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Comparison of urban and rural soils based on speciation of heavy metals by BCR sequential extraction procedure: A case study in the historical and industrial city of Sisak, Croatia

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Abstract

Within the framework of the pan-European project “URban GEOchemistry (URGE) in Europe – Soil, children, health”, pedological and geochemical investigations of the soils of the city of Sisak and its adjacent surroundings were carried out, and three urban and two rural soil profiles were examined. The mineralogical composition and concentration of selected potentially toxic elements (PTEs) Cr, Cu, Ni, Pb and Zn in the soil were determined. The Community Reference Bureau of Reference (BCR) sequential extraction procedure (SEP) of these PTEs was undertaken and the potential risk to human health and the environment was assessed.

The concentrations of Cr and Ni are generally similar in urban and rural soil profiles, while the concentrations of Cu, Pb and Zn in soil horizons/layers are higher in urban profiles. The extracted fractions of PTEs gave the following general distribution: in urban soil profiles residual (RES) > reducible (ORG) or oxidisable (FEMN) > exchangeable (CARB), except for Cu where ORG > RES > FEMN > CARB, while in rural soil profiles RES > FEMN or ORG > CARB, except for Pb where FEMN > RES or ORG > CARB.

The differences between soils in urban and rural profiles depend mainly on the historical land use, i.e. on the duration and intensity of anthropogenic influences on the soil and, to a lesser extent, on the geogenic origin of the parent material and the pedogenic processes. The studied elements in the urban soil profiles are predominantly of anthropogenic origin, indicating a possible influence of the ancient settlements of Segestica and Siscia and of heavy industry in the 20th century. The anthropogenic influences on the rural profiles are low and geogenic influences dominate.

Risks to the environment were assessed in the soil profiles based on PTE concentrations in the CARB fraction and the sum of the CARB, ORG and FEMN fractions from BCR SEP. All calculated risks to human health and the environment were rated as no-risk, very low risk and low risk.

Keywords: SEP, potentially toxic elements, soil profiles, anthropogenic influences, risk assessment

1. INTRODUCTION

The pan-European pilot project URGE was carried out with the aim of assessing the quality of urban soil through geochemical mapping in different European cities. The main objective of the project was to harmonise the methodology for urban geochemical surveys and to compare the results obtained at European level. The Geochemical Expert Group of EuroGeoSurveys coordinated the implementation of the whole project, and the Croatian Geological Survey (HGI-CGS) carried out the surveys in the city of Sisak, Croatia. According to ŠORŠA & HALAMIĆ (2014), the concentration of PTEs in the topsoil (0–10 cm) in the city of Sisak and its rural surroundings is the result of the geological background and strong anthropogenic influences caused by the long urban, transport, and industrial history of Sisak. Geochemical mapping of the topsoil in the city of Sisak was extended to investigation of the subsoil layers. The aim of the extended investigations was to determine the changes in the concentration of PTEs in the soil by depth and to assess the potential risk to human health and the environment. In addition, the geochemical fractions of Cr, Cu, Ni, Pb, and Zn in the subsurface soil layers were determined using the Community Reference Bureau of Reference

sequential extraction procedure. The exchangeable fraction, the reducible fraction, the oxidisable fraction and the residual were determined by BCR SEP in the soil horizons/layers of three urban and two rural soil profiles.

In the broadest sense, the term urban soils refers to soils that have developed in urban areas or under strong anthropogenic influence. Depending on the objective of a study dealing with urban soils, there are many different definitions of the term (CRAUL, 1992; SOBOCKA, 2003; LEHMANN & STAHR, 2007; POUYAT et al., 2010; GREINERT, 2015; GREINERT & KOSTECKI, 2019; O’RIORDAN et al., 2021). Here, the term “urban soils” is used for all soils in the urban area of Sisak, while the term “rural soils” is used for the soils in the adjacent rural area of Sisak.

The purpose of SEP is to study how metals are released into the environment under different environmental conditions. Knowing the total concentration of a metal in soil is not sufficient to accurately assess its impact on the environment and its potential contamination. The mobility and bioavailability of a metal are crucial for soil contamination. The SEP is a chemical technique that successively extracts metals and other elements from

solid samples (soil, sediment, waste) in order of solubility in different geochemical fractions. Each successive fraction dissolves a particular phase with metals bound to it and removes them from the system. This method can be used to extract metals sequentially in 2, 3, 4, 5, 6 or 7 fractions. There are several developed methods for SEP and the most commonly used are Tessier, BCR, Short, Galán, and Geological Society of Canada (GCS) (ZIMMERMAN & WEINDORF, 2010).

The European Commission (2001) has proposed the BCR SEP method, which differs from the Tessier method (TESSIER et al., 1979) by merging Tessier's first and second fractions i.e., the exchangeable and the carbonate fractions (URE et al., 1993; ZIMMERMAN & WEINDORF, 2010). The aim of developing BCR SEP is to compare the results of SEP of sediment and soil analysis data at EU level. BCR SEP defines three successive extractions of metals from the sample and residual. Fraction 1 – CARB extracts metal ions adsorbed in the soil and metals bound to carbonates. Fraction 2 – FEMN separates metals bound to iron or manganese oxides that form nodules, concretions, cement between particles or a coating around particles. Fraction 3 – ORG comprises metals bound to organic material and sulphides (TESSIER et al., 1979; GLEYZES et al., 2002). Organic matter readily accumulates metals that are degraded under oxidation conditions. The last fraction is residual – RES. Once the first three fractions are removed, the residue should consist of primary and secondary minerals containing metals in the crystal lattice. These metals are not expected to be released into the environment under conditions prevailing in nature.

Contaminated soils or soils enriched with PTEs pose a potential risk of poisoning some plants, soil microorganisms, animals, and humans. Human health can be threatened by contaminated soils in several ways: by inhalation, through the skin, or by consumption of food and drink. A potential environmental risk is defined as the possibility of harming flora, fauna or human health through exposure to high concentrations of harmful ele-

ments (RAPANAT et al., 2008). The potential risk to the environment also depends on the mobility, bioavailability and ecotoxicity of PTEs. The risk of poisoning is lower when PTEs are fixed in the soil and not mobile. Their release into the mobile phase of the soil depends mainly on the Eh value, pH and buffer capacity of the soil, then on the content of Mn-Fe oxyhydroxide, clay and organic material in the soil. Based on the results of the BCR SEP analyses, the risk of a potential mobilisation of PTEs into the environment could be assessed. The potential risk of release of PTEs into the mobile phase was calculated as a function of the CARB fraction (RATH et al., 2009; LIU et al., 2010) and as a function of the sum of the CARB, FEMN and ORG fractions (MIKO et al., 2003).

According to the study by ŠORŠA (2014) on the distribution of elements in topsoil, their origin and potential risk for the environment and human health, 5 PTEs were selected for BCR SEP. The first was Cr, which is predominantly of geogenic origin, the second was Ni, which is partly of geogenic and partly of anthropogenic origin, while the remaining three elements (Cu, Zn and Pb) are predominantly of anthropogenic origin. The objective of the study was to determine any differences in the distribution of these elements by depth in soils in urban and rural soil profiles, their origin in the soil profiles, and the sources of possible contamination. In addition, the risk of release of metals into the environment will be assessed based on the results of the BCR SEP.

1.1 Study area

The city of Sisak lies at latitude 45° 29' N and longitude 16° 20' E and is located in the Posavina region, 57 km south-east of Zagreb (Fig. 1). The study area includes the urban part of the city and the adjacent rural surroundings. The terrain is lowland. The largest part of the study area lies at an altitude of about 100 m above sea level and the Rivers Kupa, Sava and Odra occasionally flood the lower parts of the Sisak area. Quaternary sediments predominate in the region of the city of Sisak. The deposits com-



Figure 1. Geographic location of the study area of Sisak, Croatia.

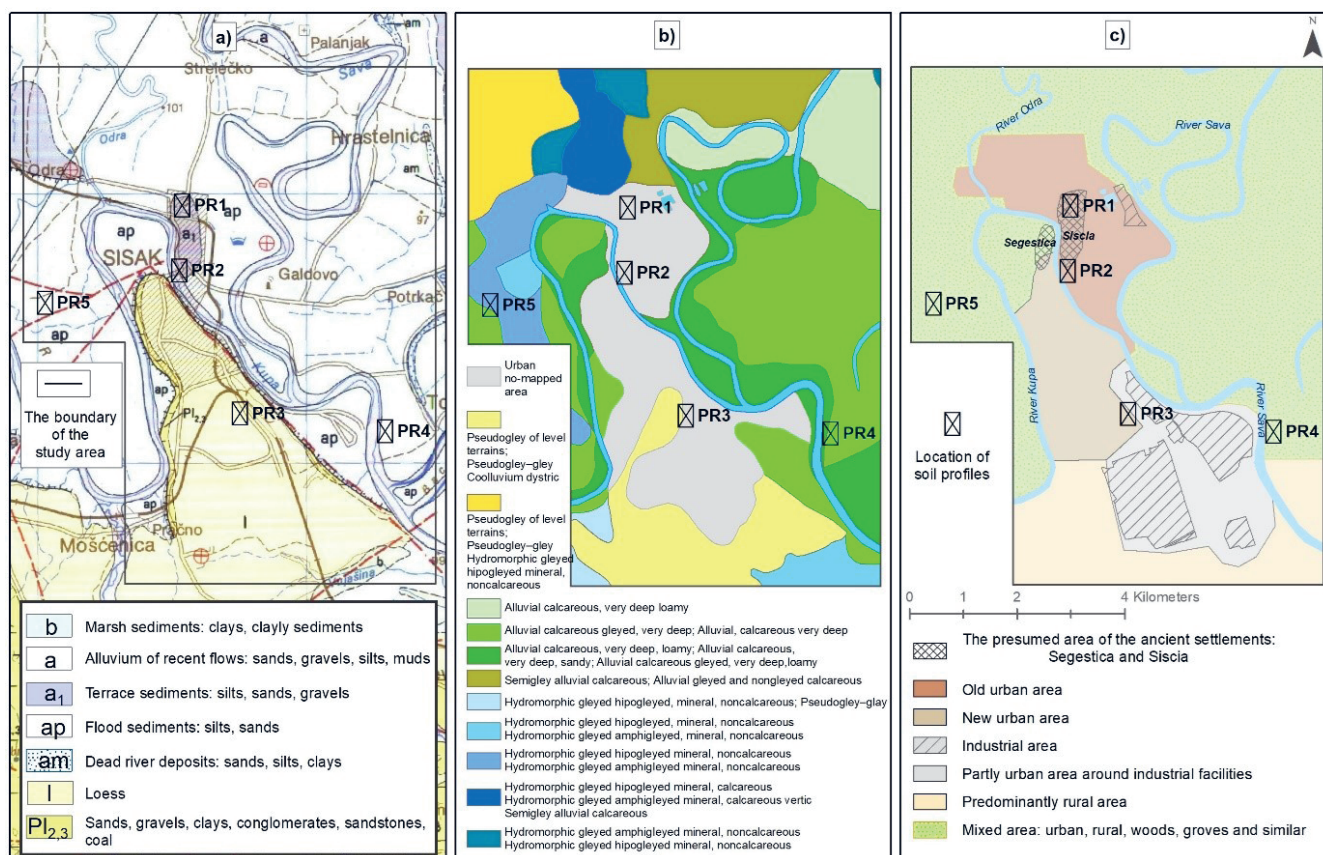


Figure 2. a) Geological map (PIKIJA, 1987a, b), b) pedological map (HUSNJAK, 2012) and c) the map showing historical and current land use (ŠORŠA, 2014) of the study area in Sisak with the locations of the soil profiles.

prise carbonate alluvium of the River Sava in the east, siliciclastic alluvium of the Rivers Kupa and Odra in the west and north, and loess deposits in the central part, within the large meander of the River Kupa (Fig. 2a; PIKIJA, 1987a, b). Based on the pedological map, hydromorphic soils, i.e., the classes of pseudogleyic, undeveloped, semigley and gley soils predominate in the rural surroundings of Sisak, and technogenic soils dominate in the urban part (Fig. 2b; HUSNJAK, 2012). The climate in Sisak is moderately warm and rainy, without extreme dry periods (LISAC & HERIĆ-NEKIĆ, 1995). According to the Sisak meteorological station, the most frequent wind directions are NE 15.4% of the time and N 13.0% of the time.

In accordance with the official land use in the city of Sisak (KAMINSKI-KIRŠ, 2002), the urban soil profiles PR1, PR2 and PR3 are located in the parks and recreation areas, and the rural soil profiles PR4 and PR5 are placed in the area with soils for agricultural production. According to the historical and current land use observed during fieldwork, the urban area of Sisak includes “the old urban area; new urban area, industrial area, and partly urban area around the industrial facilities”, while the rural area includes “the predominantly rural area, and mixed area: urban,

rural, woods, groves and similar” (Fig. 2c). According to the current land use, the urban soil profiles are located in the urban area and the rural soil profiles in the rural area of Sisak.

The soils of the three urban soil profiles PR1, PR2 and PR3 and the two rural soil profiles PR4 and PR5 are classified according to the WRB (IUSS Working Group WRB, 2014) and the Croatian Soil Classification (CSC; HUSNJAK, 2014) and already presented in HUSNJAK et al. (2018) and ŠORŠA (2014) (Tab. 1).

2. MATERIALS AND METHODS

2.1. Sampling

The locations of the profiles were chosen to achieve an even distribution of soil profiles throughout the study area, consistent with historical and current land use, geological, and pedological characteristics (Fig. 2a, b, c; Tab. 1). Two profiles PR1 and PR2 were located in the old urban area on the terrace sediments of the River Kupa and were classified as Urbic and Lincic technosols, respectively. Profile PR3 was excavated on the boundary between the new urban area and the partially urban area around the industrial facilities on the loess and classified as a Hypereutric regosol.

Table 1. Classification of urban and rural soils from profiles in Sisak according to the World Reference Base for soil resources 2014 (IUSS Working Group WRB, 2014) and the Croatian Soil Classification (HUSNJAK, 2014) taken from (HUSNJAK et al., 2018; ŠORŠA, 2014).

Type of soil profile	Soil profile	WRB classification	Croatian Soil Classification
Urban soil profiles	PR1	Urbic Technosols (Loamic, Calcaric, Grossartefactic, Humic)	Humus-accumulative soils; the type Rendzina
	PR2	Lincic Technosol (Calcaric, Ruptic)	Technogenic soils; the type Deposol
	PR3	Hypereutric Regosol (Siltic, Relocatic, Ruptic) over Hypereutric Relictistagnic Retisol (Siltic)	Humus-accumulative soils; the type Rendzina
Rural soil profiles	PR4	Haplic Fluvisol (Anthric, Calcaric, Hypereutric, Siltic)	Hydromorphic soil (Semiglay)
	PR5	Haplic Fluvisol (Anthric, Humic, Hypereutric, Endoarenic)	Hydromorphic soil (Semiglay)

Two profiles were excavated in predominantly rural areas - PR4 in the south, on the carbonate alluvium of the Sava River, and PR5 in the north on the siliciclastic alluvium of the River Kupa and both were classified as Haplic fluvisols.

The soil profiles in the urban areas (PR1, PR2 and PR3) have only weakly developed horizons and were therefore described and sampled mainly in recognised layers. The urban soil profile PR1 was located in the park in the Roman Siscia area. The entire profile PR1 is anthropogenic, carbonate, and the soil is black. The profile was dug to a depth of 120 cm and 1 horizon and 5 layers were sampled. The urban soil profile PR2 was taken in the park near the old bridge. The part of the profile to a depth of 105 cm was excavated and then drilled between 105 and 120 cm. The parent material for the soil is mainly of anthropogenic origin. Five soil layers were sampled. The urban soil profile PR3 was located in the park in front of the school in Caprag. It was dug to 102 cm and the rest was drilled to 200 cm. The settlement of Caprag was built in the 50s and 60s of the last century for the workers of the ironworks of Sisak. Therefore, the upper part of the profile is anthropogenically influenced. Six soil samples were collected from four horizons and two layers.

The rural soil profiles (PR4 and PR5) have developed horizons. Rural soil profile PR4 was located in the south-eastern part of the study area on agricultural land and about 200 m from the River Sava. It was dug to a depth of 115 cm and further drilled to 220 cm. Six soil samples were collected in six horizons. Rural soil profile PR5 is located in the north-western part of the study area, about 1,300 m from the River Kupa. Soil profile PR5 was only drilled to a depth of 130 cm, and three soil samples were collected.

The amount of anthropogenically sourced detritus (bricks, stones, pieces of iron and other material of anthropogenic origin) was often very large in urban areas, so a larger volume of soil weighing up to 4 kg was sampled in urban soil profiles. In soil profiles in rural areas, the weight of the soil samples was about 2.5 kg. Twenty-six soil samples were collected from identified soil horizons and layers.

2.2. Analyses

The samples were air dried at room temperature, gently crushed, sieved through a 2-mm sieve, homogenised, powdered and split for all analyses.

The mineralogical composition was determined by X-ray powder diffraction (XRD) in the laboratory of the Croatian Geological Survey. The samples for XRD analyses were ground using a McCrone mill. Semi-quantitative XRD analysis was performed using a PANalytical vertical X-ray goniometer (type X³Pert) equipped with a Cu-tube and PW 3018/00 PIXcel detector. The experimental conditions were: 45 kV, 40 mA, primary beam divergence 1/4° and continuous scan (step 0.02 °2θ/s). The semi-quantitative composition of the samples was carried out according to the method of SCHULTZ (1964).

The 5 g of samples for chemical analyses were digested in 90 ml *aqua regia*, then heated and boiled in a bath (at 95°C) for one hour. After cooling, up to 300 ml of 5% HCl was added to the solution. Chemical analyses were performed by inductively coupled plasma mass spectroscopy (ICP MS) for a range of 53 chemical elements at ACME Analytical Laboratories, Vancouver, Canada (the procedure is described in detail in ŠORŠA, 2014; ŠORŠA et al., 2017).

Table 2. Sequential extraction scheme combined with the residual fraction.

Step	Reagent	Soil phase	Label
1.	Acetic acid (0.11 mol/l)	Acid soluble	CARB
2.	Hydroxylammonium chloride (0.5 mol/l)	Reducible	FEMN
3.	Hydrogen peroxide (8.8 mol/l), followed by extraction with ammonium acetate (1 mol/l)	Oxidisable	ORG
4.	<i>Aqua regia</i> (HNO ₃ : HCl = 1:3)	Residual	RES

To determine the different forms of metals in soils, a slightly modified three-step procedure described in the Report EUR 19775 EN of the EUROPEAN COMMISSION (2001) was used for acid-soluble, reducible and oxidisable soil fractions. What remained after these three steps is the residual fraction (RES) which was analysed after the *aqua regia* treatment (NIEUWENHUIZE et al., 1991). This treatment does not completely dissolve all the remaining mineral phases. The efficiency of the digestion varies from element to element and depends on the mineralogy of the sample material. The result obtained is therefore considered as near-total. The extraction scheme is presented in Tab. 2. It should be noted that the results obtained are operationally defined and therefore the significance of the analytical results is related to the extraction scheme used. The sequential extraction scheme recommended by BCR is sufficiently repeatable and reproducible for use in speciation studies (DAVIDSON et al., 1994).

The resulting solutions were analysed for Cr, Cu, Ni, Pb and Zn on an AAnalyst 700 Perkin Elmer flame absorption spectrometer (AAS) using an air-acetylene flame. The sum of all fractions gave the total metal content of the sample.

For statistical purposes analytical data, the value of which was below the DL was assigned half of the DL value.

2.2.1. Quality control

Quality control (QC) for chemical analyses with ICP MS was carried out for all topsoil and soil samples from soil profiles collected within the project URGE in the Sisak study area. The coefficient of variation of the precision of the technique and the accuracy of the standards were satisfactory (the QC is described in detail in ŠORŠA, 2014; ŠORŠA et al., 2017).

Soil samples from soil profiles were analysed in geochemical fractions obtained by BCR SEP for the five metals Cr, Cu, Ni, Pb and Zn with the AAS. The correlation of the results obtained with both analytical techniques can serve as an additional quality control. The comparison of the results can be done by graphical representation or statistical tests such as the t-test or the Wilcoxon test (REIMANN et al., 2008). Due to the small number of samples, only a graphical representation of the comparison of the measurement results was made and no statistical tests were performed. Comparing the results of the analysis of samples measured with the ICP MS with the results of the analysis of the same samples measured with the AAS, a slight difference in the measurements can be observed (Fig. 3). The concentrations of Cr determined with ICP MS were higher than those measured with AAS for all samples. The results for Cu and Pb agreed, except in profile PR2 and partly in PR1, where the element contents determined with AAS are generally slightly higher than those with ICP MS. Nickel and Zn behave in the same way in the two sets of results. In profiles PR1 and PR2 these metals have higher concentrations when analysed with AAS, and their concentrations measured with AAS are lower than those determined with ICP MS in profiles PR2, PR3 and PR4.

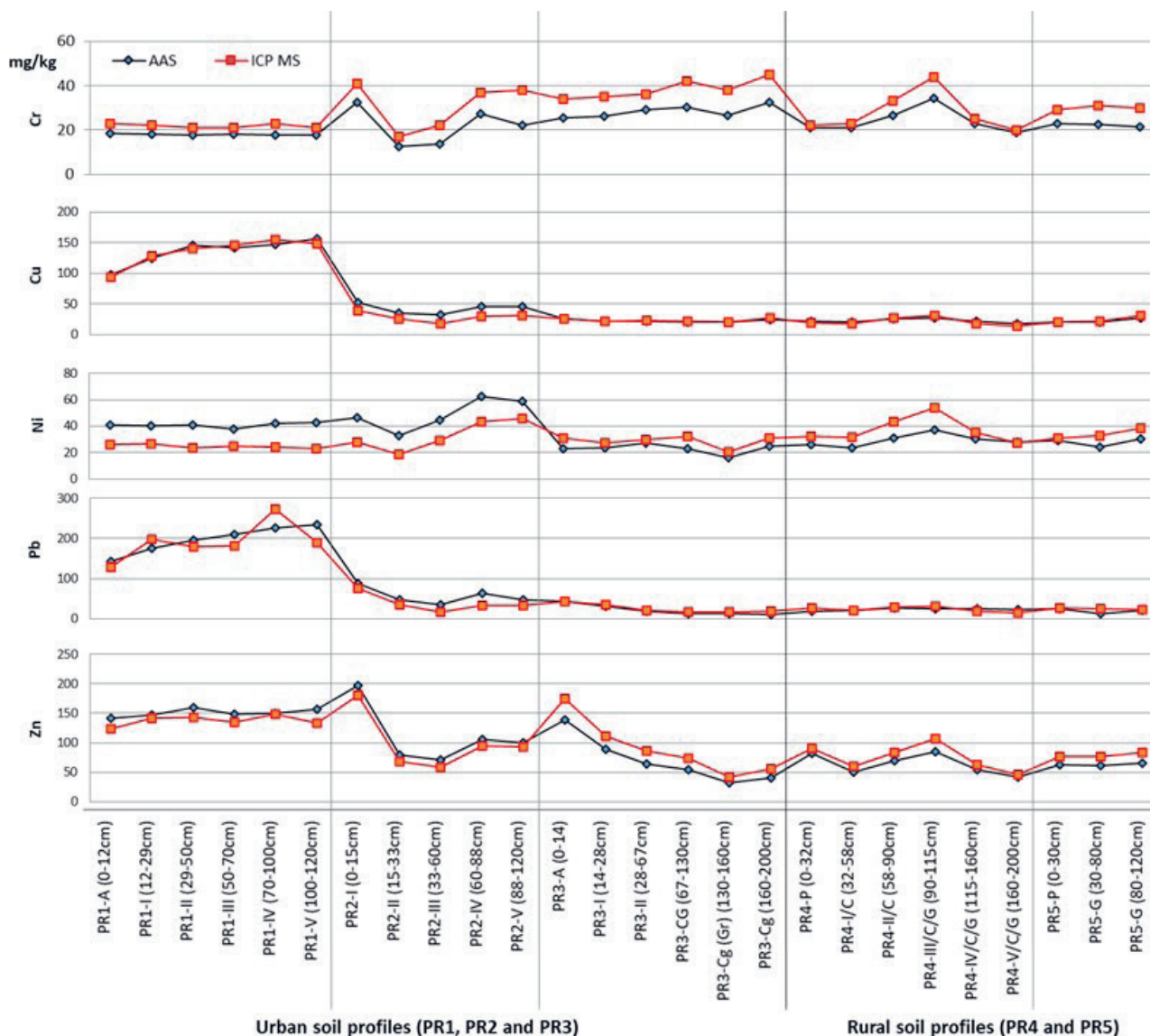


Figure 3. Quality control for elements analysed with two analytical techniques by graphic comparison of Cr, Cu, Ni, Pb and Zn concentration measurements obtained by AAS and ICP MS.

Chromium shows the greatest difference in the measurements with AAS and ICP MS. The reason for this result is the concentration of Cr in resistant minerals that are difficult to dissolve in acids (chromite, magnetite, ilmenite). *Aqua regia* was used to dissolve the soil sample before measurement with ICP MS and to dissolve the residual fraction for measurement with

AAS. A slight change in the ratio of HCl: HNO₃, the temperature or the dissolution time probably led to a deviation in the measurements. The differences in the measurements for Cu, Ni, Pb and Zn were small. On average, the differences in the measurements were small and the measured concentrations of the metals showed the same trend of increase or decrease for both analytical techniques.

Table 3. Quality control for the BCR SEP - Certified and measured concentrations of the standard sample BCR-701 in urban and rural soil profiles.

Element	Concentration in standard BCR - 701	Geochemical fraction				
		CARB	FEMN	ORG	RES	SUM
Cr	Measured	0.75	15.7	136	52.4	205
	Certified	2.26	45.7	143	62.5	253
Cu	Measured	33.3	80.9	82.0	48.4	245
	Certified	49.3	124	124	38.5	267
Ni	Measured	11.8	18.8	18.9	41.0	90.5
	Certified	15.4	26.6	15.3	41.4	98.7
Pb	Measured	5.06	84.6	19.8	39.7	149
	Certified	3.18	126	9.30	11.0	149
Zn	Measured	154	115	52.6	100	422
	Certified	205	114	45.7	95.0	460

The precision of BCR SEP was determined by measuring a soil sample with AAS in three consecutive replicates. The accuracy of the results of SEP was determined by comparison with a standard sample BCR-701 (Tab. 3). Certified and measured concentrations of the standard sample BCR-701 for Cr, Cu, Ni, Pb and Zn by geochemical fractions in soil samples have a large overlap (PUEYO et al., 2001). The lowest accuracy was found for Cr, probably due to the resistivity of Cr minerals. Other PTEs show generally good accuracy.

2.3. Risk assessment

The risk to the environment and human health was assessed based on the results of BCR SEP in the soil profiles according to Risk Assessment Code (RAC) which includes only CARB fraction and according to the sum of the concentration of the CARB,

FEMN and ORG fractions. In both risk assessment methods, the horizons or layers in the soil profiles were treated the same, they were all considered as surface horizons/layers. The potential risk to human health is in urban soil profiles due to land use for recreational purposes and in rural areas due to cultivation of crops for human and animal consumption. In addition, mobilisation of metals in case of contamination in deeper horizons/layers poses a risk to groundwater during the flood season.

2.3.1. Risk Assessment Code

The assessment of risk to the environment due to the potential mobilisation of PTEs from soil can be based on the metal concentration in the carbonate fraction obtained by the BCR (RATH et al., 2009; LIU et al., 2010). In the CARB fraction, the metals are only weakly bound to the surface of the soil particles or incorporated in the structure of minerals soluble in acids and can be easily mobilised into the environment. The formula for calculating the content of metal in a given fraction is $E = (CM/\Sigma CM) \times 100$; where (E) is the percentage of metal extraction in the fraction, (CM) is the metal concentration in the fraction, and (ΣCM) is the total metal concentration in the whole sample ($\Sigma CM = CARB + FEMN + ORG + RES$) (LIU et al., 2010). The risk assessment of metal release to the environment is based on the percentage of extraction (E) of the selected metal in the CARB frac-

tioning to land use. HOOKER & NATHANAIL (2006) suggested that environmental risk can be expressed as relative risk (RR) for selected elements (i), calculated using the following formula: $RR_i = (\text{total concentration in soil})_i / (\text{soil target value})$ for each land use.

3. RESULTS AND DISCUSSION

A soil profile in a naturally developed soil has characteristic horizons that depend, among others, on pedogenesis on a particular parent material, while a soil profile in an urban area usually has no formed horizons, only layers (Figs. 4 and 5). In the urban soil profile PR1, the anthropogenic influences are so strong that the soil is a mixture of soil and anthropogenic material. In PR2, the upper layers have been recently disturbed and filled with material brought from elsewhere. Soil profile PR3 is under anthropogenic influence in its upper half and shows natural pedogenesis in its lower half. The profiles in the urban area (PR1, PR2 and PR3) have a shallow surface horizon that developed in a relatively short time. It formed in PR1 after the last excavation in 1974, in PR2 the upper layers were backfilled in 2009 and in PR3 during the construction of the Caprag settlement in the 1950s and 1960s. Soil profiles PR4 and PR5, which are exposed in rural areas, have a natural pedogenic development. Their surface horizon is thicker

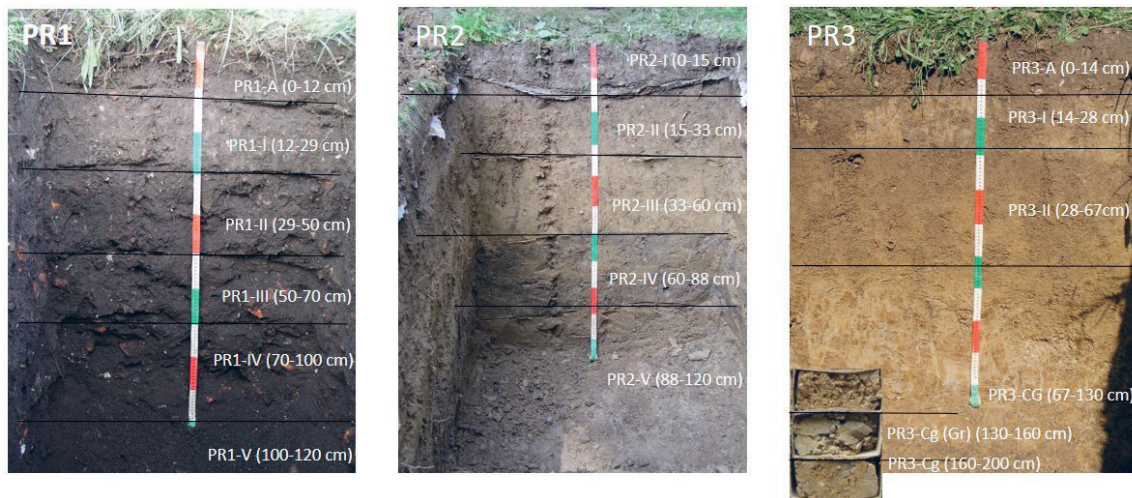


Figure 4. Urban soil profiles PR1, PR2 and PR3 with their determined horizons/layers.

tion. There is no risk if the $E < 1\%$. Low, medium, high and very high risk applies to $E = 1-10\%$, $E = 11-30\%$, $E = 31-50\%$ and $E > 50\%$, respectively (RATH et al., 2009).

2.3.2. Risk assessment based on the sum of concentrations in the fractions CARB, FEMN and ORG

MESIĆ et al. (2008) proposed legal limits for total metal concentrations in soils according to land use. The proposed classification of land use distinguishes soils for agricultural production, children's playgrounds, residential areas, parks and recreation areas, and areas for industrial and commercial purposes.

The BCR SEP of samples from soil profiles revealed four fractions in which the PETs Cr, Cu, Ni, Pb and Zn were bound. Metals in RES fraction can be mobilised only by strong acids, but such conditions are unlikely in the environment. A realistic assessment of the risk to the environment and human health was obtained by summing the concentration of the first three fractions: CARB + FEMN + ORG (MIKO et al., 2003), and comparing these with the prescribed limits for total concentration ac-

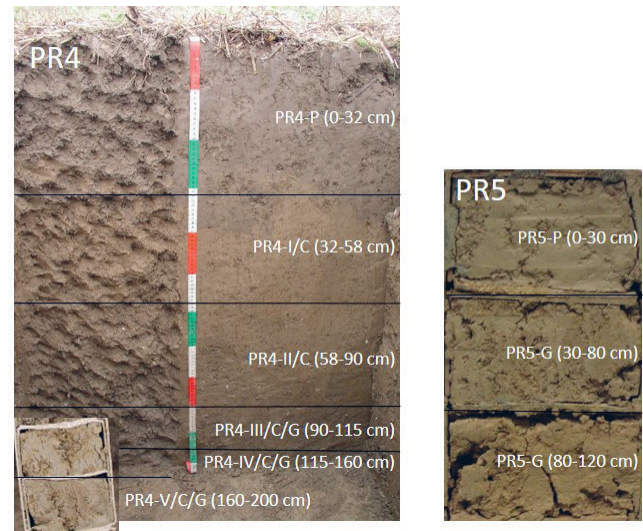


Figure 5. Rural soil profiles PR4 and PR5 with their determined horizons.

and also developed under anthropogenic influence (ploughing), but is genetically related to the rest of the profile.

The influences on the pedogenic development of the soil profiles were multiple. The urban soil profiles PR1 and PR2 are located on the river terrace, PR3 on the slightly elevated loess and the rural profiles PR4 and PR5 in the floodplain. The parent material was brought in by the Rivers Kupa and Sava or by wind, and deposited in their alluvium. The transport and sedimentation were of varying intensity.

In addition to the geogenic background, there are numerous anthropogenic influences, which include a long urban history, the construction of dikes for flood protection, the various embankments of streams, ravines and profiles, and industrial development. The pedogenic development of the profiles has been strongly influenced by surface and high-level groundwater. For this reason, mainly hydromorphic soils have developed. In such soils, the migration of ions, colloids and other small particles to the depth of the profile was facilitated. All this has influenced the oscillation and irregularity of the mineralogical composition and the amount of PTEs along the horizons/layers in these soils.

3.1. Urban soils

3.1.1. Mineralogy

The following minerals were determined in the samples from the urban soil profiles: quartz, phyllosilicates, calcite, dolomite, plagioclase and cristobalite (Fig. 6 and Supplements 1; Supplements 2). Quartz is the predominant mineral in all profiles. Besides quartz, phyllosilicates were the most abundant mineral phases in the soil profiles. Most of the samples contain 14 Å, 10 Å and 7 Å diffraction maxima that are characteristic of phyllosilicates. The diffraction maxima of 14 Å indicates the presence of swelling minerals (smectite and/or vermiculite) and/or chlorite. Diffraction maxima of 10 Å indicates illitic material, and 7 Å indicates the presence of kaolinite and/or chlorite (MOORE & RAYNOLDS, 1997; STARKEY et al., 1984). In sample PR2-II (15-33 cm) the diffraction maximum of 14 Å is not visible. Samples PR1-IV (70-100 cm) and PR1-V (100-120 cm) do not contain the diffraction maximum of 7 Å. The phyllosilicate content is highest in profile PR3. In PR1, the phyllosilicate content is largely uni-

form over the entire depth. In general, the content of phyllosilicate increases with depth in profiles PR2 and PR3. Calcite and dolomite are present in soils of profiles PR1 and PR2, but were not found in PR3. Plagioclase is present in PR1, PR2 to a lesser extent than in the soil of PR3, which is probably a consequence of the different parent materials since profiles are located on different sediments (Fig. 2a, PIKIJA, 1987a, b) or more intense weathering. A low content of cristobalite was only observed in soil profile PR3. The cristobalite in profile PR3 located on loess (Fig. 2a, PIKIJA, 1987a, b) is probably of volcanic origin. As there are several potential cristobalite sources within a relatively short distance of 5 to 15 km from soil profile PR3, the cristobalite may have been deposited together with other loess material.

The urban profiles PR1, PR2 and PR3 show anthropogenic influences in their mineralogical composition (Fig. 2b, c). Profile PR1 has a uniform content of all minerals throughout its depth, which is a consequence of the mixing of materials due to constant digging over. In the layer PR2-II (15-33 cm), the calcite content is greatly increased and the phyllosilicate content is reduced due to anthropogenic influences. This layer was filled with carbonate sand mixed with the existing parent material. The layer is then covered with nylon and compacted soil to form the surface layer PR2-I (0-15 cm). The lower part of profile PR2 is natural. Soil profile PR3 is disturbed to a depth of 67 cm in the upper three layers and therefore contains less phyllosilicates than in the lower three layers, which are natural. The mineralogical composition in the urban soil profiles PR1 and PR2 is consistent with the mineralogical composition of the siliclastic alluvium of the Rivers Kupa and Odra on which profiles are located (Fig. 2a, PIKIJA, 1987a, b). Similarly, the mineralogy of profile PR3 also corresponds to the mineralogical composition of loess (Fig. 2a, PIKIJA, 1987a, b; ŠORŠA et al., 2018). Anthropogenic influences are large in profile PR1 and in the upper part of profiles PR2 and PR3.

3.1.2. Total concentration of the selected PTEs

As soil profiles vary according to parent material, pedogenic development, anthropogenic influence and land use (Figs. 2a, b, c), there is not even much regularity in the content of selected PTEs

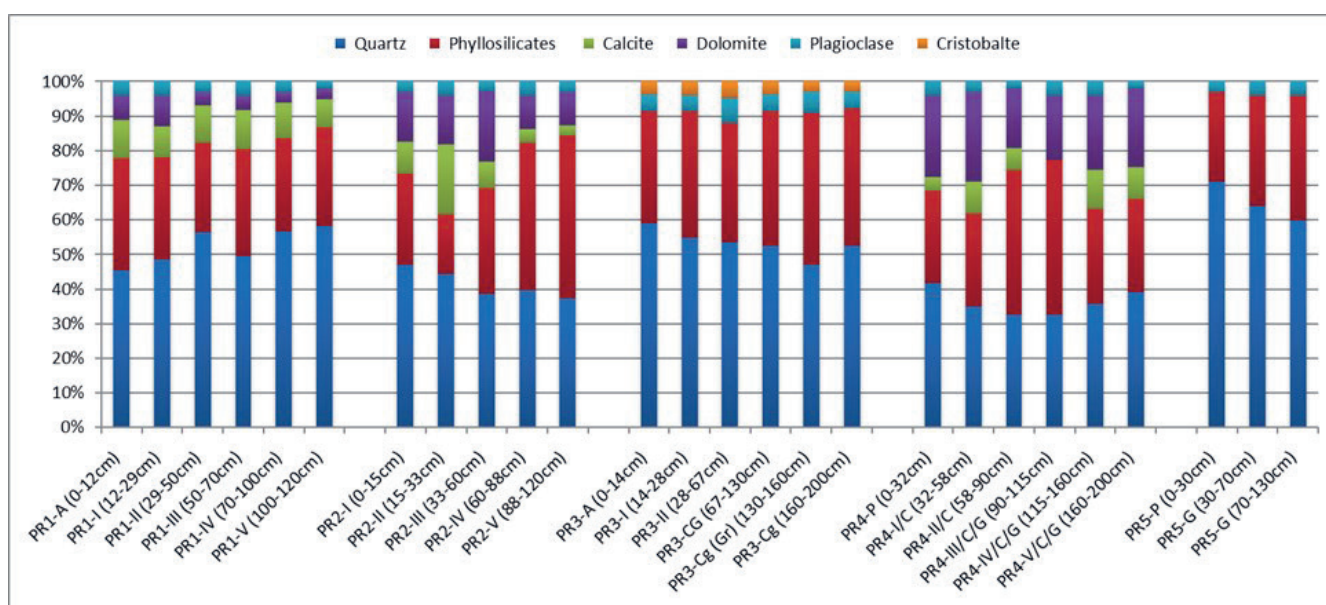


Figure 6. The mineral composition in soil samples in urban and rural soil profiles determined by X-ray diffraction.

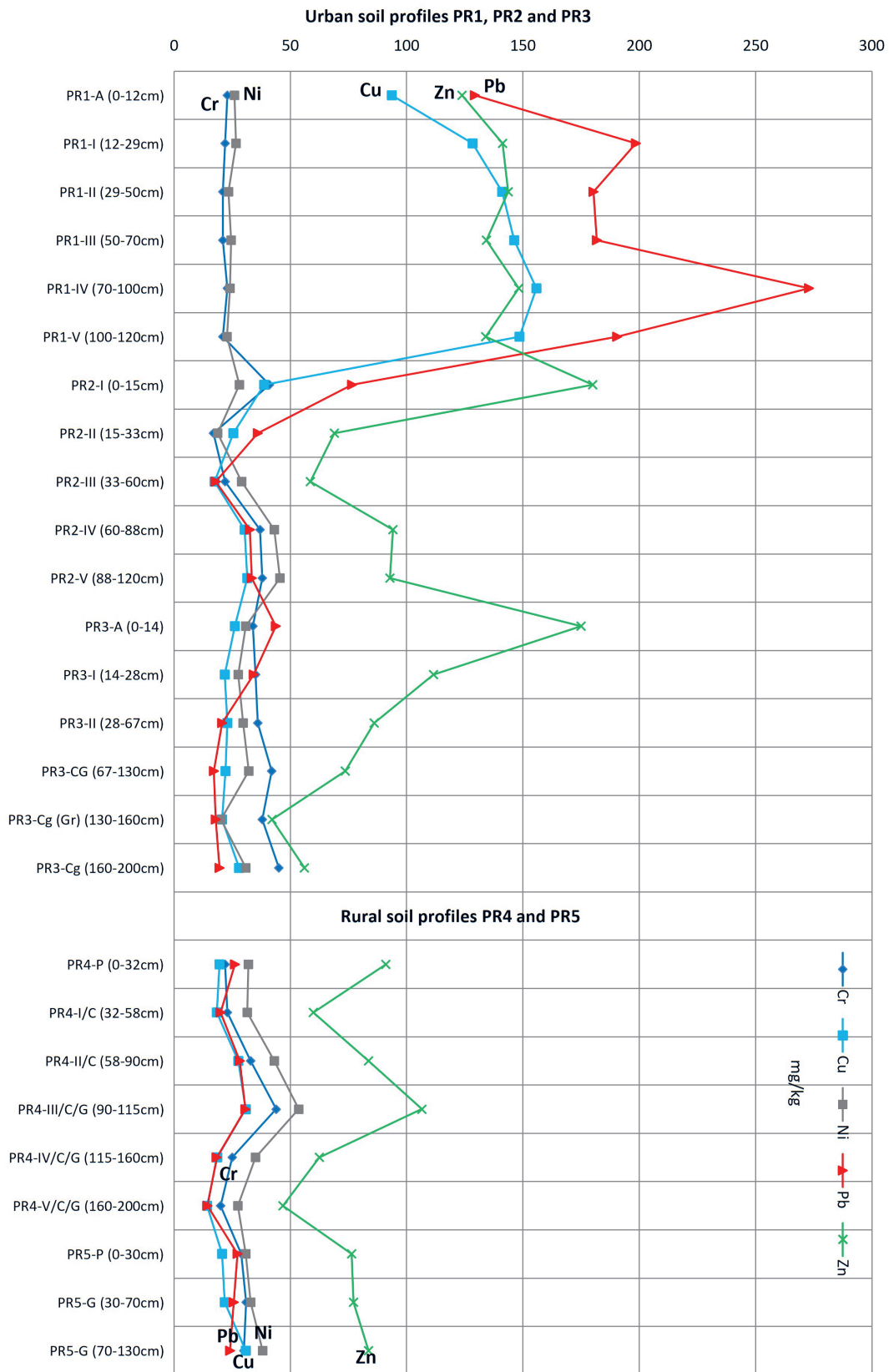


Figure 7. The concentration of the Cr, Cu, Ni, Pb and Zn in soil samples in urban and rural soil profiles measured with ICP MS.

(Fig. 7; Tab. 4). The surface horizon of soil profiles in urban areas often has elevated levels of contaminants (LEHMANN & STAHR, 2007). The concentration and distribution of selected PTEs along the horizons and layers in urban soil profiles PR1, PR2 and PR3 were strongly influenced by human excavation and contamination (Fig. 8).

Soil profile PR1 has significantly higher levels of PTEs: Cu, Pb and Zn than the other profiles (Fig. 7; Tab. 4). According to the geochemical maps of the spatial distribution of elements on the surface (ŠORŠA & HALAMIĆ, 2014), profile PR1 is located in the area with increased Cu and Pb concentration. In this profile, the surface horizon is not enriched with PTEs, their concen-

Table 4. The concentration of the Cr, Cu, Ni, Pb and Zn in soil samples in urban and rural soil profiles measured by AAS and ICP MS.

Type	PTEs	Cr		Cu		Ni		Pb		Zn	
		mg/kg									
	Soil profile	AAS	ICP MS	AAS	ICP MS	AAS	ICP MS	AAS	ICP MS	AAS	ICP MS
Urban soil profiles	PR1-A (0-12cm)	18.4	23.0	97.9	93.7	40.6	26.1	144	129	142	124
	PR1-I (12-29cm)	18.2	22.0	125	128	40.5	26.7	176	199	147	141
	PR1-II (29-50cm)	17.6	21.0	146	141	40.7	23.4	196	180	159	144
	PR1-III (50-70cm)	18.1	21.0	142	146	37.6	24.6	210	182	148	13
	PR1-IV (70-100cm)	17.6	23.0	147	156	41.9	24.1	226	273	150	148
	PR1-V (100-120cm)	17.6	21.0	157	149	42.5	22.8	235	191	157	134
	PR2-I (0-15cm)	32.6	41.0	52.2	38.8	46.1	28.2	88.2	76.5	197	180
	PR2-II (15-33cm)	12.7	17.0	35.9	25.6	32.7	18.7	47.5	36.1	78.8	68.9
	PR2-III (33-60cm)	13.7	22.0	32.7	17.5	44.6	29.1	34.9	17.9	70.5	58.6
	PR2-IV (60-88cm)	27.2	37.0	45.6	30.3	62.2	43.2	64.6	32.6	105	94.2
Rural soil profiles	PR3-A (0-14)	25.5	34.0	25.7	26.2	23.3	30.9	42.8	43.8	139	175
	PR3-I (14-28cm)	26.1	35.0	21.4	21.9	23.3	27.6	32.1	34.2	89.2	112
	PR3-II (28-67cm)	29.2	36.0	22.2	22.9	27.1	29.8	19.0	20.7	64.0	86.1
	PR3-CG (67-130cm)	30.2	42.0	21.1	22.2	22.7	32.2	11.9	17.2	54.9	73.7
	PR3-Cg (Gr) (130-160cm)	26.6	38.0	20.1	20.7	16.1	20.3	12.2	17.9	32.3	42.2
	PR3-Cg (160-200cm)	32.5	45.0	24.1	28.0	24.6	30.8	11.8	19.5	40.6	56.0
	PR4-P (0-32cm)	21.0	22.0	22.7	19.6	26.1	32.0	19.7	26.2	82.4	91.1
	PR4-I/C (32-58cm)	21.0	23.0	21.0	18.4	23.9	31.5	20.9	20.0	50.8	59.9
	PR4-II/C (58-90cm)	26.6	33.0	26.5	27.6	30.9	43.1	26.6	28.3	70.2	83.7
	PR4-III/C/G (90-115cm)	34.1	44.0	27.7	30.9	37.4	53.7	24.1	30.7	84.3	106.6
PR4-IV/C/G (115-160cm)	22.9	25.0	21.4	18.5	30.7	35.1	24.4	18.4	55.1	62.5	
PR4-V/C/G (160-200cm)	18.9	20.0	18.2	14.3	27.9	27.5	22.4	14.5	42.5	46.9	
PR5-P (0-30cm)	22.7	29.0	20.9	20.7	28.9	30.8	25.4	27.4	63.0	76.4	
PR5-G (30-80cm)	22.4	31.0	21.3	21.8	24.3	32.9	13.7	25.8	61.3	77.2	
PR5-G (80-120cm)	21.4	30.0	27.9	30.9	30.6	38.1	21.4	24.0	65.6	83.6	

tration is elevated deeper in the profile. All elements with increased content in the PR1 profile belong to anthropogenic factor 1 (Heavy industry), and the element Pb also belongs to anthropogenic factor 6 (Roman mints) (factors defined by ŠORŠA et al., 2017). The concentration of all PTEs by layer does not vary significantly, except for the enrichment in the layer at 70-100 cm depth (Figs. 4 and 7; Tab. 4). In the urban soil profile PR1, PTEs have accumulated in the soil over a long period of time. It is located in the park, close to a parcel of archaeological excavations

dating back to Roman times. The land has been in continuous use for over 2,000 years. It was once the site of the Roman Siscia, and for the last 150 years (until 1974) it was a cemetery. Today it is a city park near industrial facilities. Therefore, the amount and distribution of PTEs in profile PR1 are mainly of anthropogenic origin (ŠORŠA, 2014). Copper, Pb and Zn are elevated due to smelting furnaces and mints in Roman times, industry, transport, fossil fuel combustion and other wastes. It is difficult to determine the extent of the influence of cemeteries on PTEs concentrations in the profile. In the absence of detailed descriptions of burial methods and the use of coffins, gravestones, etc., one can only speculate on the amount of PTEs of “cemetery” origin.

In soil profile PR2, the surface horizon is slightly enriched in all elements compared to the underlying horizons (Fig. 7; Tab. 4). Moreover, the concentration of all selected metals, after the previously described drop from the surface layer, increases with depth, with slight variations. The anthropogenic formation of the upper two horizons/layers and the strong influence of the third layer after the flower exhibition in 2009, when the upper two layers were partially filled, had the greatest influence on observed variation in the content of the elements at depth. Therefore, the contents of the elements of the surface horizon and the surrounding area cannot be compared.

The surface horizon of PR3 is slightly enriched in Cu, Ni, Pb and Zn compared to the rest of the profile. This content in the surface horizon is consistent with the geochemical maps of the surrounding area (ŠORŠA & HALAMIĆ, 2014). Most of the

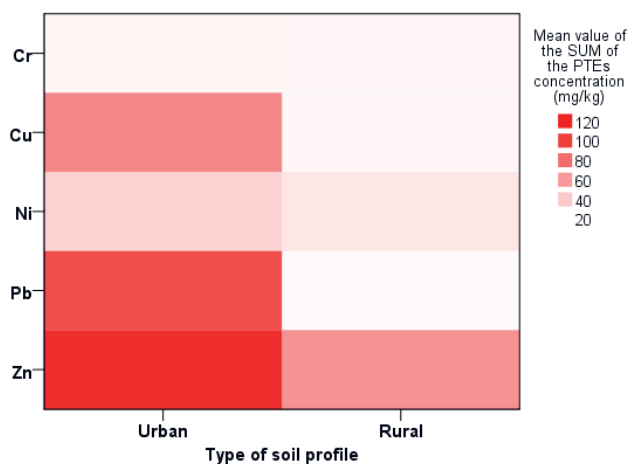


Figure 8. Heatmap of total concentration of the Cr, Cu, Ni, Pb and Zn in soil samples in urban and rural soil profiles measured with AAS.

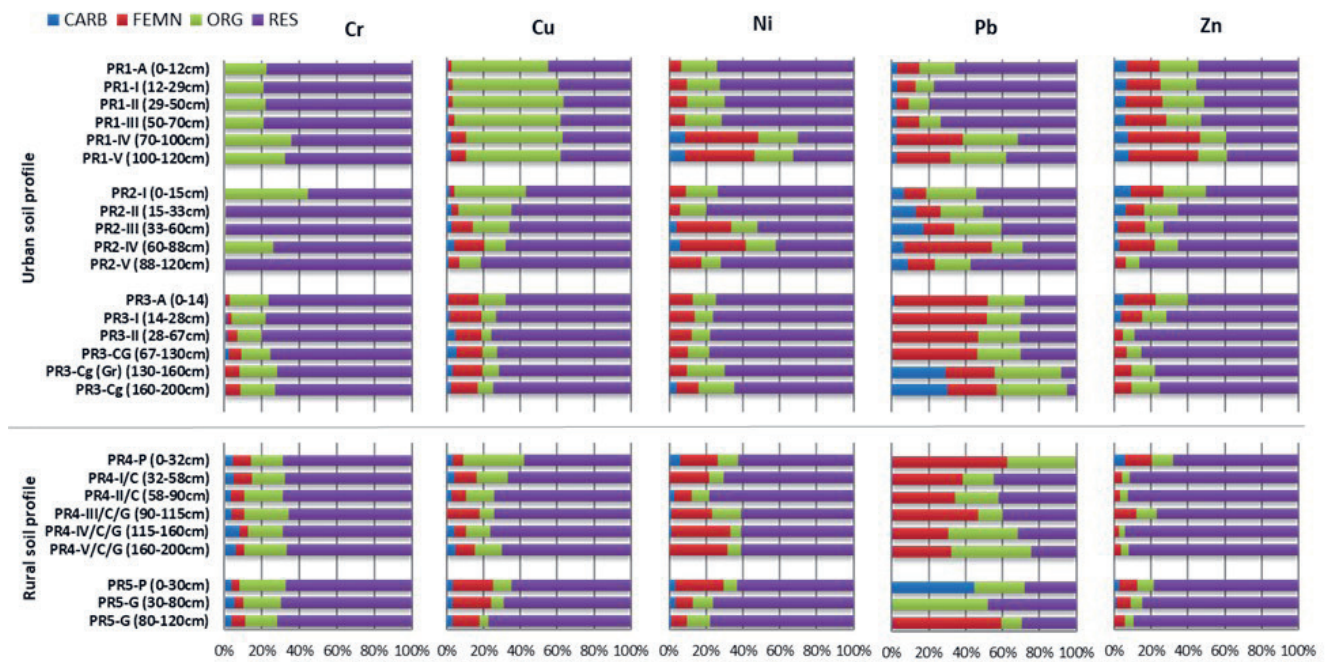


Figure 9. The diagrams of percentage concentration of Cr, Cu, Ni, Pb and Zn in the CARB, FEMN, ORG and RES geochemical fractions in soil samples from horizons/layers in urban and rural soil profiles determined with BCR SEP.

PTEs belong to anthropogenic factor 1 (Heavy industry) (ŠORŠA et al., 2017). At a depth of 67 cm in the PR3 profile, the concentration of Zn drops sharply, while the concentrations of Cr, Cu, Ni and Pb decrease only slightly. At this depth, there are no anthropogenic influences and they originate from the parent material.

3.1.3. BCR Sequential extraction procedure of the selected PTEs

The concentration of Cr, Ni, Pb, and Zn in the urban soil profile PR1 is highest in the fraction RES, while the concentration of Cu is highest in the fraction ORG (Fig. 9; Supplements 4.a). This is followed by the fractions RES for Cu and ORG, in which in addition to Cu, Cr and partly Zn, Ni and Pb are bound.

Profile PR1 is richest in humus and nitrogen (ŠORŠA, 2014), so the content of metals bound in the fraction ORG is significantly higher there than in the other profiles (KHADHAR et al., 2020). In the FEMN fraction there is a lot of Ni, Pb and Zn and Cu in much lower concentrations, and Cr is almost absent in the lower two layers. Zinc is almost evenly bound in the FEMN and ORG fractions, and the concentrations of Pb, Ni, Cu and Cr decrease to zero, respectively, in the upper horizon/layers. Nickel in the fraction RES is predominantly of geogenic origin and bound to silicates since nickel of anthropogenic origin has a high affinity for binding to Fe- and Mn-oxy-hydroxides (McGRATH, 1997). This is probably the reason why its content in the FEMN fraction is elevated in the lower two layers of profile PR1. Nickel concentration in the FEMN fraction is related to the Fe_2O_3 and MnO content in these horizons/layers (Supplements 3; ŠORŠA, 2014). With increasing Fe-Mn oxide content, the Ni concentration in the FEMN fraction also increases. Lead concentration in PR1 is significantly higher than in the other profiles. Lead of anthropogenic origin, especially Pb from metallurgical processes, has a higher binding affinity to Fe-Mn-oxides than to organic material (ETTLER et al., 2005). Consequently, although the profile PR1 contains a high content of humus and nitrogen, more Pb is present in the FEMN than in the fraction ORG. The lowest concentration of all elements was found in the CARB fraction. It is associated

with a low content of Zn and Pb, then with Ni and Cu in the lower layers, while Cr is absent.

There is not much regularity in terms of fractions and profile depth. In general, the fraction RES decreased and the fraction ORG of Cu and Cr as well as the fraction FEMN of Ni, Pb and Zn increased. The amount of PTEs in the fractions in the urban soil profile PR1 is not the result of pedogenic processes in the parent material. The fluctuating concentrations in the fractions are the result of repeated excavations in the area where the profile is located and the repeated mixing of the parent material with anthropogenic artefacts. Considering that profile PR1 has been under strong anthropogenic influence for over 2,000 years, it is likely that some of the metals were only weakly bound.

In general, the distribution of metal concentration by fraction in the PR1 profile is as follows: RES > ORG > FEMN > CARB, except for Cu, which is ORG > RES > FEMN > CARB.

In soil profile PR2, the largest fraction of metals is in the fraction RES (Fig. 9; Supplements 4a). The content of humus and nitrogen is highest in the surface horizon, and the concentration of PTEs in the fraction ORG is also highest there. Chromium is not present in the FEMN fraction, while other metals are similarly present in the FEMN and ORG fractions. Only Pb and significantly less Zn, Cu and Ni are bound in the CARB fraction. The urban soil profile PR2 is characterised by an enrichment of all the studied PTEs in the surface layer. However, the two upper layers and part of the third layer were infilled in 2009 and have no fixed genetic relationship with the rest of the profile. It is likely that some of the material from the immediate vicinity of the profile was used to level the site and some was brought in from elsewhere. However, one can observe an increase in metals bound to the FEMN fraction with increasing depth and a strong decrease in the deepest layer, which is consistent with the amounts of Fe_2O_3 and MnO in the profile (Supplements 3; ŠORŠA, 2014). The distribution of fractions in profile PR2 is RES > FEMN > ORG > CARB.

In soil profile PR3 PTEs Cr, Cu, Ni and Zn are mainly concentrated in the RES fraction and Pb in the FEMN fraction or in

deeper horizons in ORG (Fig. 9; Supplements 4.a). Chromium, Cu, Ni and Zn are almost equally presented in the FEMN and ORG fractions. This is a consequence of the concentration of organic matter and Fe and Mn oxides in the soil. The content of humus and nitrogen is relatively low, except in the two upper horizons. The content of Fe₂O₃ and MnO is slightly increased in the whole profile compared to the other urban profiles PR1 and PR2 (Supplements 3; ŠORŠA, 2014). The lowest amount of PTEs is bound in the CARB fraction. The exception is Pb in the two deepest horizons, where it is almost absent in the RES fraction, but evenly distributed in the other three. Zinc, Pb and Cu are enriched in the surface horizon, probably due to the proximity of the iron-works (Fig. 7; Tab. 4). In the deeper horizons, the metals are predominantly of geogenic origin, with the exception of Pb, which is predominantly of anthropogenic origin throughout the profile. The dominant distribution of geochemical fractions in the PR3 profile is RES > FEMN > ORG > CARB, with the exception of Pb, which is FEMN > ORG > RES > CARB.

The predominant distribution of the studied PTEs concentration by fraction in the urban soil profiles is as follows: RES > ORG or FEMN > CARB, except for Cu, where ORG > RES > FEMN > CARB.

The leaching content of PTEs by the fractions shows a large variability due to the different chemical composition of the soil samples. The ranges of variation between the minimum and maximum values are generally large, which is another indicator of the diversity of soil composition by horizon/layer. Lead shows large ranges for all fractions, Cu for the RES and ORG fractions, Ni and Zn for RES and FEMN. Chromium shows the lowest concentration ranges in all fractions compared to the other PTEs, probably because it is predominantly of geogenic origin. Based on the geological background and the results of total concentrations of PTEs in soil and on BCR SEP it can be concluded that Ni is also partly of geogenic origin, while Cu and Zn are mainly of anthropogenic origin. The content and “behaviour” of Pb in all fractions differs from that of the other PTEs. Lead is almost uniformly present in the fractions RES, FEMN and ORG and varies irregularly in the profiles. Lead is predominantly of anthropogenic origin.

3.2. Rural soils

3.2.1. Mineralogy

Soil profiles PR4 and PR5 are located on agricultural land and anthropogenic influences are mainly limited to the surface horizons. The minerals identified in the horizons of the rural soil profiles were quartz, phyllosilicates, calcite, dolomite and plagioclase (Figs. 6 and Supplements 1; Supplements 2). Quartz is less abundant in PR4, but predominates in profile PR5. This change is followed by the change in phyllosilicate content. The amount of phyllosilicate in PR4 is the highest in the horizons with the lowest quartz content (at a depth of 90 - 115 cm). The content of phyllosilicates in PR5 increases with depth. Calcite and dolomite are present in profile PR4, but not in PR5. Plagioclase feldspars are present in both rural profiles. The rural soil profile PR4 is located on carbonate alluvium of the Sava River and its mineralogical composition is consistent with the parent material (Fig. 2a; Supplements 3; PIKIJA, 1987a, b; ŠORŠA et al., 2018). Hence, it has the highest dolomite content compared to the other profiles. The mineralogy of the second soil profile PR5 indicates that the parent material probably originates from the siliciclastic alluvium of the River Kupa (Fig. 2a, PIKIJA, 1987a, b; ŠORŠA et al., 2018).

3.2.2. Total concentration of the selected PTEs

The surface horizon of profile PR4 is slightly enriched in metals compared to the lower horizons (Fig. 7; Supplements 4b). Subsequently, the content of metals increases strongly in the pseudogley horizon PR4- II /C (58-90 cm) and relict gley horizon PR4- III /C/G (90-115 cm) (Figs. 5 and 7; Tab. 4). The concentration of all PTEs then gradually decreases in the two deepest horizons. The highest concentrations of all PTEs in the entire PR4 profile were measured in the relict gley horizon. The origin of the metals in the profile, especially their high content in this horizon, is questionable. The high content of metals accumulated in the relict gley horizon corresponds to the siliciclastic parent material of the floodplain of the River Kupa, although the PR4 profile was excavated in the carbonate floodplain of the River Sava (Fig. 2a, PIKIJA 1987a, b; ŠORŠA, 2014). The reason for this could be the high groundwater table in this area and the frequent floods, which lead to a mixing of water and drained material from both rivers. Additionally, the mouth of the River Kupa shifted downstream over time and was once located 1 km further north than today (SLUKAN ALTIĆ, 2004).

The concentration and distribution of PTEs in the PR4 soil profile was influenced by several factors/processes: the carbonate parent material, then the pedogenic processes with a high groundwater table leading to the development of gley soils, frequent flooding and siliciclastic material brought by the River Kupa, and intensive agricultural production.

Only three horizons (Fig. 5) were developed in the drilled soil profile PR5, which is located in the north of the study area, on agricultural land that developed on the siliciclastic alluvium of the River Kupa (Fig. 2 a,b,c). The concentrations of selected PTEs are low. The geochemical maps show a similar distribution of elements in the vicinity of the profile site (ŠORŠA & HALAMIĆ, 2014). The concentration of Cu, Zn, Ni, increases with depth, while Pb and Cr decrease (Fig. 7). The proportion of geogenic elements increases with depth, while elements of partial or complete anthropogenic origin decrease.

3.2.3. BCR Sequential extraction procedure of the selected PTEs

The predominant fraction for Cr, Cu, Ni and Zn in the rural soil profile PR4 is RES, with the exception of Pb, which prevails in the FEMN or ORG fractions (Fig. 9; Supplements 4.b). The second most important fraction is the FEMN, except for Cr and partially Cu, which is the most important for Pb and the smallest for Zn. The concentration of bound metals in ORG fraction is slightly lower than that of FEMN. The distribution of the fractions by depth is variable. The concentration of all measured metals increased in the gley horizons in the ORG and FEMN fractions and decreased in the RES fraction. It is likely that the metals were increasingly dissolved out of the residual minerals. Mobilised metals are bound to organic material, clays, and Fe-Mn oxides due to changes in reduction and oxidation conditions in this horizon. Lead and Zn are not present (except in the surface horizon), and very few other metals are present in the CARB fraction. Generally, the distribution in profile PR4 is RES > FEMN > ORG > CARB except for Pb, which is FEMN > RES > ORG > CARB.

In rural soil profile PR5, the dominant fraction of metals is RES, with the exception of Pb (Fig. 9; Supplements 4.b). Lead is distributed among the fractions RES, FEMN, ORG and CARB depending on the horizons. The concentration of Cu, Ni and Zn in the FEMN fraction is higher than in the ORG fraction, which is related to the affinity of each metal and the content of clay, organic matter and Fe- Mn-oxy-hydroxides (Supplements 1 and 3).

Chromium is preferentially bound in the ORG fraction, Cu and Ni in the FEMN fraction, Zn equally in both (McGRATH, 1997; ETTLER et al., 2005; ŠORŠA, 2014; KHADHAR et al., 2020). The concentration of metals in the RES fraction increases with depth, except for Pb, while it decreases in the fractions FEMN and ORG, except for Cr and Ni. The metal content in the CARB fraction is generally very low. The high content of Pb and partly of other PTEs in the CARB fraction in the surface horizon is probably brought in with the dust and adsorbed to soil particles (TESSIER et al., 1979). The distribution of PTEs in profile PR5 is RES > FEMN > ORG > CARB except for Pb, which is RES > ORG > FEMN > CARB.

The predominant distribution of metal concentration by fraction in the rural geochemical profiles is as follows: RES > ORG or FEMN > CARB, except for Pb which is FEMN > RES or ORG > CARB.

The large variability of Pb and partly also of Cu, Ni and Zn in the fractions in rural soil profiles is due to their anthropogenic or partly anthropogenic origin. Rural soil profiles were developed in rural area and therefore the anthropogenic influences were mostly limited to the surface horizons. The parent material and pedogenic development had a dominant influence on the distribution of PTEs in the horizons, except for Pb.

3.3. Risk assessment

3.3.1. Risk Assessment Code

The environmental risk of the selected PTEs was assessed based on the concentration of PTEs in the CARB fraction (RATH et al.,

2009; LIU et al., 2010). The risk of PTEs in soil profiles varied according to the depth and each PTE (Tab. 5). The risk assessment by RAC in the profiles ranges from no risk to high risk. The RAC is highest in urban soil profiles PR1 and PR2, followed by rural profile PR5, and profiles PR3 and PR4 have almost the same RAC.

In the urban soil profiles, there is no risk for Cr and Ni in most horizons/layers, and the risk for Cu and Zn is low. The RACs for Pb range from no risk in the middle horizons in profile PR3, to low risk (from 1 to 10) in the entire urban soil profile PR1, the upper and two lower layers in PR2, and the upper horizon in PR3. A medium risk (from 11 to 30) exists in the middle layers of profile PR2 and in the two lowest horizons of PR3.

There is no risk for Pb in most horizons of rural soil profiles PR4 and PR5, but only in the upper horizon of profile PR5 is there a high risk of Pb mobilisation (from 31 to 50). There is a low risk for Cr, Cu and partially for Ni. There is a low risk of release of Zn from the CARB fraction to the environment in the upper horizons of PR4 and PR5.

According to the calculated RAC, the risk of mobilisation of metals to the environment in urban soil profiles is in the following order: Pb > Zn > Cu > Ni > Cr, considering the magnitude of the risk. The risk of mobilisation of PTEs in rural soil profiles varies as follows: Cr > Cu > Ni > Zn > Pb.

3.3.2 Risk assessment based on the sum of concentrations in the fractions CARB, FEMN and ORG

In the urban area, based on the official land use in the city of Sisak (KAMINSKI-KIRŠ, 2002), the urban soil profiles PR1, PR2

Table 5. The percentage of the metals Cr, Cu, Ni, Pb and Zn in the CARB fraction in soil profiles and assessment of the risk of release of PTEs into the environment (RAC).

Type	Soil profile	CARB Cr	CARB Cu	CARB Ni	CARB Pb	CARB Zn
		*E _M (%) = CARB _M / (CARB _M + FEMN _M + ORG _M + RES _M) x 100				
Urban soil profile	PR1-A (0-12 cm)	0.20	0.73	0.00	¹ 2.92	6.67
	PR1-I (12-29 cm)	0.20	0.99	0.00	2.73	6.64
	PR1-II (29-50 cm)	0.20	1.05	0.00	2.44	6.35
	PR1-III (50-70 cm)	0.20	1.01	0.00	2.39	5.77
	PR1-IV (70-100 cm)	0.20	2.23	8.54	2.22	7.58
	PR1-V (100-120 cm)	0.20	2.21	8.38	2.14	8.02
	PR2-I (0-15 cm)	0.11	1.74	0.00	6.40	9.02
	PR2-II (15-33 cm)	0.28	2.65	0.00	² 12.9	6.30
	PR2-III (33-60 cm)	0.26	2.94	4.14	16.9	2.10
	PR2-IV (60-88 cm)	0.13	4.54	5.95	6.61	2.70
	PR2-V (88-120 cm)	0.16	1.20	0.00	8.70	0.67
	PR3-A (0-14 cm)	0.78	1.24	0.43	1.40	5.52
	PR3-I (14-28 cm)	1.15	1.64	0.06	0.11	3.64
	PR3-II (28-67 cm)	1.54	4.55	0.05	0.19	0.00
	PR3-CG (67-130 cm)	2.29	5.51	0.06	0.31	0.01
PR3-Cg (Gr) (130-160 cm)	0.56	3.48	0.08	28.9	0.01	
PR3-Cg (160-200 cm)	0.92	2.40	3.66	30.0	0.01	
Rural soil profile	PR4-P (0-32 cm)	4.53	3.09	6.25	0.19	5.54
	PR4-I/C (32-58 cm)	4.90	4.52	0.06	0.17	0.01
	PR4-II/C (58-90 cm)	3.65	2.83	2.75	0.14	0.00
	PR4-III/C/G (90-115 cm)	4.08	0.00	1.55	0.15	0.00
	PR4-IV/C/G (115-160 cm)	7.96	4.34	1.47	0.15	0.01
	PR4-V/C/G (160-200 cm)	6.05	4.84	0.05	0.16	0.01
	PR5-P (0-30 cm)	3.79	3.16	3.64	³ 44.8	2.53
	PR5-G (30-80 cm)	5.58	3.20	3.33	0.27	0.93
	PR5-G (80-120 cm)	4.21	3.26	1.47	0.17	0.00

* The percentage of metal M extraction in the CARB fraction; M = Cr, Cu, Ni, Pb, Zn.

¹ bold numbers – low risk; ² red coloured numbers – medium risk; ³ yellow highlighted numbers – high risk

and PR3 are located in the parks and recreational areas. The prescribed limits for these land use for Cr, Cu, Ni, Pb and Zn are 500, 300, 200, 500 and 700 mg/kg dry soil, respectively (MESIĆ et al., 2008). In the rural area of Sisak, the rural soil profiles PR4 and PR5 correspond to the official land use in areas with soils for agricultural production (KAMINSKI-KIRŠ, 2002). MESIĆ et al. (2008) set limits for Cr, Cu, Ni, Pb and Zn of 100, 60, 50, 100 and 200 mg/kg dry soil, respectively, for soils for agricultural production.

The total concentrations determined with AAS (Tab. 4) were below the limits for the corresponding land use in all horizons/layers of both urban and rural soil profiles. Consequently, the sum of the concentration of CARB, FEMN and ORG is lower than the total concentration of the element (Tab. 4 and Supplements 4.a, b). The risk ratio for all selected PTEs in urban and rural soil profiles is $RR \leq 0$. There is no risk of contamination in all soil profiles.

The estimated risks for the release of PTEs to the environment and the risk to the environment and human health are negligible or very low. The soils in the soil profiles are neutral to slightly alkaline, they have a large buffering capacity, a high content of carbonates, humus and nitrogen (ŠORŠA, 2014), so the risk of PTE mobilisation and the impact on human health are low.

4. CONCLUSION

4.1. Urban soils

(a) The soil in the urban soil profiles PR1, PR2 and PR3 has mostly no developed horizons, only slightly different soil layers have formed. The pedogenesis of the whole profile PR1 and the upper layers of profiles PR2 and PR3 has been mainly influenced by human activities from ancient times until today, while the influence of the parent material on the soil properties is minor.

(b) The mineralogical composition in soil profiles PR1 and PR2 is consistent with the mineralogical composition of the siliciclastic alluvium of the Rivers Kupa and Odra. The mineralogy of profile PR3 corresponds to the mineralogical composition of loess. The urban profile PR1 was under strong anthropogenic influence throughout its depth, while the profiles PR2 and PR3 show anthropogenic influences in their mineralogical composition in their upper part. The lower part of profiles PR2 and PR3 is natural.

(c) The concentration of the PTEs Cr and Ni is similar in all soil profiles, but the concentration of Cu, Pb and Zn is higher in the urban soil profiles than in the rural profiles. The distribution of metals along the horizons/layers in the urban profiles PR1 and the upper parts PR2 and PR3 is irregular and strongly influenced by humans' excavation and contamination.

(d) The general distribution of PTEs concentration by fraction, determined by BCR SEP in urban soil profiles, is as follows: $RES > ORG$ or $FEMN > CARB$, except for Cu where $ORG > RES > FEMN > CARB$. Based on the geological background, pedogenesis, anthropogenic influences and the results of the analyses of BCR SEP, it can be concluded that the source of Cr is predominantly geogenic and that of Ni is partly geogenic and partly anthropogenic. Copper and Zn are mainly anthropogenic and to a lesser extent geogenic in origin. Lead was accumulated in the soil predominantly by anthropogenic input.

4.2. Rural soils

(a) The soil in rural soil profiles PR4 and PR5 has developed soil horizons. In addition to the parent material, groundwater and sur-

face water had a significant influence on the pedogenic development of the soil in profile PR4. The rural soil profile PR5 shows natural pedogenesis.

(b) The mineralogical composition in soil profiles PR4 and PR5 is consistent with the mineralogical composition of the carbonate alluvium of the River Sava and the siliciclastic alluvium of the Rivers Kupa and Odra, respectively. The rural soil profiles PR4 and PR5 are located on agricultural land and the anthropogenic influences are mainly limited to the surface horizons/layers.

(c) The concentration of PTEs Cr and Ni is similar in all studied soil profiles, but the concentration of Cu, Pb and Zn is lower in the rural soil profiles than in the urban profiles. Pedogenesis in rural soil profile PR4 was shaped by the high groundwater level and the distribution of metals in the horizons was influenced by frequent flooding. Profile PR5 shows natural pedogenesis and was influenced by humans only in the surface horizon.

(d) Distribution by geochemical fraction, determined using BCR SEP in rural soil profiles, is $RES > FEMN$ or $ORG > CARB$, except for Pb where $FEMN > RES$ or $ORG > CARB$. Based on the parent material, pedogenic development, limited anthropogenic influences and the results of the analyses of BCR SEP, it can be concluded that the parent material and pedogenic development had a predominant influence on the distribution of geochemical fractions in the horizons, except for Pb.

4.3. Urban vs. rural soil profiles

Soil horizons were undeveloped or weakly developed in the urban soils, in contrast to the developed horizons in the rural soil profiles. The differences in the mineralogical composition of the urban and rural soil profiles are primarily due to the fact that the parent material in the urban soil profiles was more anthropogenically influenced. The geological background has the greatest influence on the similar concentration of Cr and Ni in urban and rural soil profiles, but the concentration of Cu, Pb and Zn was significantly higher in urban soil profiles than in rural ones, due to historical land use and repeated excavation and contamination. The distribution by geochemical fraction for Cr, Ni and Zn was similar in all profiles. The distribution of fractions for Cu in urban soil profiles and for Pb in rural soil profiles was predominantly anthropogenically influenced.

4.4. Risk assessment

(a) According to the calculated RAC of the studied PTEs in urban soil profiles, the magnitude of risk is in the following order: $Pb > Zn > Cu > Ni > Cr$. The risk of mobilisation of PTEs in rural soil profiles varies as follows: $Cr > Cu > Ni > Zn > Pb$. The high risk is recorded only in one surface horizon of one rural profile.

(b) The results of the total concentration of selected PTEs determined by AAS were below the limits for the corresponding land use in all horizons/layers of both urban and rural soil profiles. Consequently, the sum of the concentration of CARB, FEMN and ORG is below the prescribed limits. The calculated risk ratio for all studied PTEs in urban and rural soil profiles is $RR \leq 0$. There is no risk of metal release in any soil profile.

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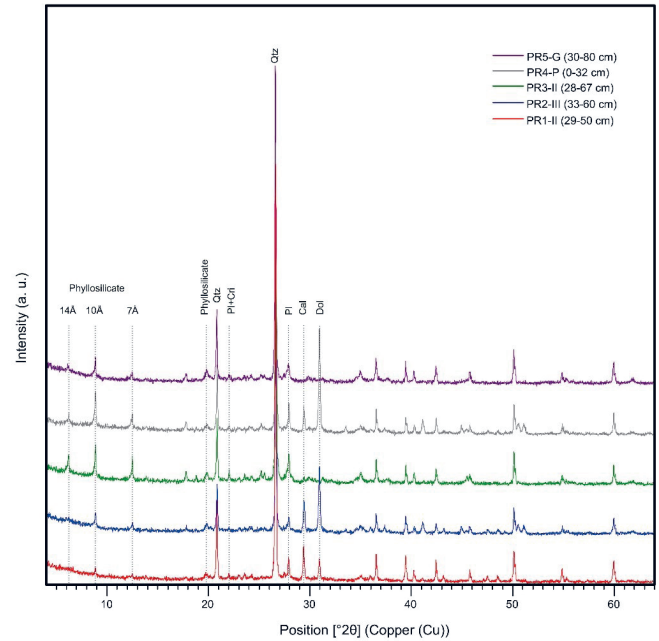
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Supplement 1. Mineral composition of soil from urban and rural soil profiles PR1, PR2, PR3, PR4 and PR5 determined by X-ray diffraction.

Type of soil profiles	Soil samples from soil horizons/layers	wt. %					
		Qtz	Phil	Cal	Dol	Pl	Cri
Urban soil profiles	PR1-A (0-12 cm)	46	32	11	7	4	-
	PR1-I (12-29 cm)	48	30	9	9	4	-
	PR1-II (29-50 cm)	56	26	11	4	3	-
	PR1-III (50-70 cm)	49	31	11	4	4	-
	PR1-IV (70-100 cm)	57	27	10	3	3	-
	PR1-V (100-120 cm)	58	29	8	3	2	-
	PR2-I (0-15 cm)	47	27	9	14	3	-
	PR2-II (15-33 cm)	45	17	20	14	4	-
	PR2-III (33-60 cm)	38	31	8	20	3	-
	PR2-IV (60-88 cm)	40	42	4	10	4	-
	PR2-V (88-120 cm)	37	47	3	10	3	-
	PR3-A (0-14 cm)	59	32	-	-	5	4
	PR3-I (14-28 cm)	55	37	-	-	4	4
	PR3-II (28-67 cm)	53	35	-	-	7	5
	PR3-CG (67-130 cm)	52	39	-	-	5	4
PR3-Cg (Gr) (130-160 cm)	47	44	-	-	6	3	
PR3-Cg (160-200 cm)	52	40	-	-	5	3	
Rural soil profiles	PR4-P (0-32 cm)	42	27	4	23	4	-
	PR4-I/C (32-58 cm)	35	27	9	26	3	-
	PR4-II/C (58-90 cm)	33	42	6	17	2	-
	PR4-III/C/G (90-115 cm)	33	45	-	19	4	-
	PR4-IV/C/G (115-160 cm)	36	28	11	21	4	-
	PR4-V/C/G (160-200 cm)	39	27	9	23	2	-
	PR5-P (0-30 cm)	71	26	-	-	3	-
	PR5-G (30-70 cm)	64	32	-	-	4	-
	PR5-G (70-130 cm)	60	36	-	-	4	-

Abbreviations: Qtz, quartz; Phil, phyllosilicates; Cal, calcite; Dol, dolomite, Pl, plagioclase and Cri, cristobalite.

Supplement 2. X-ray diffraction patterns of selected representative soil samples: PR1-II (29-30 cm), PR2-III (33-60 cm), PR3-II (28-67 cm), PR4-P (0-32 cm) and PR5-G (30-80 cm). Abbreviations for minerals are the same as in Supplement 1.



Supplements 3. The concentration (in wt. %) of major elements oxides and Ba in soil samples from soil profiles PR1, PR2, PR3, PR4 and PR5.

	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	TiO ₂	P ₂ O ₅	Cr ₂ O ₃	Ba	*LOI	SUM
Soil profile / Detection limit	0.1	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.001	0.01	0.1	0.01
PR1-A (0-12 cm)	58.2	8.89	3.64	6.17	1.95	0.79	1.45	0.09	0.62	0.70	0.012	0.03	16.5	99.0
PR1-I (12-29 cm)	58.4	8.35	3.52	7.28	1.95	0.75	1.39	0.10	0.57	0.81	0.017	0.03	15.8	99.0
PR1-II (29-50 cm)	60.4	7.92	3.36	7.04	1.46	0.72	1.31	0.10	0.48	1.04	0.012	0.03	15.6	99.5
PR1-III (50-70 cm)	62.0	7.87	3.28	6.81	1.30	0.74	1.32	0.10	0.52	1.07	0.011	0.03	14.5	99.5
PR1-IV (70-100 cm)	61.5	7.92	3.21	6.34	1.17	0.70	1.33	0.09	0.59	1.07	0.010	0.02	14.9	98.3
PR1-V (100-120 cm)	62.0	7.75	3.25	6.81	1.27	0.71	1.34	0.10	0.48	1.07	0.013	0.03	14.8	98.9
Urban soil profiles														
PR2-I (0-15 cm)	49.8	9.47	3.84	10.1	3.60	0.89	1.49	0.10	0.60	0.24	0.013	0.03	19.7	99.5
PR2-II (15-33 cm)	51.8	7.05	2.80	13.5	3.82	0.96	1.17	0.07	0.45	0.12	0.007	0.02	17.6	99.3
PR2-III (33-60 cm)	47.2	9.99	3.72	11.3	5.34	0.83	1.59	0.08	0.66	0.11	0.015	0.03	18.5	99.4
PR2-IV (60-88 cm)	54.6	14.7	5.45	3.80	2.54	0.87	2.19	0.11	0.95	0.19	0.018	0.04	13.0	98.4
PR2-V (88-120 cm)	53.8	14.8	5.66	4.08	2.90	0.83	2.23	0.12	0.86	0.19	0.019	0.04	13.7	99.3
PR3-A (0-14 cm)	62.8	13.7	5.39	1.14	1.43	1.23	2.08	0.13	1.08	0.16	0.014	0.05	9.92	99.1
PR3-I (14-28 cm)	63.7	14.6	5.76	0.97	1.44	1.29	2.19	0.11	1.13	0.15	0.012	0.06	7.88	99.3
PR3-II (28-67 cm)	64.2	15.1	5.73	0.72	1.56	1.33	2.34	0.10	1.18	0.15	0.015	0.05	6.90	99.3
PR3-CG (67-130 cm)	63.4	15.8	5.70	0.63	1.56	1.38	2.39	0.08	1.16	0.11	0.024	0.05	6.92	99.2
PR3-Cg (Gr) (130-160 cm)	62.5	17.6	4.44	0.50	1.10	0.94	2.18	0.03	1.20	0.03	0.018	0.05	8.55	99.1
PR3-Cg (160-200 cm)	60.3	17.4	5.78	0.56	1.29	0.98	2.29	0.03	1.07	0.05	0.025	0.05	9.16	98.9
PR4-P (0-32 cm)	48.5	9.37	3.49	10.2	5.34	0.83	1.65	0.08	0.62	0.20	0.010	0.03	18.9	99.2
PR4-I/C (32-58 cm)	44.5	10.6	3.93	11.9	5.57	0.82	1.74	0.09	0.65	0.11	0.014	0.03	19.4	99.4
PR4-II/C (58-90 cm)	45.8	14.8	5.44	7.29	4.70	0.74	2.35	0.05	0.75	0.14	0.017	0.04	17.4	99.5
PR4-III/C/G (90-115 cm)	52.6	17.5	7.12	1.78	2.12	0.78	2.51	0.15	0.89	0.16	0.021	0.05	13.5	99.2
PR4-IV/C/G (115-160 cm)	42.5	11.2	4.32	12.4	5.56	0.77	1.77	0.12	0.69	0.11	0.013	0.03	20.1	99.5
PR4-V/C/G (160-200 cm)	44.5	9.32	3.48	13.0	6.10	0.80	1.52	0.08	0.63	0.10	0.013	0.03	19.9	99.5
Rural soil profiles														
PR5-P (0-30 cm)	67.6	13.1	4.69	0.52	1.07	1.03	2.21	0.12	0.97	0.16	0.016	0.04	7.72	99.2
PR5-G (30-70 cm)	66.6	13.9	5.15	0.52	1.17	1.01	2.34	0.11	0.95	0.12	0.015	0.04	7.20	99.1
PR5-G (70-130 cm)	64.5	15.0	5.97	0.46	1.29	0.97	2.52	0.09	0.90	0.11	0.015	0.04	7.08	98.9

* LOI – Loss on ignition

Supplements 4a. The concentration in (mg/kg) of Cr, Cu, Ni, Pb and Zn as PTEs in geochemical fractions, obtained with BCR SEP, of soil samples from urban soil profiles PR1, PR2 and PR3.

Soil profile	Chromium (mg/kg)				Copper (mg/kg)				Nickel (mg/kg)				Lead (mg/kg)				Zinc (mg/kg)			
	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES
PR1	* < DL	< DL	4.08	14.2	0.71	1.70	51.5	44.0	0.00	2.75	7.80	30.0	4.20	17.4	28.1	94.2	9.44	25.5	29.2	77.4
PR1-A (0-12cm)	* < DL	< DL	4.08	14.2	0.71	1.70	51.5	44.0	0.00	2.75	7.80	30.0	4.20	17.4	28.1	94.2	9.44	25.5	29.2	77.4
PR1-I (12-29cm)	< DL	< DL	3.70	14.4	1.24	2.93	71.5	49.3	0.00	3.95	7.16	29.4	4.82	17.8	18.0	136	9.79	27.1	28.7	81.7
PR1-II (29-50cm)	< DL	< DL	3.79	13.8	1.53	3.54	87.7	53.6	0.00	3.91	8.41	28.4	4.79	13.6	21.6	156	10.1	31.4	35.8	82.0
PR1-III (50-70cm)	< DL	< DL	3.74	14.2	1.44	4.50	82.0	54.2	0.00	3.30	7.43	26.8	5.00	26.7	23.8	154	8.55	33.4	28.1	78.0
PR1-IV (70-100cm)	< DL	< DL	6.20	11.3	3.28	12.4	77.2	54.6	3.58	16.7	9.00	12.7	5.02	81.5	68.1	71.4	11.4	58.4	21.0	59.0
PR1-V (100-120cm)	< DL	< DL	5.64	11.9	3.46	12.9	80.8	59.6	3.56	16.2	8.82	13.9	5.03	68.9	71.5	89.1	12.6	59.3	24.1	61.1

Soil profile	Chromium (mg/kg)				Copper (mg/kg)				Nickel (mg/kg)				Lead (mg/kg)				Zinc (mg/kg)			
	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES
PR2	< DL	< DL	14.4	18.1	0.91	1.22	20.5	29.6	0.00	4.10	8.19	33.9	5.65	10.7	24.2	47.7	17.8	34.6	45.5	98.9
PR2-I (0-15cm)	< DL	< DL	14.4	18.1	0.91	1.22	20.5	29.6	0.00	4.10	8.19	33.9	5.65	10.7	24.2	47.7	17.8	34.6	45.5	98.9
PR2-II (15-33cm)	< DL	< DL	< DL	12.6	0.95	1.27	10.3	23.4	0.00	1.92	4.72	26.1	6.12	6.55	10.8	24.1	4.96	7.7	14.8	51.4
PR2-III (33-60cm)	< DL	< DL	< DL	13.6	0.96	3.71	6.4	21.6	1.85	13.3	6.12	23.4	5.90	5.83	9.08	14.1	1.48	10.3	7.1	51.6
PR2-IV (60-88cm)	< DL	< DL	6.98	20.2	2.07	7.31	5.29	30.9	3.70	22.0	10.3	26.2	4.27	30.6	11.0	18.7	2.84	20.4	13.0	68.7
PR2-V (88-120cm)	< DL	< DL	< DL	22.0	0.56	2.63	5.43	37.9	0.00	10.3	6.37	42.4	4.06	6.78	8.99	26.9	0.67	5.8	7.3	86.7

Soil profile	Chromium (mg/kg)				Copper (mg/kg)				Nickel (mg/kg)				Lead (mg/kg)				Zinc (mg/kg)			
	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES
PR3	0.20	0.57	5.19	19.5	0.32	4.18	3.71	17.5	0.10	2.94	2.86	17.4	0.60	21.6	8.50	12.1	7.65	23.8	23.8	83.5
PR3-A (0-14cm)	0.20	0.57	5.19	19.5	0.32	4.18	3.71	17.5	0.10	2.94	2.86	17.4	0.60	21.6	8.50	12.1	7.65	23.8	23.8	83.5
PR3-I (14-28cm)	0.30	0.80	4.61	20.4	0.35	3.65	1.71	15.7	< DL	3.16	2.38	17.8	< DL	16.5	6.00	9.60	3.25	10.3	11.7	64.0
PR3-II (28-67cm)	0.45	1.63	3.76	23.4	1.01	3.19	1.19	16.8	< DL	3.38	2.57	21.2	< DL	8.87	4.25	5.88	< DL	3.05	3.85	57.1
PR3-CG (67-130cm)	0.69	2.08	4.62	22.8	1.16	2.96	1.59	15.4	< DL	2.31	2.55	17.8	< DL	5.50	2.79	3.57	< DL	3.69	4.42	46.8
PR3-Cg (Gr) (130-160cm)	0.15	1.94	5.46	19.1	0.70	3.19	1.81	14.4	< DL	1.51	3.31	11.3	3.53	3.27	4.41	1.00	< DL	3.07	4.12	25.1
PR3-Cg (160-200cm)	0.30	2.49	6.01	23.7	0.58	3.45	2.01	18.1	0.90	3.07	4.67	15.9	3.53	3.14	4.51	0.60	< DL	3.75	6.31	30.6

* Detection limit (DL) in mg/kg of Cr<0.072; Cu<0.010; Ni<0.027; Pb<0.073; Zn<0.006.

Supplements 4b. The concentration in (mg/kg) of Cr, Cu, Ni, Pb and Zn as PTEs in geochemical fractions, obtained with BCR SEP, of soil samples from rural soil profiles PR4 and PR5.

Soil profile	Chromium (mg/kg)				Copper (mg/kg)				Nickel (mg/kg)				Lead (mg/kg)				Zinc (mg/kg)			
	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES
PR4	0.95	2.06	3.59	14.4	0.70	1.34	7.49	13.1	1.63	5.30	2.76	16.4	< DL	12.3	7.30	< DL	4.56	12.1	9.86	55.9
PR4-P (0-32cm)	0.95	2.06	3.59	14.4	0.70	1.34	7.49	13.1	1.63	5.30	2.76	16.4	< DL	12.3	7.30	< DL	4.56	12.1	9.86	55.9
PR4-I/C (32-58cm)	1.03	2.06	3.67	14.2	0.95	2.49	3.48	14.1	* < DL	5.12	1.94	16.8	< DL	8.02	3.45	9.40	< DL	2.01	2.22	46.6
PR4-II/C (58-90cm)	0.97	1.87	5.49	18.2	0.75	2.09	4.04	19.7	0.85	2.98	2.93	24.2	< DL	9.10	6.25	11.2	< DL	2.16	3.07	64.9
PR4-III/C/G (90-115cm)	1.39	2.24	8.03	22.5	0.00	4.97	2.16	20.5	0.58	8.16	5.92	22.8	< DL	11.3	3.17	9.62	< DL	10.0	9.27	65.0
PR4-IV/C/G (115-160cm)	1.82	1.11	4.16	15.8	0.93	1.34	2.74	16.4	0.45	9.71	1.84	18.7	< DL	7.46	9.24	7.71	< DL	1.44	1.74	51.9
PR4-V/C/G (160-200cm)	1.14	0.90	4.24	12.6	0.88	1.94	2.61	12.7	< DL	8.89	2.03	17.0	< DL	7.16	9.75	5.50	< DL	1.54	1.71	39.2

Soil profile	Chromium (mg/kg)				Copper (mg/kg)				Nickel (mg/kg)				Lead (mg/kg)				Zinc (mg/kg)			
	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES	CARB	FEMN	ORG	RES
PR5	0.86	0.93	5.70	15.2	0.66	4.63	2.06	13.6	1.05	7.41	2.13	18.3	11.4	< DL	6.86	7.12	1.59	6.28	5.81	49.3
PR5-P (0-30cm)	0.86	0.93	5.70	15.2	0.66	4.63	2.06	13.6	1.05	7.41	2.13	18.3	11.4	< DL	6.86	7.12	1.59	6.28	5.81	49.3
PR5-G (30-80cm)	1.25	1.06	4.43	15.7	0.68	4.42	1.50	14.7	0.81	2.33	2.61	18.6	< DL	< DL	7.07	6.60	0.57	4.92	3.91	51.9
PR5-G (80-120cm)	0.90	1.45	3.71	15.3	0.91	4.01	1.35	21.6	0.45	2.46	3.91	23.8	< 0.073	12.7	2.34	6.30	< 0.006	3.73	3.26	58.6

* Detection limit (DL) in mg/kg of Cr<0.072; Cu<0.010; Ni<0.027; Pb<0.073; Zn<0.006.