



The interaction of heavy metals and metalloids in the soil–plant system in the São Domingos mining area (Iberian Pyrite Belt, Portugal)

Peter András¹ · João Xavier Matos² · Ingrid Turisová¹  · Maria João Batista³ · Radoslava Kanianska¹ · Sherif Kharbish⁴

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Abstract

São Domingos belongs among the most important historic Iberian Pyrite Belt Cu mines. The anthrosoil is contaminated by a very high content of heavy metals and metalloids. The study was focused on evaluating the interaction of some chemical elements (Ca, Mg, Fe, Mn, Cu, Pb, Zn, Ag, Cd, Ni, Co, As, Sb) in the system soil vs. five autochthonous dominant plant species: *Pinus pinaster* Aiton, *Quercus rotundifolia* Lam., *Agrostis* sp., *Juncus conglomeratus* L. and *Juncus effusus* L. The plants are heavily contaminated by Cu, Pb, As and Zn. The bioconcentration factor proved that they exhibit features of metal tolerant excluders. The trees are accumulators of Ag, whereas the graminoids are hyper-accumulators of Ag and *Juncus effusus* of Co. The translocation factor confirmed that the selected elements are immobilised in the roots except for Mn and Zn in *Pinus pinaster* and Mn in *Quercus rotundifolia* and *Juncus conglomeratus*. The bioaccumulation of Mn, Zn and Cu at low pH increases. The increased content of Ca and Mg in the soil inhibits, in the case of some metals and metalloids, their intake to plants. Although the studied plants, despite their fitness and vitality at the contaminated sites, are not suitable for phytoextraction (except Co and Ag), they can be used for phytostabilisation at the mining habitats.

Keywords Bioconcentration factor · Translocation factor · Contamination factor · Geoaccumulation index · Pollution load index · pH · Ca–Mg-caused inhibition

Introduction

The São Domingos mine was exploited since the Roman Age and later, between 1857 and 1966, by the Mason and Barry Company. The ore body is formed by a sub-vertical E-W direction body, associated with black shales and volcanic felsic and basic rocks of the IPB volcano–sedimentary complex (Strunian to Upper Visean age; Matos et al. 2006, 2008;

Fig. 1). These rocks are surrounded by thrust faults, SW-vergent, by shales and quartzites of the Phyllite–Quartzite Formation of the Famennian epoch. The mineralisation is represented by massive sulphide and stockwork ore (pyrite, chalcopyrite, sphalerite, galena, tetrahedrite, arsenopyrite and sulphosalts). Intense oxidation and supergene enrichment are related to deposit erosion and represented by haematite and limonite gossan and a covellite/chalcocite zone. The mining products consisted of pyrite, roasted pyrite, sulphur and copper. Native copper was obtained by cementation from ore leaching at the Moitinha plateaus (Matos et al. 2006). Related to the mining process, intense acid mine drainage occurred and large areas are occupied by different mine wastes (Quental et al. 2003; Matos 2004). The extractive activities affected a total area of 3,076,900 m², from the São Domingos to the Chumbeiro dam, located 11 km downstream. A total of 14.7 Mm³ of mining waste has been estimated. The São Domingos mining waste related with the exploitation of the gossan open pit is dispersed in the northern mine area, near the old open pit and close to the village of São Domingos. Evaluated by the Conasa company, the total inferred mineral resource is estimated at 2.38 Mt of non-conditioned volumes,

Responsible editor: Philippe Garrigues

✉ Peter András
peter.andras@umb.sk

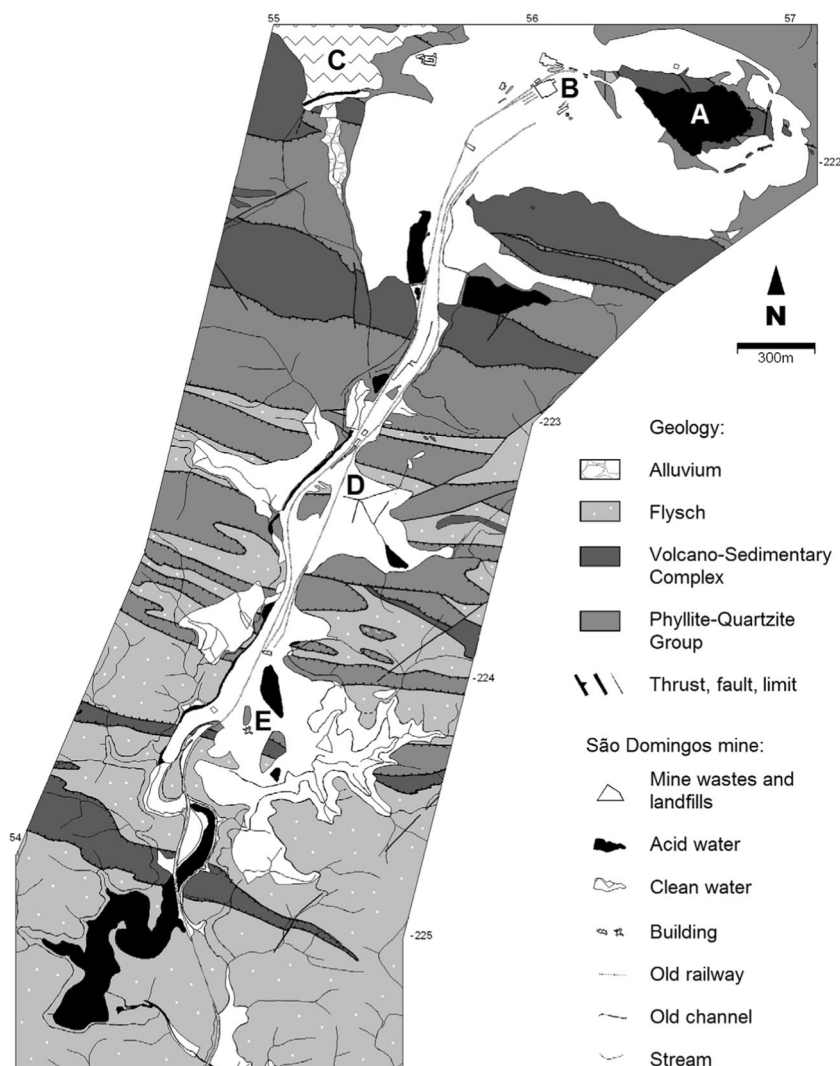
¹ Faculty of Natural Sciences, Matej Bel University in Banská Bystrica, Tajovského 40, 974 01 Banská Bystrica, Slovakia

² Laboratório Nacional de Energia e Geologia (Portuguese Geological Survey), Ap. 104, 7801-902 Beja, Portugal

³ Laboratório Nacional de Energia e Geologia (Portuguese Geological Survey), Ap. 7586, 2721-866 Alfragide, Portugal

⁴ Geology Department, Faculty of Science, Suez University, El Salam City, Suez Governorate 435 18, Egypt

Fig. 1 Geological setting of São Domingos mining area



with an average grade of 0.77 g t^{-1} gold and 8.26 g t^{-1} silver, totalling a metal content of 59,489 oz t gold and 633,488 oz t silver (Matos 2004; Álvarez-Valero et al. 2008, Vieira 2015, Vieira et al. 2015). According to these authors, considering non-conditioned mine waste (including tailings located in urban areas), a total of 4.0 Mt of waste is present in the mine's northern area, with an average grade of 0.64 g t^{-1} Au and 7.30 g t^{-1} Ag.

Surrounding the São Domingos Cu deposit is one of the most contaminated localities by mining activity in all of Europe, helping to enable the study on the impact of heavy metals on country components.

The soil profile is poorly developed, showing commonly < 1 m profiles as is usual in the south Portugal Alentejo region. The parental rocks of the soils are as follows: shales, quartzites and volcanic rocks in the northern area and shales and greywackes in the southern area. The anthrosoil composition is intimately also connected with the spoil material, strongly affected by primary and secondary ore minerals, whose decomposition saturates the country by high heavy metal content and produces great acidity levels.

In the mining area, acid mine drainage is the most important element mobility factor (Abreu et al. 2010; Bálintová et al. 2012; Batista et al. 2012b; Holub et al. 2015). Seepage waters were formed by surface rain water run-off in and under the tailings and slags in the limit between the consolidated bedrock material and unconsolidated weathered material run into the main São Domingos stream with the lowest pH values and the highest Fe and sulphur ion concentrations (Quental et al. 2003; Matos et al. 2006; Álvarez-Valero et al. 2008; Abreu et al. 2010; Mateus et al. 2011; Batista et al. 2012a, b). Microbial analysis indicates the presence of microorganisms, capable of surviving at $\text{pH} < 1$, Fe and S oxidates (*Acidithiobacillus ferrooxidans*), Fe oxidates (*Leptospirillum ferrooxidans*) and S oxidates (*Acidithiobacillus thiooxidans*) and also moderate acidophiles ($\text{pH} 3$ to 6; Bryan et al. 2006). The oxidation processes, combined with the inability of carbonates to neutralise, results in acid production that lowers the pH of the water and raises the conductivity and metal concentration in the solution (Batista et al. 2012a, b). Groundwater concentrations are low in metals, except for Mn, and at some

locations, the Zn and redox potential and high pH also indicate that the contaminated water is confined to the main São Domingos stream (Martins et al. 2007). Several studies (e.g. Batista et al. 2007, 2012b, 2013; Abreu et al. 2008, 2012; Gonzalez-Fernandez et al. 2011; Alvarenga et al. 2012, 2014; Santos et al. 2014; Andráš et al. 2016) show significant impacts on plants, especially in areas that are proximal to mine waste with sulphide mineralisation, where soils present high grades of As, Cu, Pb and Zn.

The aim of the research was to identify dominant autochthonous conifers, broadleaves and graminoids at the São Domingos mining area and reference site and study the input of selected metals/metalloids on these plant species, their bioaccumulation and translocation processes with respect to pH and to the ability of Ca/Mg to inhibit their transfer in the system soil–plants. Consequently, the obtained results were used to identify the suitable type of phytoremediation application.

Material and methods

Sampling of soil and plants

The data sampling was planned considering the local waste disposal and mine site characteristics according to the existing geological and mining mapping (Matos 2004). The key selected sectors were the mine open pit and São Domingos Valley where the tailings, landfills and acid water lagoons are located. The reference area was situated to a locality which is not affected by ore mineralisation (Fig. 2), situated about 1.5 km from the northern border of the São Domingos mining area in the western direction.

Thirty soil (from the root ball of individual sampling plants) and 30 individual plant samples from 5 taxa (roots, shoots or leaves/needles from 8 individuals of *Agrostis* sp., 4 *Juncus conglomeratus*, 4 *J. effusus*, 5 *Pinus pinaster*, 9 *Quercus rotundifolia*) were collected from the mining area (Fig. 2). The field work was done in August 2013 at the time when the above-ground organs of individuals were fully developed. From each locality, one clump of graminoids and samples from one adult tree was collected. The averaged root sample was prepared from five individual drilling holes to the lateral roots. The analysed branch samples represent averaged samples from five 3-year-old branches and from the terminal parts of branches were collected the leaves/needles. The plant species were collected from sites which represented the variability of the habitats at the São Domingos mining area (varying from dry scratchy groves with a dominion of *Pinus pinaster* and *Quercus rotundifolia*, xerophilous and mesophilous open grassland habitats with *Agrostis* sp. up to wetlands with *Juncus conglomeratus* and *J. effusus*). We also took into account the minimum distance of 10 m between the

trees and the 5 m between the herbs. The reference area was selected to reflect the same rock type as the studied mining area. From the reference area, only three plant species were collected, because the area is dry, without wetlands with *Juncus* spp.

The nomenclature of vascular plants is according to Euro+Med PlantBase database (Domina 2011).

Handling of soil and plant samples and analytical methods

The soil from the roots was carefully removed by means of a soft brush and then washed three times in distilled water. The plants were cut into little pieces and dried for 2 weeks at room temperature. They were consequently dried for 6 h in drying plant, model ED, APT Line II, Binder at a temperature of 40 °C.

The soil samples marked as SDO-1 to SDO-35 were dried at the laboratory temperature. The rinse pH of the soil was determined in water suspension and the paste pH in 1 M KCl (64 g KCl/1000 ml H₂O) lixivium. Fifteen millilitres of distilled water or 1 M solution of KCl was added to 5 g of the sample in a glass bake, and this suspension was mixed by electromagnetic stirrers for 2 h, then both pH and Eh were measured in the laboratories of the Geological Institute of the Slovak Academy of Science in Banská Bystrica using pH metre EUTECH instruments according to Sobek et al. (1978). The determined pH and Eh values were re-counted for standard hydrogen electrode count according to Pitter (2009).

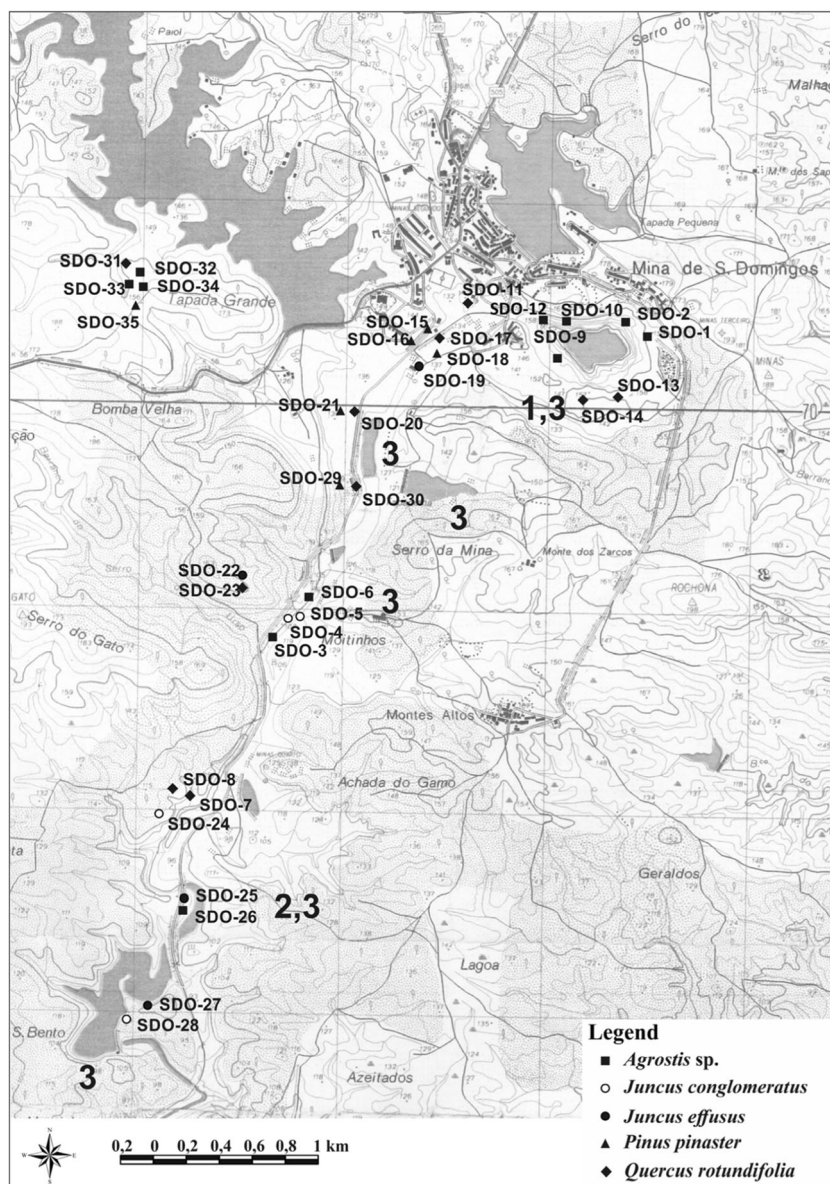
The pH measured in the water suspension is known as rinse pH, whereas the pH in the KCl-soil (NaCl-soil) suspension is known as the paste pH. The paste pH not only represents the balance between the concentration of hydrogen (H⁺) and hydroxyl (OH⁻) ions in the solution but it also reflects the function of the adsorbed Al³⁺ ions in the colloidal complexes of the soil. Al³⁺ ions could be released into the soil solution through the activity of hydrolytically neutral salts (NaCl, KCl, CaCl₂). As Eh is also dependant on the pH of the soil solution, we can use the rH₂ factor for a better comparison between Eh values at different pH:

$$rH_2 = Eh/30 + 2pH$$

In well-aerated soils, rH₂ ranges between 28 and 34, whereas in non-altered soils, the rH₂ value is < 20 (Richter and Hlůšek 2003).

The paste pH_(KCl) of anthropogenic soil enables the determination of the ionic composition of the soil sorption complex and the cation exchange capacity (McNeill and Khakee 1992; Čurlík and Šefčík 1999; Čurlík et al. 2003). The pH_{H₂O} – pH_{KCl} difference is expressed by the D_{pH} value. A positive value is equal to the occurrence of soil

Fig. 2 Samples localisation at São Domingos mining area: 1—mine open pit; 2—Achada do Gamo plant; 3—acid waters lagoons/dams. Topography adapted from IgeoE 557 1/25000 scale map



colloids with a negative charge, and a negative value reflects the occurrence of colloids with a positive charge.

The ICP-MS analyses of soil/technosoil samples were realised in the ACME Laboratory (Vancouver, Canada) from samples of 2 g in weight. The samples were homogenised and dried at the laboratory temperature. The grinding in an agate mill was realised in the laboratory of the Geological Institute of the Slovak Academy of Science in Banská Bystrica.

Two grammes of rock powder was wetted with a few drops of water and then digested into dry vapour in a H_2O – HF – $HClO_4$ – HNO_3 mixture with a rate of 2:2:1:1. After adding 10 ml of 50% HCl , the samples were slowly heated on a water bath under continual mixing. The cooled solution was refilled with HCl to an exact volume and ICP-MS was analysed.

Contamination indices and indices of environmental impact soil–plant

The environmental impact of heavy metals or metalloids and the degree of the pollution of the soil (sediments) can be described with the help of several parameters: the contamination factor (CF) or enrichment factor, pollution load index (PLI) and geoaccumulation index, I_{geo} .

The CF is a ratio of the element content in the soil of the contaminated area divided by the content of the element in the background soil (Kalender and Çiçek Uçar 2013). Some authors designate this value as the enrichment factor (Kisku et al. 2000; Singh et al. 2010). It is calculated according to the following formula:

$$CF = C_{\text{heavy metal in contaminated soil}} / C_{\text{background}}$$

According to Hakanson (1980) and Varol (2011), the $CF < 1$ means low contamination, $1 < CF < 3$ is a moderate contamination, $CF > 3$ to 6 is a considerable contamination and $CF > 6$ means a very high contamination.

For the whole studied area, the PLI can be calculated as follows:

$$PLI = (CF_1 \cdot CF_2 \cdot CF_3 \dots CF_n)^{1/n}$$

According to Tomlinson et al. (1980) and Varol (2011), pollution exists when $PLI > 1$.

The geoaccumulation index (I_{geo}) is possible calculate according to the following equation:

$$I_{geo} = \text{Log}_2(C_n)/1.5(B_n),$$

where C_n is the metal content in soil/sediment from the contaminated area and is the metal content in the background soil (Nowrouzi and Pourkhabbaz 2014). The 1.5 factor is the background matrix correction factor. According to the I_{geo} index value, Varol (2011) distinguishes the following classes:

- $I_{geo} \leq 0$ —unpolluted
- $0 < I_{geo} < 1$ —unpolluted to moderately polluted
- $1 < I_{geo} < 2$ —moderately polluted
- $2 < I_{geo} < 3$ —moderately to heavily polluted
- $3 < I_{geo} < 4$ —heavily polluted
- $4 < I_{geo} < 5$ —heavily to extremely polluted
- $5 > I_{geo}$ —extremely polluted

For the bioaccumulation calculation, two parameters are important: the bioconcentration factor (BCF) and the translocation factor (TF). BCF, separately for every species, was calculated three ways: (i) as the ratio of average element concentration in an entire plant (shoot plus roots in herbaceous species or leaves/needles plus branches plus root in trees) vs. average element concentration in soil samples from the root ball of this species, (ii) as the ratio of average element concentration in the roots vs. the element content in the soil and (iii) as the ratio of average element concentration only in the aerial parts of plants to the average element concentration in the soil (Brooks 1998; Boussen et al. 2013; Boim et al. 2016). If $BCF < 1$, the plant is an excluder; if $BCF = 1$, the plant is an indicator; and if $BCF > 1$, the plant is an accumulator to hyper-accumulator (Baker 1981). The first and second ways define the plants that are generally suitable for phytostabilisation, while the third way defines plants suitable for phytoextraction.

The translocation factor (TF) reflects the rate of the chemical concentration of the contaminant in the leaves or shoots vs. the concentration of the contaminant in the roots (Singh et al. 2010). This parameter shows in which part of the plant the contaminant (in the case of this study, the individual heavy metals or metalloids) is preferentially accumulated.

Statistical analysis

The correlation analyses were done in IBM SPSS Statistics, version 19.0 (IBM Corp. Released 2010).

Results

Soil contamination assessment

Soil samples collected in the surrounding of the open pit mining area (SDO-1 to SDO-30) show a rinse $pH_{(H_2O)}$ ranging between 2.74 and 7.10 (on average 4.29). The paste $pH_{(KCl)}$ varies from 2.69 to 7.02, on average 4.19 (Tab. 1); thus, the soil has an acidic character.

The $Eh_{(H_2O)}$ ranges from -10.7 to 243.4 (on average 153.3) and $Eh_{(KCl)}$ values from -5.6 to 225.7 (on average 172.9). Eh values indicate mainly suboxic conditions.

The values of the rH_2 factor (13.43–15.39) confirm badly aerated conditions. The D_{pH} values, with the exception of two negative values in samples SDO-21 and SDO-25, are as follows: 0.05 to 0.85 (on average 0.34). Such values indicate the presence of soil colloids with a negative surface charge. Two soil samples (SDO-13 and SDO-25) seem to be extraordinary in comparison with the rest of the samples. Not only are the D_{pH} values negative or low, but the pH in these samples is also not strongly acid but close to a neutral value, and the Eh is relatively low. These samples represent not contaminated “isles”, e.g. in the surrounding of the Achada do Gamo old sulphur factory area (Fig. 2).

Analytical data in Table 1 presents the content of selected chemical elements in the soil from São Domingos. The content of heavy metals and metalloids decreases in the range $Fe > Pb > As > Zn > Cu > Mn > Sb > Bi > Ni > Co > Ag > Cd$. The top soil shows the highest values except for Fe (3.29–25.24%) and Pb. The variability for Pb ranges from 80.1 mg kg^{-1} (sample SDO-26) to $>10,000 \text{ mg kg}^{-1}$ (samples SDO-4 and SDO-5). Accordingly, the top highest concentration of Cu ($6204.7 \text{ mg kg}^{-1}$) was evaluated in the same sample SDO-13.

The soil at the reference area has close to a neutral pH ($pH_{(H_2O)}$ 6.91 and $pH_{(KCl)}$ 6.61 on average) and contains a substantially lower content of heavy metals and metalloids (Table 2), mainly Pb (82 times lower), Sb (36 times), As (29 times), Bi (25 times), Cu (18 times) and Zn (7 times). Here, the content of heavy metals and metalloids decreases in the range $Fe > Mn > Zn > As > Pb$ and $Ni > Cu > Co > Sb > Bi > Cd > Ag$. It points to a higher content of Mn (four times) and Ni (two times) on this site. The rH_2 index not only is higher—varying from 17.61 to 20.84 (on average 19.13)—but it also detected that the soil is not well aerated. The D_{pH} index value is very similar (on average 0.30) to the value from the contaminated area.

Table 1 pH, Eh, rH₂ and D_{pH} values and ICP-MS analyses of soil samples from the contaminated area (in mg kg⁻¹; Ca, Mg, Fe in %)

Sample	pH (H ₂ O)	Eh	pH (KCl)	Eh	rH ₂	D _{pH}	Ca	Mg	Fe	Mn	Cu	Pb	Zn	Ag	Cd	Ni	Co	As	Sb	Bi
SDO-1	5.05	108.7	4.56	137.2	14.67	0.49	0.05	0.19	11.80	292	370.5	2737.3	414	9.6	0.4	25.4	25.9	1004	125.2	28.2
SDO-2	4.96	114.4	4.68	130.4	14.27	0.28	0.14	0.30	7.45	722	27.4	726.1	69	1.7	0.6	49.1	21.7	100	20.1	4.0
SDO-3	3.30	210.6	3.17	218.1	13.87	0.13	0.06	0.48	6.70	565	265.7	6695.1	153	2.6	1.1	32.8	11.4	551	278.8	87.6
SDO-4	2.74	243.4	2.69	246.5	13.70	0.05	0.30	0.31	9.59	174	793.3	>10,000.0	772	6.5	2.6	14.4	11.4	1742	667.3	251.0
SDO-5	4.33	150.9	4.18	159.8	13.99	0.15	0.39	0.20	8.22	125	874.1	>10,000.0	1470	7.8	3.8	13.2	12.7	1965	1094.9	369.0
SDO-6	5.43	86.7	5.28	95.9	14.06	0.15	1.95	0.19	20.43	426	1481.2	8498.8	8760	5.1	3.9	12.1	66.3	916	388.2	134.0
SDO-7	4.92	117.7	4.07	166.4	15.39	0.85	0.12	0.69	4.68	1164	147.9	136.5	97	0.2	0.2	52.5	18.1	76	8.7	2.8
SDO-8	3.68	188.9	3.15	219.8	14.69	0.53	0.03	0.48	6.62	298	112.6	360.0	88	1.5	0.2	34.6	6.6	628	34.1	8.4
SDO-9	5.31	93.8	4.79	124.2	14.76	0.52	0.04	0.10	9.41	16	57.4	3193.9	16	5.1	0.1	1.1	0.6	1751	17.6	25.4
SDO-10	4.19	159.7	3.81	181.3	14.42	0.38	0.08	0.11	8.44	101	256.9	2304.5	74	5.1	0.3	8.6	3.9	1540	57.1	84.6
SDO-11	4.33	150.5	3.95	173.1	14.43	0.38	0.16	0.08	16.64	92	216.4	9407.3	85	7.9	0.3	4.9	2.5	3906	225.0	63.8
SDO-12	4.29	153.3	3.71	187.1	14.82	0.58	1.14	0.07	25.24	182	1665.0	6255.1	4503	6.6	1.6	6.5	49.2	1768	196.5	46.8
SDO-13	7.10	-10.7	7.02	-5.6	14.01	0.08	0.90	0.24	10.25	1386	6204.7	1501.0	312	3.5	0.8	23.0	98.9	343	50.4	12.5
SDO-14	5.40	88.9	4.81	123.3	14.91	0.59	5.39	0.47	6.25	1878	1283.6	714.5	1463	1.2	2.6	62.3	36.7	273	43.9	6.1
SDO-15	4.22	157.4	3.75	183.6	14.56	0.47	1.18	0.26	20.57	268	1207.7	1516.0	4162	3.0	0.8	16.0	73.9	507	48.7	11.2
SDO-16	3.44	203.0	3.21	216.1	14.08	0.23	0.28	0.18	9.30	130	347.1	2995.4	648	4.7	0.4	15.5	10.9	1474	62.8	32.1
SDO-17	3.90	176.2	3.40	205.1	14.64	0.50	0.21	0.07	21.37	547	728.9	2008.1	574	3.0	1.0	75.4	23.7	922	74.5	22.9
SDO-18	4.20	158.8	3.83	180.4	14.41	0.37	0.11	0.14	10.15	220	546.4	6712.0	217	14.3	0.8	15.2	8.2	2631	102.9	54.3
SDO-19	4.84	121.3	4.38	147.8	14.61	0.46	0.17	0.02	14.78	56	279.2	4024.8	815	3.5	0.4	2.9	9.2	2405	112.1	85.8
SDO-20	3.19	217.5	3.05	225.7	13.90	0.14	0.05	0.11	8.76	59	229.9	572.5	168	2.3	0.1	8.3	3.4	1647	57.4	96.4
SDO-21	3.50	198.5	3.58	194.6	13.49	-0.08	0.29	0.14	7.82	150	233.7	718.9	169	3.0	0.4	8.4	7.9	1187	65.0	35.4
SDO-22	3.82	180.9	3.37	207.1	14.54	0.45	0.05	0.16	3.29	126	335.0	516.1	75	0.8	0.1	15.6	4.0	362	43.0	8.7
SDO-23	3.89	176.9	3.48	200.4	14.46	0.41	0.88	0.15	13.46	165	757.1	2122.6	2533	5.6	0.5	9.0	44.4	439	156.4	17.6
SDO-24	3.38	206.2	3.24	214.6	13.91	0.14	0.10	0.29	5.43	170	82.0	292.9	68	0.7	0.2	12.7	3.6	1865	63.4	3.1
SDO-25	6.02	52.6	6.21	41.6	13.43	-0.19	0.64	1.20	5.88	858	190.3	322.3	386	0.6	1.3	45.7	18.9	247	14.0	2.8
SDO-26	3.89	176.6	3.63	191.6	14.17	0.26	0.21	1.20	5.47	463	227.1	80.1	245	0.4	0.3	43.4	16.6	65	6.5	0.9
SDO-27	3.33	209.0	3.05	225.5	14.18	0.28	0.09	0.25	6.73	112	149.4	1295.1	102	0.9	0.9	9.3	3.5	4366	234.1	16.4
SDO-28	4.70	129.8	4.10	164.5	14.88	0.60	0.14	0.61	4.59	553	161.8	162.0	159	0.4	0.2	31.2	13.7	86	8.5	1.6
SDO-29	3.42	204.3	3.17	218.1	14.11	0.25	0.13	0.18	7.33	139	263.3	1789.7	102	3.7	<0.1	9.4	3.6	780	48.9	13.8
SDO-30	3.93	174.6	3.26	213.0	14.96	0.67	0.12	0.47	5.33	346	186.9	510.7	94	1.3	0.1	33.5	9.2	189	19.4	5.4
x	4.29	153.3	4.19	172.9	13.86	0.34	0.51	0.31	10.07	393	650.1	3048.5	960	3.75	0.9	23.1	20.7	1191	144.2	51.1

Table 2 pH, Eh, rH₂ and D_{pH} values and ICP-MS analyses of soil samples from the reference area (in mg kg⁻¹; Ca, Mg, Fe in %)

Sample	pH (H ₂ O)	Eh	pH (KCl)	Eh	rH ₂	D _{pH}	Ca	Mg	Fe	Mn	Cu	Pb	Zn	Ag	Cd	Ni	Co	As	Sb	Bi
SDO-31	7.05	106.5	6.99	127.3	17.65	0.06	0.16	0.37	3.41	813	28.3	52.6	53	1.0	0.3	25.5	14.2	26	4.1	1.6
SDO-32	6.96	110.8	6.68	120.0	17.61	0.28	0.18	0.51	1.78	513	24.1	18.4	43	0.3	0.2	13.7	5.8	8	3.5	2.2
SDO-33	6.88	212.5	6.72	216.4	20.84	0.16	0.15	0.27	4.84	2001	39.4	66.7	137	0.9	0.6	44.2	25.6	68	4.2	3.8
SDO-34	6.74	202.2	6.48	232.7	20.21	0.26	0.06	0.25	5.23	1497	39.3	69.1	139	0.4	0.6	47.7	27.3	84	4.4	2.4
SDO-35	6.93	163.8	6.18	179.5	19.32	0.75	0.11	0.46	4.90	2403	48.2	48.1	128	0.4	0.8	55.4	27.1	17	4.8	3.1
x	6.91	159.2	6.61	175.2	19.13	0.30	0.13	0.37	4.03	1445	35.86	51.0	100	0.6	0.5	37.3	20.0	40.6	4.2	2.6

The high correlation degree was described between couples Cu/Co ($r = 0.817$), Pb/Sb ($r = 0.788$), Pb/Bi ($r = 0.707$) and Fe/Zn ($r = 0.679$) at São Domingos. The highest negative correlation was found between couples Ni/As ($r = -0.567$) and Mn/As ($r = -0.518$).

The average of the Ca content at São Domingos is 0.51% and of Mg 0.31%. The Ca/Mg ratio is 1.645, but the degree of Ca/Mg correlation (Fig. 3) is only low ($r = 0.07$). At reference area, the Ca content is lower (0.13%) and Mg a little higher (0.37%), that is Ca/Mg ratio is also higher ($r = 0.351$).

Among Ca and Cu, Pb, Ag and As, negative correlations were described, because Ca inhibits their input to plant organs, especially in *Pinus pinaster*. The moderate degree of negative correlation between acidity (pH) and bioconcentration factor, therefore a higher bioavailability at a lower pH, was determined in the case of Mn ($r = -0.411$), Zn ($r = -0.307$) and Cd ($r = -0.219$). The other metals did not show this dependence (e.g. Cu; Fig. 4).

Contamination indices

The values of the calculated CF show the high contamination of the mining area mainly by Pb, Sb, As, Bi, Cu, Zn and Ag; moderate contamination by Fe, Cd and Ni; and low contamination by Mn (Table 3). The Co content in the soil of the reference area is low (20 mg kg⁻¹ in average), but a little bit

higher as compared to the mining area (23.1 mg kg⁻¹); the CF = 0.62 (low contamination). Ca and Mg are, from the viewpoint of the contamination present in the country, not relevant.

In addition, the pollution load index PLI = 1.56 confirms that the studied area is strongly contaminated.

The geoaccumulation index I_{geo} proved that the soil in the mining area is extremely polluted by Pb, As, Sb and Bi, heavily polluted by Cu, moderately to heavily polluted by Zn and Ag as well as moderately polluted by Fe and Cd (Table 3).

Chemical elements in plant organs and their interaction in the system soil–plant

The content of selected elements in individual parts of the studied plants is presented in Table 4.

According to Table 4, the highest Fe, Cu, Pb, Zn and Ni contents were determined in the roots of *Agrostis* sp., Co in the needles of *Pinus*, Mn in the leaves of *Quercus*, As in the roots of *Juncus effusus* and Sb in the roots of *Juncus conglomeratus*. The lowest heavy metal and metalloid content were found in *Pinus* and *Quercus* (except for Mn).

The sequence of the element content in plants differs more according to the individual species than according to the studied sites, among which this sequence is almost identical (Table 5). Fe, Ca and Mg generally show the highest degree of bioavailability as well as the ability to transport these elements to the shoots. In descending order, Mn follows as bioaccumulation in woody plants and *Agrostis* sp. (no in roots *Juncus* spp.), whereas Pb is the following one as far as herbs are concerned. Pb remains more or less immobile in the roots, and Mn is efficiently transported to the shoots (with the exception of *Juncus effusus*), just like Zn (with the exception of *Agrostis* sp.). Zn and Mn in *Quercus* are mainly accumulated in the leaves.

The heavy metal and metalloid accumulation in the system soil–plants is, with the exception of several few cases, low (Table 6). The trees are Ag accumulators, whereas the graminoids are the hyper-accumulators (the Ag content in roots is 400–700 times higher as in soil). The translocation of Ag from the roots to the shoots was not confirmed. Mn is

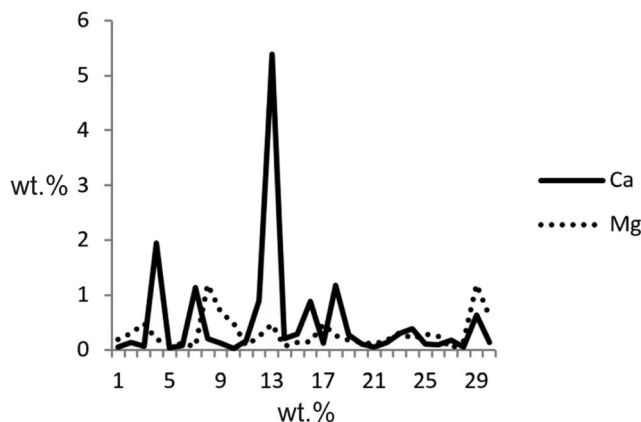


Fig. 3 Ca/Mg correlation in soil from São Domingos

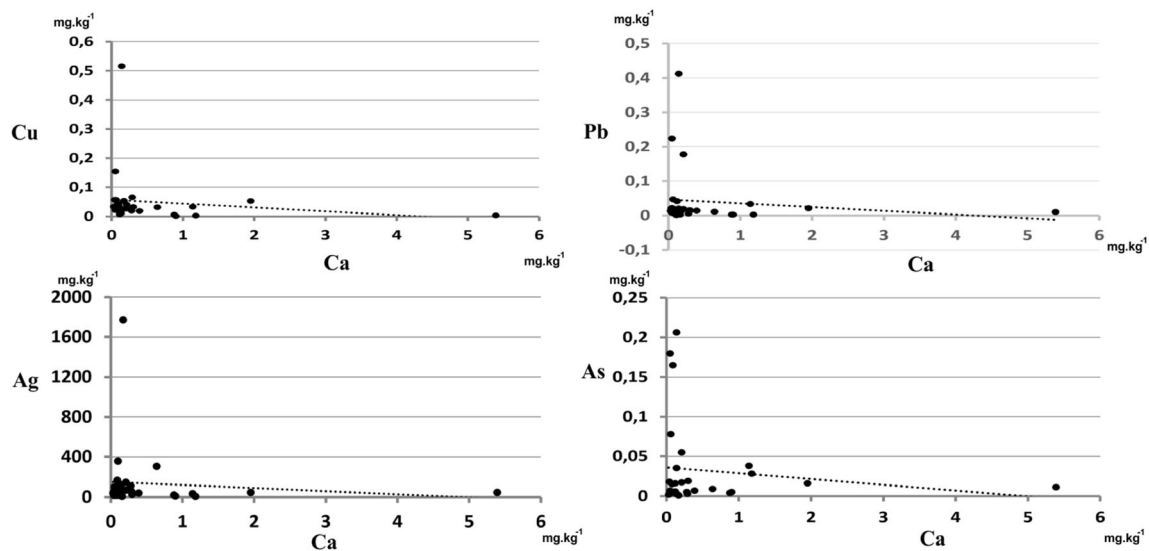


Fig. 4 Relation of Ca vs. heavy metal and metalloid content (Cu, Pb, Ag, As) in *Pinus pinaster* from São Domingos

also relatively mobile and its accumulation decreases in the following order: *Pinus pinaster*, *Juncus conglomeratus* and *Quercus rotundifolia*. This element is also well translocated into the aerial parts of this species. *Juncus effusus* accumulates Co very well in all organs ($BCF > 9$). Thus, it may serve as the potential plant species for the phytoremediation of cobalt-contaminated areas. *Pinus pinaster* is an accumulator of Cd and an indicator for Co in São Domingos (Table 4).

All of the studied heavy metals and metalloids are preferentially accumulated in the roots, except for Mn, which is mainly accumulated in the leaves or shoots (not in *Agrostis* sp. and *Juncus effusus*). In the trees, Zn and Co (in *Pinus*) are also mainly transported to assimilation organs.

Discussion

For growth and development, each plant needs the appropriate amounts of mineral salts, i.e. macronutrients and micronutrients. The mining processes exposed thousands of tons of nutrient-poor waste rock and subsoil to weathering.

The transfer and accumulation of heavy metals and metalloids to the plant organs influence numerous factors, for example the heavy metal content in the soil and soil properties (e.g. the mould content, the content of the organic matter of clay minerals, the cation exchange capacity and Ca and Mg presence). The input of heavy metal and metalloids to plants is

usually and substantially influenced by Ca and Mg and respectively by the Ca/Mg ratio in the sorption complex (Čurlík et al. 2015).

Heavy metals and metalloids are mainly represented in the soil in the form of salts, which are usually unavailable for plant uptake. Only their limited portion is present in the form of an aqueous phase. The uptake of heavy metals and metalloids is controlled both by biological–chemical processes in the root system and by the influence of the presence of some heavy metals or metalloids in soils or in plants. The lack of some micronutrients in the soil can cause the excessive accumulation of individual metals in organs of plants (Fijalkowski et al. 2012).

On the other hand, at the contaminated sites (such as the São Domingos mining area), the excess of numerous heavy metals and metalloids caused disturbances in the metabolism of plants and influenced both the transport and assimilation of heavy metals and metalloids in the organs of plants (Padmavathiamma and Li 2007). The correlation among metallic elements and macroelements (e.g. Ca, Mg) is variable.

The main factor which controls the distribution and mobility of heavy metals and metalloids is pH. Soil type, soil moisture (at São Domingos, the soil is very dry), the presence of individual minerals as well as their content, the intensity of the weathering process, organic matter in the soil, characteristics of edaphone, its composition and the uptake of metals by plants substantially affect the distribution of heavy metals and metalloids. The increase of H^+ ion concentration causes

Table 3 The values of geoaccumulation index (I_{geo}) and contamination factor (CF)

Index/factor	Fe	Mn	Cu	Pb	Zn	Ag	Cd	Ni	Co	As	Sb	Bi
I_{geo}	0.74	-2.46	3.59	5.78	2.68	2.06	0.26	-1.26	-0.53	4.28	4.59	4.09
CF	2.48	0.27	18.05	82.39	9.60	6.25	1.80	1.04	0.62	29.05	36.05	25.55

Table 4 The content of selected elements in the plant species on contaminated and reference area (in mg kg⁻¹; Ca, Mg, Fe in %)

Sample	Organ	Ca	Mg	Fe	Mn	Cu	Pb	Zn	Ag	Cd	Ni	Co	As	Sb
<i>Quercus rotundifolia</i> —contaminated area														
SDO-7	Root	0.85	0.19	0.10	509.00	22.00	8.00	19.00	29.00	0.36	5.40	10.80	2.20	0.58
	Branch	1.66	0.27	0.04	847.00	4.00	6.00	21.00	75.00	0.42	4.50	0.90	1.10	0.37
	Leaves	0.51	0.19	0.02	1825.00	3.00	6.00	28.00	26.00	0.07	3.10	0.50	1.20	0.28
SDO-8	Root	0.53	0.14	0.10	1735.00	9.00	15.00	51.00	122.00	0.95	6.40	4.80	8.70	0.97
	Branch	0.61	0.19	0.02	2029.00	6.00	6.00	49.00	57.00	0.86	6.80	1.80	1.30	0.27
	Leaves	0.53	0.15	0.02	2987.00	4.00	5.00	59.00	60.00	0.20	3.80	1.10	1.50	0.25
SDO-11	Root	1.40	0.09	0.14	81.00	17.00	57.00	43.00	147.00	0.18	4.60	0.60	18.50	1.39
	Branch	1.97	0.11	0.05	140.00	10.00	18.00	40.00	132.00	0.24	3.10	0.70	5.70	0.44
	Leaves	1.24	0.13	0.05	497.00	5.00	25.00	72.00	68.00	0.09	2.10	0.60	8.50	0.49
SDO-13	Root	0.43	0.06	0.06	55.00	147.00	13.00	12.00	71.00	0.04	1.70	1.50	2.40	0.51
	Branch	0.68	0.16	0.02	328.00	9.00	3.00	27.00	77.00	0.10	1.90	1.60	1.00	0.12
	Leaves	0.39	0.13	0.03	514.00	5.00	4.00	25.00	37.00	0.02	1.30	0.90	1.60	0.15
SDO-14	Root	2.60	0.08	0.17	131.00	79.00	51.00	223.00	169.00	0.83	4.30	1.70	21.40	4.88
	Branch	1.12	0.24	0.03	112.00	9.00	7.00	57.00	127.00	0.36	3.10	0.80	2.50	0.20
	Leaves	0.70	0.24	0.03	213.00	5.00	7.00	68.00	54.00	0.10	18.00	0.60	3.00	0.31
SDO-17	Root	0.62	0.08	0.34	60.00	53.00	82.00	74.00	362.00	0.22	5.20	1.60	31.20	2.29
	Branch	0.86	0.18	0.02	8.00	5.00	5.00	13.00	133.00	0.33	0.40	3.60	1.00	0.15
	Leaves	0.99	0.20	0.23	561.00	19.00	38.00	136.00	203.00	0.17	2.40	0.90	16.10	1.70
SDO-21	Root	0.56	0.09	0.18	70.00	103.00	45.00	136.00	1082.00	0.54	2.70	3.90	26.20	2.66
	Branch	0.97	0.19	0.02	110.00	28.00	6.00	105.00	650.00	0.75	2.50	3.80	1.70	0.19
	Leaves	0.86	0.23	0.04	371.00	15.00	11.00	175.00	168.00	0.13	2.00	2.50	3.00	0.39
SDO-23	Root	1.76	0.06	0.17	120.00	25.00	45.00	82.00	196.00	0.27	1.70	1.80	8.60	1.62
	Branch	0.86	0.18	0.01	111.00	9.00	8.00	35.00	98.00	0.53	5.70	3.00	1.80	0.16
	Leaves	0.76	0.06	0.03	664.00	4.00	6.00	115.00	112.00	0.21	0.90	1.10	1.80	0.20
SDO-30	Root	0.64	0.10	0.10	320.00	25.00	61.00	42.00	273.00	0.25	6.30	2.50	5.30	0.93
	Branch	0.71	0.13	0.02	1068.00	9.00	8.00	35.00	103.00	0.28	5.90	3.10	1.10	0.17
	Leaves	0.52	0.10	0.03	2496.00	5.00	7.00	42.00	21.00	0.09	3.70	1.40	1.10	0.24
x	Root	1.40	0.10	0.15	342.00	53.00	42.00	76.00	272.00	0.40	4.30	3.20	13.80	1.76
x	Branch	1.50	0.18	0.03	528.00	10.00	7.00	42.00	161.00	0.43	3.80	2.10	1.90	0.23
x	Leaves	0.72	0.16	0.05	1125.00	7.00	12.00	80.00	83.00	0.12	4.10	1.10	4.20	0.45
x ∑		0.94	0.15	0.08	665.00	23.00	20.00	66.00	172.00	0.32	4.10	2.20	6.60	0.81
<i>Quercus rotundifolia</i> —reference area														
SDO-31	Root	0.67	0.12	0.08	161.00	15.50	1.65	29.00	20.00	0.17	2.38	1.14	2.10	0.32
	Branch	1.42	0.21	0.06	628.00	17.70	3.16	33.30	16.00	0.14	6.42	0.45	≤1	0.11
	Leaves	0.71	0.15	0.06	1154.00	11.20	1.51	33.80	13.00	0.04	3.78	0.81	1.60	0.05
x ∑		0.93	0.16	0.07	648.00	14.80	2.11	32.00	16.00	0.12	4.19	0.80	1.35	0.16
<i>Pinus pinaster</i> —contaminated area														
SDO-15	Root	0.19	0.08	0.26	72.00	44.00	47.00	61.00	366.00	0.58	2.50	6.20	22.00	1.29
	Branch	0.59	0.07	0.01	32.00	6.00	5.00	14.00	81.00	0.25	0.40	3.70	1.00	0.09
	Needles	0.84	0.24	0.02	159.00	4.00	5.00	36.00	176.00	0.15	0.70	1.90	14.00	0.14
SDO-16	Root	0.10	0.06	0.36	138.00	23.00	112.00	63.00	543.00	2.82	7.50	48.50	56.00	2.28
	Branch	1.20	0.13	0.05	533.00	4.00	16.00	186.00	430.00	0.46	7.10	2.70	17.00	0.28
	Needles	0.52	0.15	0.04	825.00	7.00	17.00	278.00	522.00	2.70	4.50	8.80	8.00	0.35
SDO-18	Root	0.29	0.09	0.28	66.00	106.00	230.00	41.00	1301.00	0.83	3.00	2.80	100.00	2.83
	Branch	0.53	0.13	0.03	86.00	7.00	10.00	67.00	723.00	0.41	2.10	2.60	10.00	0.12
	Needles	0.12	0.03	0.02	407.00	4.00	9.00	135.00	1555.00	0.41	4.30	217.90	11.00	0.18
SDO-20	Root	0.31	0.07	0.40	34.00	24.00	42.00	20.00	161.00	0.53	2.90	0.70	93.00	3.50
	Branch	0.17	0.18	0.03	58.00	6.00	5.00	11.00	1512.00	0.50	1.90	1.00	9.00	0.08

Table 4 (continued)

Sample	Organ	Ca	Mg	Fe	Mn	Cu	Pb	Zn	Ag	Cd	Ni	Co	As	Sb
SDO-29	Needles	0.64	0.12	0.03	118.00	5.00	5.00	22.00	94.00	0.50	1.60	1.20	12.00	0.20
	Root	0.82	0.16	0.18	240.00	35.00	76.00	25.00	186.00	0.46	4.40	1.30	17.00	1.88
	Branch	0.19	0.08	0.03	681.00	8.00	12.00	44.00	366.00	0.76	3.00	1.40	2.00	0.20
x	Needles	0.59	0.07	0.03	1965.00	3.00	9.00	75.00	81.00	0.38	3.50	1.20	3.00	0.20
	Root	0.34	0.09	2.97	110.00	46.00	101.00	42.00	511.00	1.40	4.00	12.00	58.00	2.36
x	Branch	0.54	0.12	0.03	278.00	6.00	10.00	64.00	622.00	0.48	3.00	2.00	8.00	0.15
x	Needles	0.54	0.12	0.03	695.00	5.00	9.00	109.00	486.00	0.83	3.00	46.00	10.00	0.21
x Σ		0.47	0.11	0.12	361.00	19.00	40.00	72.00	540.00	0.90	3.00	20.00	25.00	0.91
<i>Pinus pinaster</i> —reference area														
SDO-35	Root	0.22	0.15	0.07	218.00	15.90	2.74	29.90	221.00	0.21	2.99	2.41	1.50	0.22
	Branch	0.26	0.19	0.01	283.00	12.50	1.20	46.70	242.00	0.18	2.53	1.35	≤1	0.09
	Needles	0.28	0.30	0.04	750.00	11.90	2.57	61.80	301.00	0.08	6.26	1.40	≤1	0.04
x Σ		0.25	0.21	0.04	417.00	13.40	2.17	46.10	255.00	0.16	3.93	1.71	1.00	0.12
<i>Agrostis</i> sp.—contaminated area														
SDO-1	Root	0.06	0.10	1.87	251.00	496.00	4587.00	97.00	4312.00	0.47	10.10	78.50	375.00	158.99
	Shoot	0.18	0.12	1.13	647.00	57.00	613.00	126.00	974.00	1.58	7.30	11.30	181.00	14.62
SDO-2	Root	0.04	0.10	1.68	567.00	117.00	3308.00	163.00	1311.00	0.27	6.50	4.40	198.00	106.54
	Shoot	0.07	0.11	1.12	298.00	14.00	299.00	25.00	191.00	0.93	1.30	1.60	21.00	12.62
SDO-3	Root	0.05	0.11	1.69	579.00	129.00	3419.00	175.00	1402.00	0.83	7.70	4.50	208.00	107.65
	Shoot	0.08	0.05	0.09	302.00	15.00	314.00	35.00	191.00	0.19	1.50	1.70	22.00	12.73
SDO-6	Root	0.18	0.11	1.88	260.00	507.00	4599.00	982.00	2929.00	2.33	10.30	80.60	386.00	162.21
	Shoot	0.41	0.06	1.22	153.00	77.00	182.00	769.00	228.00	0.41	2.70	10.60	14.00	8.98
SDO-9	Root	0.12	0.06	3.72	122.00	48.00	1475.00	72.00	2453.00	0.62	5.70	76.00	662.00	12.47
	Shoot	0.11	0.06	0.16	141.00	3.00	65.00	20.00	88.00	0.06	1.70	1.30	31.00	0.42
SDO-10	Root	0.15	0.08	1.62	213.00	158.00	499.00	94.00	1494.00	0.56	4.30	6.80	282.00	11.30
	Shoot	0.16	0.06	0.15	330.00	11.00	44.00	22.00	90.00	0.08	2.10	2.30	23.00	1.13
SDO-12	Root	0.38	0.06	7.99	255.00	464.00	1704.00	1339.00	1786.00	0.45	6.10	18.20	558.00	43.32
	Shoot	0.23	0.04	0.59	116.00	55.00	206.00	167.00	219.00	0.06	1.40	11.70	68.00	5.58
SDO-26	Root	0.21	0.31	1.73	255.00	137.00	133.00	131.00	1496.00	0.79	12.80	13.40	67.00	3.86
	Shoot	0.23	0.25	0.04	318.00	9.00	14.00	53.00	59.00	0.18	2.30	10.40	4.00	0.40
x	Root	0.15	0.12	2.77	313.00	257.00	2466.00	382.00	2148.00	0.37	7.90	35.30	342.00	75.79
x	Shoot	0.18	0.09	0.56	288.00	30.00	217.00	152.00	255.00	0.93	2.50	6.40	43.00	7.60
x Σ		0.17	0.10	1.67	300.00	144.00	1341.00	267.00	1201.00	0.65	5.20	20.80	194.00	41.43
<i>Agrostis</i> sp.—reference area														
SDO-32	Root	0.22	0.080	0.245	938	16.6	12.3	157	188	0.17	5.31	2.08	≤1	34.11
	Shoot	0.12	0.042	0.016	324	8.97	3.28	25.1	98	0.21	2.11	0.47	0	7.12
SDO-33	Root	0.28	0.104	0.958	1028	22.3	16.2	161	211	0.76	14.2	6.42	13.7	46.24
	Shoot	0.21	0.070	0.028	145	26.5	≤1.2	31	144	0.08	1.9	0.53	≤1	11.00
SDO-34	Root	0.24	0.122	0.848	460	24.7	17.33	59.6	216	0.17	14.3	6.44	17.1	25.09
	Shoot	0.16	0.095	0.112	321	12	5.04	41.3	99	0.15	3.97	1.13	3.5	7.19
x	Root	0.25	0.102	0.683	809	21.2	15.3	125.87	205	0.37	11.27	4.98	≤10.6	35.41
x	Shoot	0.16	0.069	0.052	263	15.8	≤3.17	32.47	113	0.15	2.66	0.71	≤1.5	8.44
x Σ		0.21	0.085	0.368	536	18.5	≤9.24	79.17	159	0.26	6.97	2.85	≤6.05	21.93
<i>Juncus conglomeratus</i>														
SDO-4	Root	0.04	0.07	0.38	35.00	85.00	367.00	88.00	543.00	0.69	2.20	2.60	60.00	17.20
	Shoot	0.12	0.12	0.15	79.00	25.00	154.00	29.00	177.00	0.30	0.80	3.20	33.00	10.30
SDO-5	Root	0.09	0.08	3.24	92.00	287.00	6651.00	263.00	7661.00	4.48	4.40	15.30	4280.00	306.90
	Shoot	0.15	0.06	0.05	75.00	17.00	135.00	157.00	301.00	0.94	0.60	1.40	14.00	4.82
SDO-24	Root	0.05	0.11	0.76	74.00	54.00	113.00	59.00	1940.00	0.78	3.50	3.70	192.00	7.41

Table 4 (continued)

Sample	Organ	Ca	Mg	Fe	Mn	Cu	Pb	Zn	Ag	Cd	Ni	Co	As	Sb
SDO-27	Shoot	0.22	0.19	0.02	523.00	11.00	4.00	69.00	251.00	2.29	1.80	0.90	8.00	0.20
	Root	0.04	0.00	0.65	79.00	59.00	106.00	179.00	2013.00	1.98	8.90	3.20	68.00	6.61
x	Shoot	0.12	0.13	0.02	187.00	6.00	5.00	60.00	149.00	1.50	0.90	1.50	15.00	0.80
	Root	0.06	0.07	1.26	70.00	121.00	1809.00	147.00	3039.00	1.98	4.80	6.20	1150.00	84.53
x	Shoot	0.15	0.12	0.06	216.00	15.00	75.00	79.00	220.00	1.26	1.00	1.80	18.00	4.30
x	∑	0.10	0.09	0.66	143.00	68.00	928.00	113.00	1629.00	1.62	2.90	4.00	584.00	44.30
<i>Juncus effusus</i>														
SDO-19	Root	0.17	0.04	1.75	392.00	392.00	731.00	62.00	983.00	0.25	5.10	27.00	375.00	12.40
	Shoot	0.31	0.08	0.14	15.00	15.00	48.00	51.00	177.00	0.02	2.10	17.00	28.00	1.44
SDO-22	Root	0.04	0.04	0.59	229.00	230.00	136.00	83.00	618.00	0.32	7.00	83.00	69.00	5.23
	Shoot	0.13	0.06	0.01	10.00	9.90	11.00	73.00	41.00	0.03	2.90	226.00	2.00	0.21
SDO-25	Root	0.45	0.18	0.44	68.00	68.00	107.00	180.00	1582.00	1.93	9.10	127.00	31.00	2.82
	Shoot	0.30	0.12	0.01	6.00	6.00	4.00	54.00	183.00	0.36	1.70	136.00	2.00	0.13
SDO-28	Root	0.19	0.14	0.79	74.00	74.00	85.00	42.00	392.00	0.15	8.30	208.00	35.00	2.74
	Shoot	0.17	0.10	0.01	3.00	3.00	3.00	13.00	26.00	0.02	0.70	40.00	3.00	0.22
x	Root	0.21	0.10	0.89	191.00	191.00	265.00	92.00	894.00	0.66	7.40	111.00	128.00	5.80
x	Shoot	0.23	0.09	0.05	9.00	8.00	17.00	48.00	107.00	0.11	1.90	105.00	9.00	0.50
x	∑	0.22	0.10	0.47	100.00	100.00	141.00	70.00	500.00	0.39	4.60	108.00	68.00	3.10

an increase in heavy metals and metalloid mobility (Alkorta et al. 2004; Vamerali et al. 2010). The highly contaminated, strongly acidic soils at São Domingos are relatively poor in organic matter content, so the mobility of metallic elements is substantially higher than under neutral or alkaline conditions. On the other hand, organic matter can cause both the release and immobilisation of heavy metals (Kelly 2008).

Another factor which controls the mobility of elements is the oxidation–reduction potential of the soil. According to Kavamura and Esposito (2010), the lack of oxygen in the soil causes the start up and affects an increase in the mobility of most of the heavy metals and metalloids.

The occurrence of individual heavy metals in various forms (various chemical compounds and various oxidation states) significantly affects their mobility. Typically, the most mobile metals are Cd, Zn and Mo, whereas Cr, Ni and Pb are substantially less mobile (Prasad and Freitas 2003; Batista et al. 2012a). The current study also proved the high Mn input into the organs of the plants.

The accumulation of selected metals in different plant species is very variable. It depends not only on the plant species but also on the soil characteristics (Chunilall et al. 2005), which we also confirmed. Plants have several mechanisms by which they can control heavy metals and metalloid tolerance, mainly chelation and sequestration, which are able to remove toxic metals from sensitive sites or incorporate essential metals to their specific cellular destination (Viehweger 2014).

The highest Fe content at São Domingos was recorded in the graminoids. Fe is one of the major constituents of the soil (0.5 to 5%). It is usually present in Fe³⁺ form (Greenwood and

Earnshaw 1990). The bioavailability of such an Fe oxidation status at pH values suitable for plant growth is severely limited by the low solubility of Fe hydroxides. Dicotyledons and non-graminaceous monocotyledons are characterised by an Fe³⁺ solubilisation which is usually mediated by the acidification of the rhizosphere, by completion with chelating compounds and by reduction to Fe²⁺, taken up by the roots by means of a transporter for Fe²⁺. Phytosiderophores (organic acids) are synthesised by the roots of plants and then released into the rhizosphere: there, they form complexes with Fe. The phytosiderophore-plus Fe complex moves into the root across the membrane. Movement of Fe occurs from one part of the shoot (in particularly, from senescent leaves) to other shoot parts via phloem; however, most scientists believe that Fe is not easily re-translocated into plant shoots (Hochmuth 2011). On the contrary, grasses (in our case *Agrostis* sp.) are characterised by a different mechanism for Fe acquisition, with Fe mobilising mainly by means of the roots (Pinton et al. 2007).

As far as further heavy metals are concerned, Zn is mainly acquired from the soil solution as Zn²⁺. However, zinc toxicity is rare and occurs in post-mining and smelting sites, especially with acidic soils. Here the graminaceous species are generally less sensitive to higher concentrations of Zn than most vascular plants, especially dicotyledons. Many plant metallophytes tolerate zinc, but for most cultivated species, it is toxic. Initial research has suggested that the most tolerant species are plants of the family Poaceae, as well as Lamiaceae and Caryophyllaceae, but subsequent studies did not confirm this phylogenetic predisposition to the evolution of Zn hyper-tolerance. Nowadays, zinc

Table 5 The sequence of the element contents in the individual organs of plants from São Domingos and reference area

Plant species	Site	Root	Branch	Leaves/needles	Shoot
<i>Quercus rotundifolia</i>	SD	Ca > Fe > Mg > Mn > Zn > Cu > Pb > As > Ni > Co > Sb	Ca > Mg > Fe > Mn > Zn > Cu > Pb > Ni > Co > As > Sb	Ca > Mg > Fe > Mn > Zn > Pb > Cu > As > Ni > Co > Sb	/
	RA	Ca > Mg > Fe > Mn > Zn > Cu > Ni > As > Pb > Co > Sb	Ca > Mg > Fe > Mn > Zn > Cu > Ni > Pb > As > Co > Sb	Ca > Mg > Fe > Mn > Zn > Cu > Ni > As > Pb > Co > Sb	/
<i>Pinus pinaster</i>	SD	Fe > Ca > Mg > Mn > Pb > As > Cu > Zn > Co > Ni > Sb	Ca > Mg > Fe > Mn > Zn > Cu > Ni > Pb > Co > As > Sb	Mg > Ca > Fe > Mn > Zn > Cu > Ni > Pb > Co > As > Sb	/
	RA	Ni > Pb > Co > As > Sb	Ni > Pb > Co > As > Sb	Pb > Co > As > Sb	Fe > Ca > Mg > Mn > Pb > Zn > As > Cu > Sb > Co > Ni >
<i>Agrostis</i> sp.	SD	Fe > Mg > Ca > Pb > Zn > As > Mn > Cu > Sb > Co > Ni >	/	/	Ca > Mg > Fe > Mn > Zn > Cu > Sb > Pb > Ni > Co > As
<i>Juncus conglomeratus</i>	SD	Fe > Mg > Ca > Pb > As > Zn > Cu > Sb > Mn > Co > Ni	/	/	Ca > Mg > Fe > Mn > Zn > Pb > As > Cu > Sb > Co > Ni
<i>Juncus effusus</i>	SD	Fe > Ca > Mg > Pb > Cu > Mn > As > Co > Zn > Ni > Sb >	/	/	Ca > Mg > Fe > Co > Zn > Pb > As > Mn > Cu > Ni > Sb >

SD São Domingos, RA reference area

hyper-tolerant plants from Poaceae are also available as cultural species and they are successfully used in the remediation of soils contaminated with Zn and also Pb and other heavy metals on post-mining sites (Broadley et al. 2007).

Singh et al. (2010) and Lehout et al. (2018) confirmed a significant correlation in the processes of metal translocation from root to shoot between Cd and Cr, Cu, Mn, Fe; Cr/Pb, Mn and between Pb and Fe; between Cd and Cu, Pb, Zn; and Zn and Cu. This study considered other relationships: a positive correlation in the couples Cu vs. Co, Pb vs. Sb and Bi and Fe vs. Zn and a negative correlation in the couple Ni/As and Mn/As.

A negative correlation between acidity (pH) and bioconcentration factor usually exists, and it means a higher degree of the bioavailability at lower pH values (Sobek et al. 1978; Singh et al. 2010). At the São Domingos site, it was described only in case of Mn, Zn and Cd.

The Ca/Mg > 1 ratio is characteristic of basic rocks (McCarten 1992), so it corresponds with the composition of the wall rocks at the São Domingos mining area.

Calcium is usually better soluble than magnesium, and therefore, it is also more bioavailable. Mg shows a tendency to migrate to the deeper soil horizons (Bowen 1979). This tendency is typical mainly for more acidic soils, as it also is at São Domingos. Ca is usually accumulated in the upper soil horizons. This feature is also influenced by its content in the paced plant tissues (Verbruggen and Hermans 2013).

The high Mg content can cause the strong toxicity of plants (Proctor 1971, 2003; Brooks 1987; Brady et al. 2005; Alexander et al. 2007); therefore, the relatively low Mg content in the soil at São Domingos (0.31% Mg on average) could have a positive influence on the vegetation. Actually, Mg is not harmful to plants but it inhibits Ca and K bioavailability; therefore, the symptoms of Mg toxicity are actually caused by Ca and K lack (Gunes et al. 1998; Merhaut 2007).

Arsenic is (unlike Pb, Cd and Hg) relatively mobile even in neutral or slightly alkaline soils (Yu 2005), but its mobility increases in the acidic conditions typical of São Domingos. Its bioavailability and toxicity is controlled not only by the character of soil solutions (by pH and Eh), the presence of oxyhydroxides and sorption on clay minerals (Davranchea et al. 2003; Förster and Salomons 2004), but it can be increased also by the presence of Ca²⁺, Mg²⁺ and Fe²⁺ (Dixit and Hering 2006). The relatively low bioavailability of As at the deposit is also influenced by the ability to form solid phases (Sadiq 1997; Matera and Le Hécho 2001)—secondary minerals, only slightly soluble oxides of an identical chemical formula (As₂O₃), arsenolite and claudetite, were described at the deposit by Álvarez-Valero et al. (2008).

Sb shows in acid conditions at low pH values a strong sorption ability on clay minerals as well as on Fe oxides and Fe hydroxides (Kabata-Pendias and Mukherjee 2007). It is the reason why Sb at the reference area, where the pH is higher as in the mining area, has a better bioavailability.

Table 6 The average of the bioconcentration and translocation factors in the plants from São Domingos and reference area

Plant	Site	Ratio	Fe	Mn	Cu	Pb	Zn	Ag	Cd	Ni	Co	As	Sb
Bioconcentration factor													
<i>Quercus rotundifolia</i>	SD	wp/soil	0.01	0.99	0.02	0.01	0.44	56.95	0.47	0.12	0.08	0.01	0.01
		Root/soil	0.02	0.51	0.05	0.02	0.64	90.07	0.59	0.13	0.12	0.02	0.02
		ap/soil	0.01	1.23	0.01	0.01	0.10	80.79	0.40	0.12	0.06	0.00	0.01
	RA	wp/soil	0.02	0.80	0.52	0.40	0.60	16.00	0.40	0.16	0.06	0.05	0.04
		Root/soil	0.02	0.20	0.55	0.03	0.55	1.25	0.57	0.09	0.08	0.80	0.08
		ap/soil	0.02	1.10	0.51	0.04	0.63	14.50	0.30	0.20	0.04	0.05	0.02
<i>Pinus pinaster</i>	SD	wp/soil	0.09	2.21	0.04	0.02	0.09	93.38	1.86	0.26	1.00	0.02	0.01
		Root/soil	0.27	0.67	0.09	0.04	0.04	91.25	2.48	0.31	0.60	0.04	0.04
		ap/soil	0.00	2.98	0.01	0.00	0.08	98.93	1.56	0.23	1.20	0.01	0.00
	SD	wp/soil	0.01	0.17	0.28	0.05	0.36	637.50	0.20	0.07	0.06	≤0.06	0.03
		Root/soil	0.01	0.09	0.33	0.06	0.23	552.50	0.26	0.05	0.09	0.09	0.05
		ap/soil	0.01	0.21	0.25	0.04	0.42	678.75	0.16	0.08	0.05	≤0.06	0.01
<i>Agrostis</i> sp.	SD	wp/soil	0.14	0.87	0.26	0.35	0.15	265.23	0.63	0.23	0.85	0.20	0.30
		Root/soil	0.23	0.91	0.47	0.65	0.22	474.17	0.36	0.35	1.44	0.36	0.56
		ap/soil	0.05	0.83	0.06	0.06	0.09	56.29	0.89	0.11	0.26	0.05	0.05
	RD	wp/soil	0.09	0.40	0.52	≤0.18	0.74	300.0	0.55	0.20	0.15	≤0.11	5.44
		Root/soil	0.17	0.61	0.59	0.30	1.18	386.80	0.79	0.32	0.25	≤0.19	8.79
		ap/soil	0.01	0.20	0.44	≤0.06	0.31	213.21	0.32	0.07	0.04	≤0.03	2.90
<i>Juncus conglomeratus</i>	SD	wp/soil	0.06	0.99	0.14	2.74	0.19	409.42	0.86	0.23	0.51	0.24	0.09
		Root/soil	0.17	0.48	0.26	4.56	0.24	763.57	1.05	0.39	0.80	0.46	0.16
		ap/soil	0.01	1.49	0.03	0.19	0.13	55.28	0.67	0.08	0.23	0.01	0.01
<i>Juncus effusus</i>	SD	wp/soil	0.07	0.25	0.41	0.11	0.20	376.32	0.78	0.20	9.43	0.09	0.07
		Root/soil	0.13	0.48	0.79	0.21	0.26	672.18	1.32	0.31	9.69	0.17	0.13
		ap/soil	0.01	0.02	0.03	0.01	0.13	80.45	0.22	0.08	9.17	0.01	0.01
Translocation factor													
<i>Quercus rotundifolia</i>	SD	Leaves/root	0.33	3.29	0.13	0.28	1.05	0.31	0.30	0.95	0.34	0.30	0.26
	RA	Leaves/root	0.79	7.17	0.72	0.92	1.17	0.65	0.24	1.59	0.71	0.76	0.16
<i>Pinus pinaster</i>	SD	Needles/root	0.01	6.32	0.11	0.09	2.60	0.95	0.80	0.75	3.83	0.17	0.09
	RA	Needles/root	0.55	3.44	0.75	0.94	2.07	1.36	0.38	2.09	0.58	≤0.67	0.18
<i>Agrostis</i> sp.	SD	ap/root	0.20	0.92	0.12	0.09	0.40	0.12	2.51	0.32	0.18	0.13	0.10
	RA	ap/root	0.08	0.33	0.75	≤0.21	0.26	0.55	0.41	0.24	0.14	≤0.14	0.24
<i>Juncus conglomeratus</i>	SD	ap/root	0.05	3.09	0.12	0.04	0.54	0.07	0.64	0.21	0.29	0.02	0.05
<i>Juncus effusus</i>	SD	ap/root	0.06	0.05	0.04	0.06	0.52	0.12	0.17	0.26	0.95	0.07	0.09

The values of BCF and TF > 1 or = 1 are accentuated by bold fonts and grey cell fill

SD São Domingos, RA reference area, wp whole plant, ap aerial parts of plant

The studied plants show the highest metal concentrations in *Agrostis* sp., common across the entire mining area (Turisová et al. 2014). The phytoremediation features of the relatively widespread plants of the taxons *Cistus* (4 species) and *Erica* (2 species) were studied by Abreu et al. (2008, 2012). The authors conditioned the selection by finding that they did not display visual symptoms of toxicity, in spite of the fact that they grew on very contaminated sites. Both the presently studied plant species and species studied by the above-mentioned authors did not translocate hazardous elements to the shoots to a degree, which would enable the indication of them as accumulators. Higher concentrations of the metals and metalloids were noted in *Erica andevalensis* and *Erica australis* by Anawar et al. (2010) and Anawar (2012), but these species,

together with *Juncus* sp., *Lavandula stoechas* subsp. *luisieri*, *Daphne gnidium*, *Rumex induratus*, *Ulex parviflorus* subsp. *eriodadus* and *Genista hirsuta*, are not suitable for phytoremediation but may have a major importance for the rehabilitation and recovery of the contaminated mining area.

Freitas et al. (2004a) have published the most detailed study dealing with 135 plant species from 39 families exhibiting resistance to trace metals from north–east of Portugal—a serpentinised area in which tissues were detected with a considerable content of Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. Both the present study of *Quercus rotundifolia* as well as the study of the above-mentioned authors of *Quercus pyrenaica* and *Quercus ilex* proved the high Mn content input to their organs. The highest metal content was described in *Alyssum serpyllifolium*.

According to Fecenko and Ložek (2000), manganese input is influenced by the redox potential, content of organic matters, activity of microorganisms, temperature and mainly by pH. The low pH values typical of São Domingos are very favourable for the high mobility and bioaccumulation of Mn^{2+} . The highest Mn content was usually detected in young needles/leaves (Richter and Hlůšek 2003).

In 24 plant species, also including the presently studied *Juncus conglomeratus*, *Juncus effusus*, *Pinus pinaster* and representatives from the genera *Agrostis* and *Quercus* growing in the São Domingos area, also studied by Freitas et al. (2004b), show the highest Pb and As content in the shoots of *Juncus conglomeratus* (84.8 and 23.5 mg kg⁻¹). According to our results, the Pb content in this species is very changeable (it vary from 4 to 154 mg kg⁻¹) and does not correlate with the Pb content in the soil, where it is present predominantly in the form of anglesite—PbSO₄, cerussite—PbSO₃ or leadhillite—Pb₄(CO₃)₂(SO₄)(OH)₂ (Álvarez-Valero et al. 2008). Low solubility is typical for all of these minerals. Moreover, clay minerals, Mn oxides as well as Fe and Al hydroxides are very good sorbents for Pb salts. The formation of insoluble humin complexes causes its fixation in the upper horizons of the soil (Huang et al. 2011). These features substantially influence the very limited Pb bioavailability (Rapant et al. 1996). However, according to the findings of the present study, grass *Agrostis* sp. has on average a much higher Pb and Ag content (Pb 217 mg kg⁻¹, As 43 mg kg⁻¹).

Our present study proved the relatively higher Ag, As, Ni and Zn contents in the leaves and branches of *Quercus rotundifolia* and higher Ag, As, Pb and Zn contents in *Pinus pinaster* as described by Freitas et al. (2004a) in *Quercus ilex*. Most minerals release during the weathering of Zn²⁺, which is partly sorbed on the surface of natural sorbents but in acidic conditions is very mobile and bioavailable (Tölgyessy 1989; McLean and Bledsoe 1992). The studied tree species, due to their great biomass, can be very effective for metal phytoextraction and phytostabilisation.

Conclusion

The studied dominant plant species in the polygon of the mining area accumulate high concentrations of heavy metals and metalloids (Cu, Pb, Zn, Co, As, Sb). The concentrations of these metals are accumulated predominantly in the roots. The strategy of metal accumulation in the plant organs and tissues is dependent on specific species, regardless of their life forms and preferences of habitats with different ecological conditions, as well as on the metal/metalloid geochemical behaviour. The mobility of elements (metals/metalloids) in the soil–plant system can also be controlled by pH and by the relationship between them and the Ca/Mg content in the soil. Despite the good plant fitness and vitality of the studied metal-tolerant species,

these are not suitable for phytoextraction both because of the heavy contamination of the mining and post-mining country components and due to their prevailing strategy as excluders. They may be applied only for phytostabilisation purposes.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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