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Hazardous elements speciation in sandy, alkaline coal mine overburden by using different sequential extraction procedures

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ABSTRACT

This paper deals with the problem of hazardous elements (HE) speciation in sandy, alkaline coal mine overburden destined for restoration. Two sequential extraction procedures [five stages Tesier's (T) and seven stages Zeien and Brümmer's method (ZB)] were employed that focused on potentially bioavailable HE fractions previously found in plants growing during this soil restoration process. The results showed that the selection of the extraction procedure in HE speciation is essential, due to the different potential threats of HE fractions obtained for plants. The biggest residual fraction obtained by both extractions suggest geogenic origin of Cu, Zn, Ni, Cr and Pb. Tesier's extraction procedure works reasonably well for low concentration of water soluble and exchangeable HEs, whilst giving higher values for their organically bound forms. Zeien and Brümmer's method, however, was found to be more appropriate for evaluation of the mobility of HE as Mn and Fe oxide fractions. The principal component analysis test estimated three main groups where the relationship between soil properties (pH, clay and silt), total content of element and available fractions (Zn, Ni, Cr, Pb-T and Ni-ZB) was defined as a PC 1 group. Other PC 2 and PC 3 from the PCA analysis include C_{org} and CEC, and available Cu-T and Cr, Pb-ZB, respectively. The PC 3 factor linked fine sand and available Zn-ZB. Pearson's correlation coefficients showed a high correlation between available HE and high pH(KCl) obtained by T-extraction, and Ni by Zn-extraction. Also, clay, silt and fine sand were highly correlated with the Ni-ZB available forms.

Keywords: overburden, hazardous elements, sequential extraction procedures, principal component analysis

INTRODUCTION

Worldwide surface coal exploitation has made an impact on the environment by producing massive overburden stock piles with very heterogeneous physico-geochemical properties (Ribeiro *et al.*, 2010; Quispe *et al.*, 2012; Oliveira *et al.*, 2012a,b). The restoration of such soils is usually associated with the complex problem of overburden such as bad physical properties and low fertility, especially if the humus topsoil layer has not been preserved during the coal excavation (Silva *et al.*, 2009a,b). Besides, the problem of overburden soil restoration is very often associated with increased accumulation of hazardous elements (HE) from subsoil layers (Wong, 2003). Such a coal mine sandy overburden dump,

deposited near one of the biggest thermal power plants' in Serbia (Kostolac), is planned for rehabilitation as a measure of applicable regulations (Spatial plan of RS, 1996), in order to reestablish the self-sustaining agricultural plant production on this respective area (~4,000 ha).

Generally, the excess of HE in the root zone induces a problem of overburden reclamation, especially in assessing whether crops grown there absorbs HE at a level likely to constitute a hazard to animals and humans (Bhuiyan *et al.*, 2010). Tested amelioration measures of Kostolac's overburden material, however, showed an intensive accumulation of Ni and Cr in agricultural plants despite their lower MPC total content (<50 mg kg⁻¹ of Ni, <100 mg kg⁻¹ of Cr, respectively), (Kabata-Pendias, 2011), so the problem of adequate soil

rehabilitation remains (Licina *et al.*, 2007). In fact, the obtained results stress that total concentration of HEs in soils does not give sufficient information about the mobility of elements and, in many instances, biological toxicity of the elements is related more closely to the concentrations of their particular physico-chemical forms (Žemberyová *et al.*, 2006). As the toxicity of hazardous elements in soils is dependent on their chemical form more than their total concentration, it becomes fundamental to know the element distribution between different mineral phases (Giacalone *et al.*, 2005). Consequently, element cations in soils may be present in several different physico-chemical forms (Uree and Davidson, 2008; Arenas-Lago *et al.*, 2013; Hower *et al.*, 2013; Cerqueira *et al.*, 2011, 2012) and, as a result, determining HE fractionation in soils is essential in predicting their fate, especially for long-term risk assessment (Basta *et al.*, 2005). Therefore, the speciation studies of hazardous elements in the environment are widely used in investigations by furnishing detailed information about the origin, mode of occurrence, mobilisation and their transport, and also by assessing the potentially mobile, bioavailable or ecotoxic phases of the sample (Borůvka *et al.*, 2005). Now, speciation studies are confirmed as a convenient method for the investigation of HE in agro-ecological conditions (Kierczak *et al.*, 2008). Generally, all such studies are based on the five-stage extraction procedure of Tessier *et al.* (1979), but a wide range of techniques is now available to study environmental problems in which various extraction reagents and experimental conditions are used (Kierczak *et al.*, 2008).

The determination of physico-chemical properties of the investigated overburden characteristics was attempted for rehabilitation purposes, but the main objective of this study was to assess the potential risks of the chemical forms of HE by using two sequential extraction procedures: a five-stage procedure of Tessier (1979) and a seven-step procedure of Zeien and Brümmer (1989). The employed extraction procedure focused on potentially bioavailable HE fractions, previously found as a part of non-toxic total HE concentration evaluation for plants (Licina *et al.*, 2007). Because the employed methods have a variety of different extraction reagents, the potentially toxic amounts of HEs will be interrelated with the main soil characteristics using principal component analysis (PCA) evaluation.

METHODOLOGY

Soil analysis

The studied area was located near the open coal mine pit at one of the largest national coal mine power plants (Kostolac), located about 50 km SE of Belgrade-Serbia (44° 42'56" N, 21°10'44" E). Three depths were sampled (0–30cm, 30–60cm, 60–90cm) as nine average soil profiles (three at one profile) from a 10 ha plot. Soil samples were air dried (35° C), and screened to pass through a 2-mm sieve. Particle-size distribution was determined by wet sieving and sedimentation using the pipette sampling technique.

Soil chemical properties [pH, calcium carbonate (CaCO_3), organic carbon (C_{org}), total (N_{tot}) and available nitrogen (N-NH_4 , N-NO_3) and AL-available phosphorus (P_2O_5) and potassium (K_2O)] were determined according to standard methods of soil analysis (Westerman, 1990). Soil pH was measured in water and 1M potassium chloride (KCl) solution mixed 2.5:1 with soil. Inorganic C (CaCO_3), was quantified by the Scheibler method. Total N was determined by the Kjeldahl method. Organic C was quantified by the dichromate method. Available N was determined by hot distillation after extraction in 2M KCl solution. Available P was measured by spectrophotometry after extraction in AL solution (0.1 M ammonium lactate and 0.4 M acetic acid). Available K was quantified by flame photometry after extraction in AL solution. Pseudo total element concentrations in soil samples were quantified by atomic adsorption spectrophotometry (AAS, Varian SpectraAA 202 FS), in flame acetylene/air, after digestion using nitric acid (HNO_3) conc. + hydrogen peroxide (H_2O_2) (US EPA, 1986).

The analytical quality of soil control was assured by participation in the inter laboratory proficiency testing (PT) program "15 – Soil analysis", for annual series 2011 – 2012 and 2012 – 2013, provided by BIPEA, Gennevilliers, France.

Sequential extraction procedures

Tessier's analytical procedure (1979) consists of the following steps: 1, water-soluble and exchangeable; 2, specifically adsorbed and carbonate bound; 3, elements bound to Mn and Fe oxides; 4, elements bound to organic matter; and 5, residual fraction.

Zeien and Brümmer's analytical procedure (1989) contains the following fractions: 1, water soluble and exchangeable elements; 2, easily mobilisable; 3, elements bound to Mn oxides; 4, organically-bound elements; 5, elements bound to amorphous Fe oxides; 6, elements bound to crystalline Fe oxides; and 7, residual fraction.

Statistical analysis

The statistical treatment of the data was performed using a STATISTICA program (StatSoft). In order to get information about the relationships between basic physico-chemical properties and content of HEs in different fractions, a factor analysis using Varimax normalised rotation was carried out. Varimax rotation was applied because orthogonal rotation minimises the number of variables with a high loading on each component and facilitates the interpretation of results (Micó *et al.*, 2006).

RESULTS AND DISCUSSION

Soil properties

Soil properties analysed in the study area were given in Table 1. The overburden used in the present study was highly

Table 1 Basic physic-chemical properties of analysed overburden (mean \pm standard error)

Soil layer	0–30 cm	30–60 cm	60–90 cm
pH (H ₂ O)	9.04 \pm 0.00	9.12 \pm 0.01	9.05 \pm 0.00
pH (KCl)	7.72 \pm 0.01	8.29 \pm 0.01	8.23 \pm 0.01
Clay (%)	7.87 \pm 0.21	5.81 \pm 0.40	6.32 \pm 0.60
Silt (%)	14.13 \pm 0.26	10.19 \pm 0.64	12.22 \pm 0.51
Fine sand (%)	64.02 \pm 0.83	61.63 \pm 0.76	61.25 \pm 1.04
CEC (mmol kg ⁻¹)	8.50 \pm 0.03	7.40 \pm 0.14	5.43 \pm 0.23
C _{org} (%)	0.91 \pm 0.01	0.77 \pm 0.00	0.02 \pm 0.00
N _{tot} (%)	0.02 \pm 0.00	0.03 \pm 0.00	0.01 \pm 0.00
NH ₄ -N	7.17 \pm 0.12	4.36 \pm 0.22	3.45 \pm 0.08
NO ₃ -N	6.33 \pm 0.09	2.73 \pm 0.12	0.00 \pm 0.00
P ₂ O ₅ (mg/100g)	3.37 \pm 0.22	6.10 \pm 0.06	7.32 \pm 0.09
K ₂ O (mg/100g)	7.43 \pm 0.18	4.33 \pm 0.03	4.40 \pm 0.06
Ca (mg/100g)	114.69 \pm 2.27	111.21 \pm 0.67	117.24 \pm 1.47
Mg (mg/100g)	12.08 \pm 0.02	11.18 \pm 0.36	11.84 \pm 0.23
Fe (mg kg ⁻¹)	8693.5 \pm 135.4	5897.3 \pm 271.2	7935.9 \pm 86.8
Mn (mg kg ⁻¹)	389.67 \pm 12.6	283.53 \pm 8.76	287.00 \pm 11.9
Zn (mg kg ⁻¹)	28.48 \pm 0.82	13.03 \pm 0.25	14.48 \pm 0.22
Cu (mg kg ⁻¹)	10.08 \pm 0.48	6.97 \pm 0.14	8.11 \pm 0.10
Ni (mg kg ⁻¹)	48.34 \pm 0.12	12.83 \pm 0.43	13.55 \pm 0.31
Cr (mg kg ⁻¹)	33.17 \pm 0.27	10.74 \pm 0.04	10.31 \pm 0.17
Pb (mg kg ⁻¹)	10.73 \pm 0.04	4.20 \pm 0.09	5.73 \pm 0.25

alkaline soil with very low content of organic matter and available nutrients (Table 1). According to the USDA soil classification, it belongs to sandy soils having more than 78% of sand.

The pseudo-total contents of the MHs were under the MPC values (Cu < 100 mg kg⁻¹; Zn < 300 mg kg⁻¹; Pb < 100 mg kg⁻¹; Ni < 50 mg kg⁻¹; Cr < 100 mg kg⁻¹) (Kabata-Pendias, 2011), indicating that the potential accumulation in plant organs could be expected only for Ni which was close to critical 50 mg kg⁻¹. Therefore, according to the obtained results, this overburden should not be treated as waste soils with severe HE pollution that demands a large scale of revegetation and reclamation measures.

Hazardous element characterization by using two sequential extraction procedures

Two sequential extractions are employed to assess operationally defined element fractions which can be related to potentially mobile phases. Estimated stable forms of HEs as the residual fraction in both procedures are unlikely to be released under weathering conditions. On the other hand, soluble, exchangeable and chelated fractions are quite labile and hence more available for plants and food chain (Maiz *et al.*, 2000). The results for Zn, Cu, Ni, Cr, and Pb are shown in Figure 1 as percentages of the different fractions with respect to the total amount in the soil.

Tessier's method (T) extracted more labile fractions of Zn than Zeien and Brümmer's method (Z). According to the

latter (Z), the Zn was not present in first four fractions [Zn(b)], but the similar T-fractions (exchangeable and organically bound) contained a certain amount of this element [Zn(a)]. For Cu and Ni, both extractions gave similar results, however, in a T-procedure these elements were more organically bounded [Cu(c), Ni(e)], while in Z-extraction procedure, these elements had more Mn and Fe oxides [Cu(d), Ni(f)]. Chromium bound to organic matter was not extracted by Z-procedure [Cr(h)], but T-procedure detected a part of total Cr in organic fraction in layers (0–30 cm: 13.53 %; 30–60 cm: 12.80 %; 60–90 cm: 12.29 %) [Cr(g)]. Although chromium is able to exist in several oxidation states, the most stable and common forms are trivalent Cr(III) and hexavalent Cr(VI) species, which display quite different geochemical, biological and toxicological properties. Cr(VI) is considered the most toxic form of chromium. Cr(VI) is usually associated with oxygen as chromate (CrO₄²⁻) or dichromate (Cr₂O₇²⁻) ions. In contrast, Cr(III) in the form of oxides, hydroxides or sulfates is much less mobile and exists mostly bound to organic matter in soil and aquatic environments (Ulucinar and Onar, 2005). Concerning the water soluble fraction, Pb was not identified by Z-extraction, having a lower concentration of its organically bound form [Pb(j)]. Generally, the T-procedure was exposed as more sensitive to low concentrations of water soluble and exchangeable elements and to the potentially mobile organically bound fraction compared to the Z-procedure. With three identified fractions as oxides (Mn oxides, amorphous Fe and crystalline Fe), the Z-extraction procedure is therefore more orientated to the soils rich in these fractions of HE (Kabala and Sing, 2001). Thus, the T-procedure was shown as being more appropriate for investigating this sandy alkaline type of soil revealing the possibility that potentially mobile HE fraction could be accumulated by plants. Meanwhile, both types of sequential extraction showed the highest amount of each element in the residual fraction. This consequently points out the geogenic origin of the HEs, but the presence of Pb in available fractions [Pb(i)] indicates a possible anthropogenic impact on soil as found in other investigation (Boruvka *et al.*, 2005).

Principal component analyses

The use of PCA allows a considerable reduction in the number of variables and the detection of structure in the relationships between the results of two employed sequential extraction procedures and soil characteristics. It was performed by evaluation of the principal components and computing eigenvalues. Only the eigenvalues higher than 1 (Kaiser criterion), giving a cumulative variance above 91%, were retained. Then the rotation of the principal components was carried out by the Varimax normalised method. The results, presented as factor loadings of the rotated matrix, are shown in Table 2. Factor loadings lower than 0.7 have been removed.

Three factors described satisfactory the basic soil characteristics, available and total content of elements (Table 2). The first PCA component (PC 1) accounts for the most

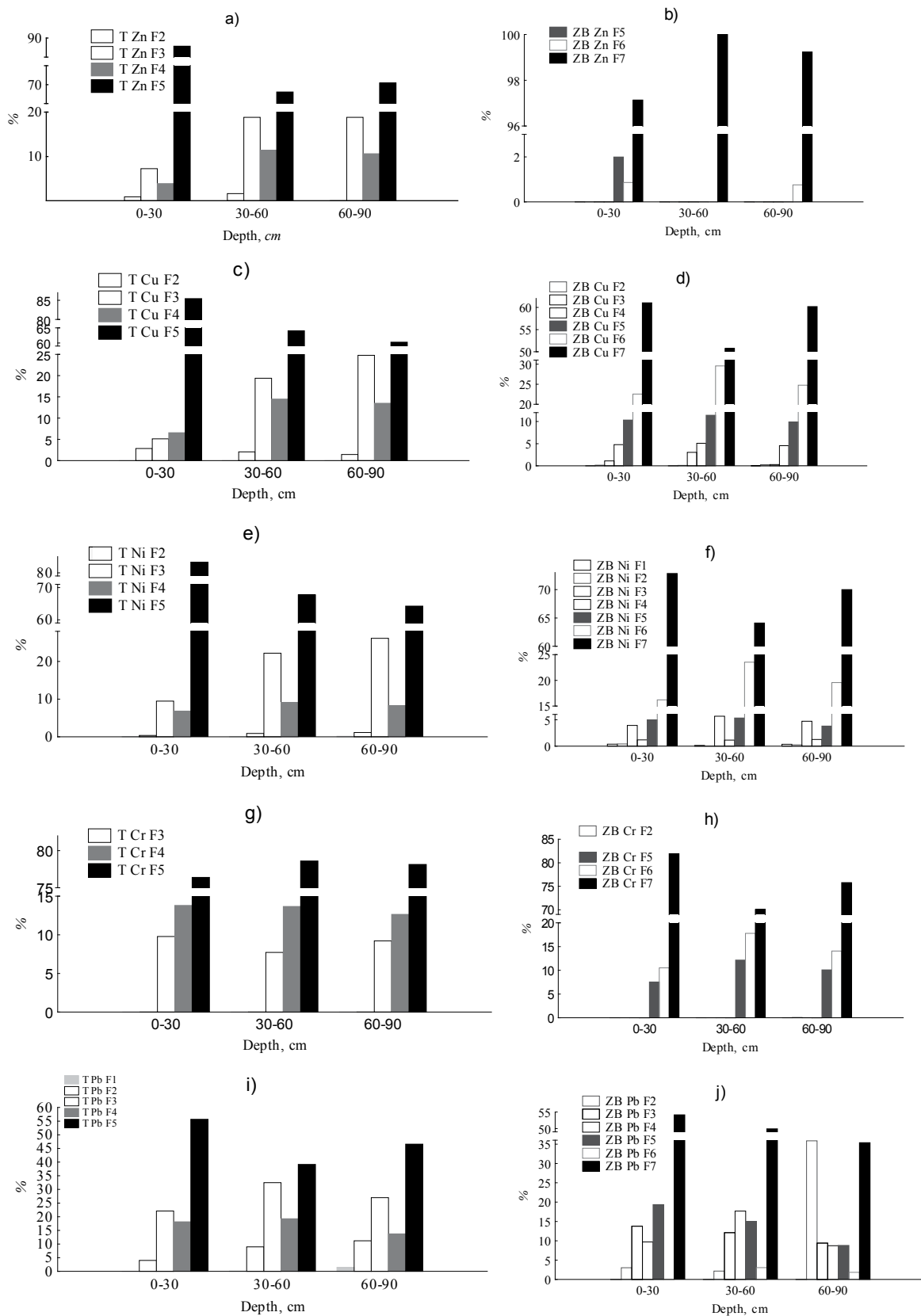


Figure 1 The percentages of the total amount of different fractions of heavy metals.

Table 2 Factor rotated matrix divided variables into three groups by principal component analysis

	PC 1	PC 2	PC 3
pH(H ₂ O)	-0.80795		
pH(KCl)	-0.91837		
C _{org}		0.92754	
CEC		0.82484	
Clay	0.72202		
Silt	0.83318		
Fine sand			0.77731
Fe	0.87682		
Mn	0.85353		
Zn T	-0.71108		
Cu T		-0.73732	
Ni T	0.88491		
Cr T	0.90134		
Pb T	0.76414		
Zn	0.89606		
Cu	0.88779		
Ni	0.88345		
Cr	0.87209		
Pb	0.94567		
Zn ZB			0.78344
Cu ZB			
Ni ZB	0.73606		
Cr ZB		-0.78926	
Pb ZB		-0.89585	
Eigenvalue	16.0775	4.7238	1.24226
% Total variance	66.9895	19.6825	5.17606
Cumulative eigenvalue	16.0775	20.80129	22.04355
Cumulative %	66.9895	86.67206	91.84812

T, heavy metal obtained by Tesier's procedure; ZB, heavy metal obtained by Zeien and Brümmer's procedure.

important associations and is strongly correlated with soil pH, contents of clay, silt and total content of HE, including available Ni obtained by both extractions, as illustrated by the high factor loading in PC 1. The first component also included available Zn, Cr and Pb according to T-extraction (Zn, Cr, Pb-T). Variables that are correlated with one another are combined into factors which are thought to be representative of the underlying correlation (Zhang, 2006). Second principal component (PC2), as organic C and CEC, were present as basic soil characteristics. This PC 2 also includes available Cu (Cu-T) and available Cr and Pb (Cr, Pb-ZB), despite that Cu retention and partitioning in soils are related to the presence of high organic matter (Impellitteri *et al.*, 2002). The third component (PC 3) is linked to fine sand and available Zn according to ZB-extraction (Zn-ZB).

Results obtained by PCA were confirmed by analysing the correlation matrix. Table 3 presents Pearson's correlation coefficients between soil characteristics (pH, C_{org}, CEC, clay, silt, sand) and available HE (Zn, Cu, Ni, Cr, Pb) according to different extraction procedure.

Generally, the availability of HE in soil is influenced by many factors, but the present high value in the soil is a principal one in T-extraction. Available forms of Ni obtained by both extractions also have a strong negative correlation with high soil pH, so the change in Ni speciation by lowering pH by root activity possibly will cause its increased uptake by plants (Pinel *et al.*, 2004). Also, although fine sand, clay and silt were not the dominant fractions in the investigated sandy soil, these fractions influenced the availability of Cr, Pb (T-extraction) and Ni, Cu (ZB-extraction), probably due to their high internal surface area (Acosta *et al.*, 2011; Riebeiro *et al.*, 2013a,b; Dias *et al.*, 2014). However, organic C and CEC have no correlation with HE availability, probably due to its very low content.

CONCLUSIONS

The present study showed that restoration of the investigated overburden area demands fertiliser nutrients and probably organic amendments application before establishing plant production. The results also showed that the selection of

Table 3 Correlation matrix–Pearson's correlation coefficients of basic soil characteristics and available heavy metals

	pH H ₂ O	pH KCl	C org	CEC	Clay	Silt	Fine sand
ZnT	0.3	0.89	-0.81	-0.87	-0.61	-0.54	-0.59
CuT	0.17	0.84	-0.89	-0.92	-0.54	-0.45	-0.6
NiT	-0.71	-0.97	0.43	0.61	0.81	0.85	0.72
CrT	-0.58	-0.98	0.61	0.75	0.78	0.77	0.62
PbT	-0.5	-0.9	0.63	0.77	0.84	0.72	0.72
ZnZB	-0.34	-0.55	0.25	0.41	0.55	0.54	0.74
CuZB	-0.7	-0.49	-0.1	-0.12	0.79	0.77	0.53
NiZB	-0.7	-0.82	0.18	0.39	0.8	0.89	0.68
CrZB	-0.49	0.03	-0.61	-0.44	0.34	0.42	0.06
PbZB	-0.43	0.15	-0.74	-0.66	0.19	0.32	-0.34

T, heavy metal obtained by Tesier's procedure; ZB, heavy metal obtained by Zeien and Brümmer's procedure.

extraction procedure in HE speciation is essential, due to the different potential threats of obtained HE fractions for plants. Zeien and Brümmer's method showed better speciation of Mn and Fe oxide fractions, while Tessier's method gives better results for organic and mobile HE fractions. However, both type of sequential extraction, confirm the geogenic origin of HEs, except for Pb(j), which represents the predominant available fraction, probably due to its anthropogenic factor.

The results of PCA indicate that main soil properties (pH, clay, silt content) have a stable relationship with the total content of HE and the presence of available forms of Ni, Zn, Cr, Pb obtained by Tessier extraction and Zn by the Zeien and Brümmer's method. Also, as long as pH and organic matter play an important role in the availability of HEs, their change through overburden restoration could change the soil condition, and consequently the availability of HEs.

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