovac and the Drina - Podrinje metallogenic zone. The contents of these elements in the residual soil reflect the geological background. In general, the isolines of these contents take the NW-SE direction, which spatially corresponds to the area of the Serbian-Macedonian geotectonic unit (Figure 7 and Figure 2). In addition, in the ore bodies of the Serbian-Macedonian metallogenic province, many chemical elements appear in the form of mineralization as an integral part of the bedrocks. Cd and Mo are the accompanying elements of polymetallic volcanogenic-sedimentary and sedimentary ore deposits. The occurrence of Sb mineralization is related to Palaeozoic shales and Triassic volcanics. In addition to Sb deposits in several places, Hg mineralization is also localized in the Palaeozoic shales.

The spatial distributions of As, Pb and Zn also show identical pattern, although the specificities of each element are visible. The expected high concentrations of these elements in Kopaonik Mtn. and the Drina - Podrinje zones are also spreading to the metallogenic zone of Šumadija. The characteristic anomalous percentile areas on the distribution maps for these elements coincide with the presence of historic (medieval) mining works and consequential mining waste. Pyrite, sphalerite and galenite are the main minerals. Arsenic largely accompanies all the above-mentioned ore mineralizations, which explains its increased presence in all metallogenic

PM

zones. The values of As, Pb and Zn peak at 155.4 mg·kg^{-1}, 143.5 mg·kg^{-1} and 182.6 mg·kg^{-1}, respectively. The geological environment of these PTEs mineralizations is made up of volcanic rocks, serpentinites, limestones and marls. Mineralization in metamorphic rocks is rare. Elevated concentrations of Pb and Zn, with concentration values ranging between 75 and 90 percentiles were also observed in areas beyond expectations that are not bound to the geological substrate. These layers are perceived by visualization in the distribution plan and are located near residential and industrial centres. The elevated Pb content was observed between the cities of Čačak and Kraljevo, and Zn in the area of Kragujevac and Jagodina, marked on the map by numbers 7 and 8, and 4 and 5 respectively (Figure 1 and Figure 7). The spatial distribution of Cu, Mn and V differs from all the previously mentioned PTEs. Their distribution is affected by the geological background and mineralization. Copper also occurs as an accompanying element in Pb-Zn ores in several samples. In diabase-chert formation, there are several Cu deposits, as well as numerous copper mineralizations with chalcopyrite-pyrite associations. Above this geological formation, the maximum concentrations of 66 mg·kg^{-1} are detected in sample # 35. Volcanogenic-sedimentary associations of the rocks of diabase-chert formations in Western Serbia and Triassic limestones in their vicinity are carriers of numerous Mn-oxide deposits. In the Šumadija zone, manganese nodules were found in many places in deep Cretaceous basins. The elevated values of V are also spatially related to the presence of ore areas and volcanic complexes.

Multivariate statistical analysis of the PTEs origin in the residual soil of Central and Western Serbia

The observed similarities and differences in PTEs spatial distributions in top residual soil in Central and Western Serbia were analysed using Pearson's correlation analysis, principal component analysis (PCA) and cluster analysis (CA).

The correlation analysis was used to identify the interrelations of the examined elements, as well as to determine the extent of causality. The results of Pearson's correlation analysis of PTEs in the top residual soil in Central and Western Serbia are shown in Table 3.

Pearson coefficients of free linear correlation yield the following:

1) A very strong positive correlation between As and Sb; Co, Cr and Ni and Cr and Ni ($0.75 < r < 1$, $p < 0.01$);

2) A moderate positive correlation between Co and Mn, Cr and Mn, Mn and Ni, and Pb and Zn ($0.50 < r < 0.75$, $p < 0.01$);

A low positive correlation ratio was not considered. Geologically present chemical associations would probably be more pronounced with increasing sampling resolution.

Considering the intensity and the level of significance

Table 3. Correlation coefficient matrix of PTEs in residual soil (n=108).

	As	Cd	Co	Cu	Cr	Hg	Mn	Mo	Ni	Pb	Sb	V	Zn
As	1												
Cd	0.157	1											
Co	-0.087	0.000	1										
Cu	0.178	0.214*	0.081	1									
Cr	-0.048	-0.013	**0.780****	0.039	1								
Hg	0.098	0.082	-0.018	-0.057	-0.053	1							
Mn	-0.091	0.267**	**0.679****	0.193*	**0.537****	0.021	1						
Mo	0.498**	0.021	-0.151	-0.009	-0.139	0.047	-0.071	1					
Ni	-0.092	-0.033	**0.854****	0.140	**0.831****	-0.040	**0.558****	-0.170	1				
Pb	0.405**	0.201*	0.227*	0.015	0.209*	0.005	0.297**	0.051	0.032	1			
Sb	**0.932****	0.133	-0.071	0.124	-0.058	0.096	-0.076	0.434**	-0.070	0.434**	1		
V	0.261**	0.151	0.109	0.029	0.260**	0.044	0.095	0.081	0.054	0.113	0.143	1	
Zn	0.425**	0.336**	0.090	0.280**	0.048	-0.056	0.242*	0.091	-0.107	**0.637****	0.389**	0.123	1

*. Correlation is significant at the 0.05 level (2-tailed)

**. Correlation is significant at the 0.01 level (2-tailed)

achieved, correlation analysis was distinguishing two groups of heavy metal pairs. Very strong correlations between some of the heavy metal pairs indicate common geogenic and natural sources, mutual dependence and identical behaviour in the weathering and residual soil formation processes.

The correlation connectivity of PTEs was also verified through PCA and CA. Principle component analysis (PCA) was used to reduce the size of the basic matrix of test results, and to account for the relationship between PTEs studied. PCA converts the tested variables to factors or major components. Correlations of the original variables are minimized by their elements and divided into smaller groups. Using the varimax rotation method with Kaiser Normalization, the load factor variance is increased between the variables for each factor. Factor analysis leads and directs to the analysis of the basic causes and the type of sources of the tested PTEs anomalous concentrations. The results of PCA of the PTEs in the top residual soil in Central and Western Serbia are shown in Table 4.

To explain the 100% variance, 13 major components are needed. The five main components (PCs) account for 75.56% of the total variance (Table 4). The other eight

Table 4. Principal component loadings of selected PTEs in residual soil (rotated component matrix) (n=108).

Parameters	PC1	PC2	PC3	PC4	PC5
Ni	**0.937**		-0.135		
Co	**0.931**		0.106		
Cr	**0.914**				
Mn	**0.695**	-0.183	0.305	0.249	0.143
As		**0.894**	0.313		0.109
Sb		**0.856**	0.343		
Mo	-0.118	**0.723**	-0.103		
Pb	0.177	0.202	**0.875**	-0.134	
Zn		0.193	**0.827**	0.271	
Cu	0.108	0.139		**0.880**	-0.146
Cd			0.400	**0.563**	0.427
Hg				-0.109	**0.824**
V	0.205	0.263			0.451
Total	3.335	3.021	1.369	1.072	1.024
% of Variance	25.657	23.238	10.534	8.250	7.877
Cumulative %	25.657	48.896	59.430	67.680	75.557

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization. a.
Rotation converged in 6 iterations.

have little relevance and are excluded from consideration.

The first PC (PC1) explains 25.66% of the total variance and consists of Cr, Ni and Co that exhibit a high correlation of 0.914, 0.931 and 0.937, respectively. Cr, Ni, and Co show their maximum values in residual soil in metallogenic zones of Mount Zlatibor area (V), Maljen Mtn.-Suvobor Mtn. area (III), Šumadija (IV) and Kopaonik Mtn. (VI) on ophiolitic massifs (Figure 2 and Figure 5). The bedrocks of the ore deposits include serpentinites, peridotites, dunites and oolitic limestones (Janković, 1977, 1982; Boev and Janković, 1996; Janković and Jelenković, 2000). Within the mentioned metallogenic regions, a series of mineralizations and ore deposits of these elements were discovered (Janković, 1990). Similarly, elevated natural concentrations of these metals in the far surroundings of the investigated area were also discovered in the soils of Croatia, Kosovo and Slovenia (Šajn, 2005; Šajn et al., 2013). These residual soils were formed by weathering processes and erosion affecting Jurassic ophiolites and Cretaceous and Neogene lithologies (Šajn et al., 2013). Manganese also shows an affinity for PC1, with a load of 0.695, and has it in PC3 (0.305) in PC4 with a slightly lower load of 0.249. Increased concentrations and mineralization of Mn parageneses are directly related to the volcanogenic-sedimentary and hydrothermal processes that took place in the areas of aforementioned metallogenic areas (Antonijević, 1995), which explains its presence in several PCs. The deposits and occurrences of manganese ore are in association with ophiolitic melange or diabase-chert formations, and Fe-Mn carbonate mines are bound by Pb-Zn sulphide deposits in the metallogenic zone of Kopaonik Mtn. (Janković et al., 1997). The presence of positive anomaly of these four elements in the residual soil of Central and Western Serbia is likely the product of lithogenic processes related to the weathering of bedrock, thus confirming their common geogenic origin.

The PC2 explains 23.24% of the total variance and consists of As, Sb and Mo. Sb and As are strongly associated with high loadings of 0.856 and 0.894 respectively. Molybdenum also shows relatively high connectivity in PC2, with a value of 0.723. The Drina-Podrinje (I) and Kopaonik Mtn. (VI) metallogenic zones are distinguished by many specific features, especially in terms of mineral composition (Janković et al., 1977; Radosavljević et al., 2007; Radosavljević, 2013). As these authors suggested, mineral paragenesis includes a large number of minerals. Antimonite and galenite are dominant. Pyrite, sphalerite, arsenopyrite, pyrrhotine, realgar, molybdenite, marcasite, magnetite, hematite and more sulphosalts were also recorded in the ores. On the other hand, the anthropogenic input cannot be recognized, although it must have been considerable in the past, when this region was a place of

intense antimony exploitation and processing, resulting in a large accumulation of tailing material.

PC3 consists of Zn, and Pb in the loads of 0.827 and 0.875 respectively. Manganese, As, Sb and Cd can also be clearly distinguished in PC3, but in somewhat lower loads of 0.305, 0.313, 0.343 and 0.400 respectively. PC3 accounts for 10.53% of the total variance. All the elements from PC3 are commonly found together in different types of ore deposits (Janković et al., 1977, 1980, 1997; Strucl, 1981; Moelo et al., 1983). These metals in residual soils are primarily defined through their natural lithogenic content in the geological substrate. We assume that the anthropogenic component is also significant. It is perceived through long-term exploitation that dates back to ancient times, then through old processing technologies and flotation of the polymetallic ore of Pb and Zn. A large amount of tailing material has been created in the area of Kopaonik Mtn. (VI), Šumadija (IV) and the Drina-Podrinje (I) that has not been properly conserved. The shape of anomalous areas on horizontal distribution maps visually suggests anthropogenic impact since they occupy large areas beyond the boundaries of the ore deposits exploitation (Figure 7). The spatial distribution of high PTEs concentrations is elongated in the NW-SE direction, which coincides with the most frequent and strongest wind directions (Figure 1), thus supporting the assumption that these elements have most likely been transported by air from unprotected debris dumps. Pb and Zn concentrations of 75-90% percentile content on distribution maps also clearly indicate anthropogenic impact. Anomalies are located far from the parent substrate and near cities. Increased Pb content is observed between Čačak (city no. 7) and Kraljevo (city no. 8), while Zn abounds near Kragujevac (city no. 4) and Jagodina (city no. 5) (Figures 1 and 5). Possible sources of Pb pollution are due to the proximity of the regional high-frequency roads, while Zn most likely is from the local motor vehicle production facilities, where the car body is galvanized.

The fourth major component explains 8.25% of the total variance and comprises Cd and Cu that show high loads of 0.563 and 0.88 respectively. Also, Mn and Zn show a positive value (0.249 and 0.271 respectively) in PC4. All these elements are found in mineralization related to the Jurassic diabase-chert formation, occurring in chalcopyrite, as well as in Tertiary volcanogenic intrusive magmatic complexes in numerous deposits of lead and zinc (Janković and Putnik, 1980; Putnik, 1981 and Janković, 1990). The geogenic origin of these elements in residual soil is also confirmed by distribution maps (Figure 7) of these elements, with the maximum values observed in the above-mentioned geological background (Figure 2).

PC5 accounts for 7.88% of the total variance and

is dominated by Hg, with a load value of 0.824. The significant presence of cinnabar is observed in the deposits of Sb, Pb and Zn, which inevitably releases Hg during oxidation processes. Anomalous Hg concentrations are spotted in the distribution maps beyond the boundaries of the mentioned deposits and the geological basement where they occur. This is probably the result of anthropogenic activities related to ore processing and smelting, with the significant airborne transfer of waste material from unprotected landfills.

Cluster analysis (CA) further confirms the observed correlation between PTEs and identifiable homogeneous groups that are similar to each other within the analysed matrix of data. The resulting clusters within the dendogram strongly correlate with the above PCA factors. The results of the top residual soil PTEs CA content were illustrated through the dendogram in Figure 8.

Ecological risk assessment (Igeo, MPI)

The analysis of the PTEs pollution impact on the top residual soils in Central and Western Serbia, as well as the detection of risk areas with possible geogenic and anthropogenic pollution, was also performed using the geoaccumulation index (Igeo) and the metal pollution index (MPI). The fluctuation of PTEs concentrations in the topsoil was examined relative to statistically estimated geochemical threshold values (Reimann et al., 2018) taken as the natural regional background distribution of the PTEs, aiming to identify unusually high element concentrations for these elements in the studied area (Table 2). The percentage pollution levels of top residual soils were obtained using the geoaccumulation index with PTEs are shown in Table 5.

The hierarchical ratio of the Igeo maximum values is, as follows:

Ni>Cd>Cr>Hg>Sb>Co>As>Mo>Pb>Mn>Cu>Zn>V. Nine PTEs (As, Cd, Co, Cr, Hg, Mo, Ni, Pb and Sb) are registered as potential pollutants. All are present at the unpolluted to moderately contaminated level (1≤Igeo<2); As, Cd, Co, Cr, Hg, Mo, Ni and Sb occur at moderately contaminated level (2≤Igeo<3); As, Cd, Co, Cr, Ni and Sb are present at moderately to heavily contaminated level (3≤Igeo<4); Cd, Cr, Ni and Sb are present at highly to extremely contaminated level (4≤Igeo<5). Only Ni in two locations has Igeo≥5 i.e. extremely contaminated environment values.

The obtained Igeo values suggest that a certain amount of pollution is expected only in a few locations. Comparing the percentage of PTEs pollution from Table 5 and the PTEs spatial pattern from Figure 7, we can safely conclude that more than 75% of the residual soil surface in the studied area is fairly uncontaminated.

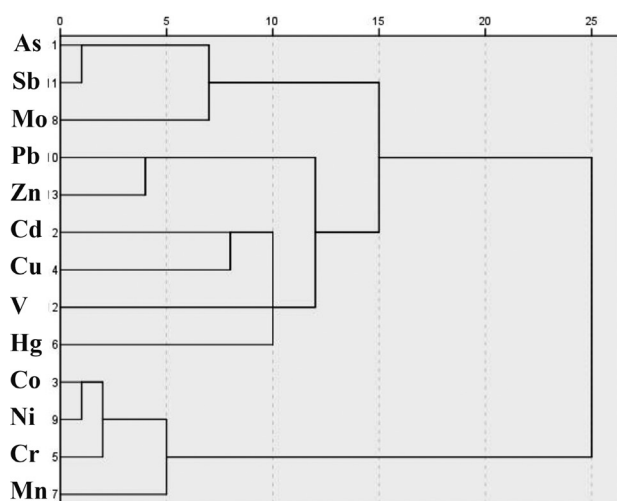The positive indices of the aforementioned PTEs,

Figure 8. Dendogram of PTEs cluster analysis in residual soil of Central and Western Serbia, using Ward Linkage Method.

activities have been present since ancient times. Antimony, Pb, Zn, and Hg have been mostly exploited, whereas other elements have been present in the secondary mineral paragenesis or have occurred independently in the basement lithologies. In these metallogenic regions (Figure 2), most primary minerals are metal sulphides (e.g. galena, sphalerite, arsenopyrite, pyrite, chalcopyrite, bornite, stibnite, molybdenite, cinnabar, realgar), which, by oxidation of primary ore, produce acid and highly soluble metal minerals - sulphate salts with great potential for soil contamination (Veličković, 1958; Dušanić, 1991; Dimitrijević, 1995; Bogosavljević-Petrović, 1995; Vujić, 2014). Moreover, huge amounts of ore exploitation waste point to significant anthropogenic influence.

In addition to the risk assessment of individual elements in the top residual soil of Central and Western Serbia, the metal pollution index (MPI) has also been calculated. The obtained MPI map (Figure 7) is similar to the maps of the spatial distribution of certain elements (Ni, Co, and Cr), which primarily point to the chemical composition of the residual soil geological substrate, bound to the ultrabasic rocks. The largest MPIs occur in Zlatibor Mtn. (V), Šumadija (IV), and Kopaonik Mtn.(VI) metallogenic areas. High concentrations of As, Hg, Mn, Pb, Sb, and Zn in these locations are the result of bedrock decomposition superimposed with the anthropogenic impact of historical and contemporary mining works.

as well as their increased proportional representation at the displayed levels, indicate that soil enrichment is principally induced by geogenic processes, and only to a certain extent by anthropogenic activities associated with ore extraction, processing and smelting. Anomalous values and elevated pollution indices are mostly noted in the vicinity of mineralizations related to the metallogenic region (Figures 2 and 7). In the explored area, mining

Table 5. Levels of geoaccumulation index (Igeo) of PTEs in top residual soils, site-by-site representation (upper part-number of sites) and percentage representation (lower part, %) (n=54).

Number of sampling sites	As	Cd	Co	Cu	Cr	Hg	Mn	Mo	Ni	Pb	Sb	V	Zn
Igeo<0	38	41	39	41	35	38	41	48	27	47	34	47	52
0≤Igeo<1	10	7	8	13	9	9	10	3	13	4	13	7	2
1≤Igeo<2	**4**	**2**	**3**	**-**	**3**	**5**	**3**	**2**	**4**	**3**	**4**	**-**	**-**
2≤Igeo<3	**1**	**2**	**2**	**-**	**2**	**2**	**-**	**1**	**2**	**-**	**1**	**-**	**-**
3≤Igeo<4	**1**	**1**	**2**	**-**	**4**	**-**	**-**	**-**	**3**	**-**	**1**	**-**	**-**
4≤Igeo<5	**-**	**1**	**-**	**-**	**1**	**-**	**-**	**-**	**3**	**-**	**1**	**-**	**-**
Igeo≥5	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**2**	**-**	**-**	**-**	**-**
%													
Igeo<0	70.4	75.9	72.2	75.9	64.8	70.4	75.9	88.9	50.0	87.0	63.0	87.0	96.3
0≤Igeo<1	18.5	13.0	14.8	24.1	16.7	16.7	18.5	5.6	24.1	7.4	24.1	13.0	3.7
1≤Igeo<2	**7.4**	**3.7**	**5.6**	**-**	**5.6**	**9.3**	**5.6**	**3.7**	**7.4**	**5.6**	**7.4**	**-**	**-**
2≤Igeo<3	**1.9**	**3.7**	**3.7**	**-**	**3.7**	**3.7**	**-**	**1.9**	**3.7**	**-**	**1.9**	**-**	**-**
3≤Igeo<4	**1.9**	**1.9**	**3.7**	**-**	**7.4**	**-**	**-**	**-**	**5.6**	**-**	**1.9**	**-**	**-**
4≤Igeo<5	**-**	**1.9**	**-**	**-**	**1.9**	**-**	**-**	**-**	**5.6**	**-**	**1.9**	**-**	**-**

CONCLUSIONS

The main outcomes of this study are as follows:

1) This study explored for the first time the geochemical spatial pattern, natural background and environmental risk assessment of PTEs, including As, Cd, Co, Cu, Cr, Hg, Mn, Mo, Ni, Pb, Sb, V, and Zn, in residual soils of Central and Western Serbia. The research was conducted on an area of about 20,000 km^2, where the bedrock is of extremely heterogeneous geological composition and complex metallogeny.

2) Natural PTEs background values in residual soils of Central and Western Serbia are as follows (mg·kg^{-1}): As (38.5), Cd (0.5), Co (36.3), Cu (51.9), Cr (170.1), Hg (0.21), Mn (1974), Mo (0.9),Ni (215.2), Pb (61.7), Sb (2.4), V (84.4), Zn (116.6). The elevated concentrations of individual PTEs in residual soil are undoubtedly natural, as they reflect the concentrations of the parent material. Compared to the Upper Continental Crust, World, European and Croatian soils, residual Serbian soils are enriched with As, Sb, Ni, and Hg; Ni, Co, As, and Sb; Ni, Co, Hg and As and Hg, Ni, As, and Cu, respectively.

3) Four groups of elements with similar spatial distributions were perceived: (As, Pb, Zn); (Cd, Hg, Mo, Sb); (Co, Cr, Ni) and (Cu, Mn, V). Cobalt, Cr and Ni have the most similar spatial distribution and can be found in the metallogenic zones of Zlatibor Mtn., Šumadija and Kopaonik Mtn. The predominant geological substrate of the residual soil in these anomaly areas is of ultrabasic composition. Cadmium, Hg, Mo, and Sb in the residual soils show their maximum concentrations in the metallogenic zones of Kopaonik Mtn., Lajkovac and Drina-Podrinje. Relatively high concentrations of As, Pb and Zn are present at Kopaonik Mtn., Drina - Podrinje and Šumadija zones. They coincide with the presence of old (medieval) mining activities and amassed mining waste. The observed elevated concentrations of Pb and Zn in those areas are surprising and are unrelated to the geological substrate. The distribution of Cu, Mn and V is determined by geological background and mineralization. The elevated values are also spatially related to the presence of ore areas and volcanic complexes.

4) According to the PCA results, five different groups are discerned. Factors PC1 (Ni, Co, Cr, Mn), PC2 (As, Sb, Mo), PC3 (Pb, Zn), PC4 (Cu, Cd), and PC5 (Hg) strongly correlate with clusters obtained within the given CA dendogram.

5) Igeo values indicate nine PTEs as potential pollutants (As, Cd, Co, Cr, Hg, Mo, Ni, Pb, and Sb). The increase in pollution is observed only in certain locations. The largest MPIs occur in Zlatibor Mtn., Šumadija and Kopaonik Mtn. metallogenic areas. High concentrations of As, Hg, Mn, Pb, Sb, and Zn in these areas have been considered a consequence of bedrock decomposition and the anthropogenic impact of historical and contemporary mining works.

In summary, our study demonstrated that the anomalous concentrations of As, Cr, Hg, Ni, Pb, Sb, and Mn are dominantly of geogenic origin, and only partially, increased contents of As, Hg, Pb, Sb, and Zn may be the result of anthropogenic activities as well, particularly in metallogenic areas (Kopaonik Mtn., Šumadija and the Drina - Podrinje metallogenic region).

In general, areas with high anomalous concentrations of individual metals and areas with a high total MPI should be the focus of future investigations as they pose a possible risk to human health and the environment. All strategic planning in the field of agriculture and tourism in this region should first and foremost be founded on detailed soil research in high resolution to ensure the preservation of biodiversity and the well-being of people.

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