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POTENTIALLY TOXIC ELEMENTS IN THE REPRESENTATIVES OF THE GENUS *PINUS* L. AND *QUERCUS* L. AT THE SELECTED SLOVAK, ITALIAN AND PORTUGUESE COPPER DEPOSITS

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Abstract: The results of the potentially toxic elements imput to the representatives of the genus *Pinus* spp. and *Quercus* spp. at four selected closed Cu-deposits: Ľubietová (Slovakia), Libiola and Caporciano (Italy) and São Domingos (Portugal) are significantly complicated. The imput of the potentially toxic elements to the plants at mining areas in comparison with reference areas usually markedly differ. At the mining areas show the plants much more bioaccumulation of toxic elements into their organs. The bioavailability of individual toxic elements is mutable but in general relatively limited. *Pinus* spp. and *Quercus* spp. are for most elements excluders (bioconcentration factor BCF<1). Only Ag show extraordinary ability to high degree of bioconcentration. Also bioconcentration factor values in *Pinus* sp. at Ľubietová ore-field show high degree of Pb and Zn accumulation in studied plants. Zinc is in *Pinus* spp. and *Quercus* spp. accumulated in needles at all studied deposits. The translocation factor (TF) indicates that the other studied toxic elements are accumulated preferentially in roots. The studied plants are suitable only for phytostabilization of the potentially toxic elements.

Key words: potentially toxic element, soil, *Pinus* spp., *Quercus* spp., bioconcentration factor, translocation factor, enrichment factor

1. INTRODUCTION

Contamination of soil or sediment by potentially toxic elements (PTE) is still world-wide an unresolved environmental problem (Švehláková & Kupka, 2014; Dadová et al., 2014). The PTE (in our case metals) are released in the mining areas from the ore mineralization to the environment and influence all country components: soil, water and, plants (Marin et al., 2010, Lacková et al., 2011, 2012a; Anithamary et al., 2012; Lichnovský et al., 2015). To find the suitable remediation management is usually a very complex problem (Lacková et al., 2012b, Urbancová et al., 2014). One of the possible solutions could be phytoremediation (Ali et al., 2013).

Phytoremediation is an innovative bioremediation process that uses various types of green plants to clean the environment and remove or transfer the polutants (e.g. metals, radio-nuclides, harmful organic contaminants…) from the contaminated country components (soil, water). In some cases it stabilize, and/or even destroy the pollutants. There are five main types of phyto-remediation techniques: phytoaccumulation or phytoextraction (the contaminants are absorbed by plant to the shoots), phytostabilization (the contaminants are immobilized in roots), phyto-degradation, phytovolatilization (the imput of the contaminants to the plants is released into the air by leaves) and rhyzofiltration (cleaning of water by roots; Lone et al., 2008; Lăcătuşu et al., 2012; Bizo et al., 2015).

Cu-Ag deposit **Ľubietová** is situated in Fatra-Tatra region of Starohorské Vrchy Mts., which forms the SW continuation of Ďumbierske Tatry Mts., underlying the Internal Carpathian Paleogene and Central Slovak Neovolcanites. Ore field Podlipa is built by greywakes and arcose slates and conglomerates near the contact with porphyric granitic rocks and porphyroides of lower terrigenous Permian (Polák et al., 2003). The Podlipa ore-field (Fig. 1) was mined by 18 galleries. Ore nests, veins, stockworks and lenses (mainly in the southern part) were 30-40 m thick. The Cu-content in hand-selected ore varied from 4 to 10%, sometimes even to 22%. The Ag content was $70 g \cdot t^{-1}$, Koděra et al., (1990) mention also occurrence of gold. From the deposit was during 500 years exploited aproximatelly 25 thousand tons of copper. The present resources are estimated to 25 thousand tons. The ore contain also probably 1750 tons of silver (Koděra et al., 1990).

Figure 1. The Podlipa dump-field at Ľubietová

The main ore minerals are chalcopyrite and minerals of the tetrahedrite-tennantite series. Next minerals are pyrite and rare galena. Andráš et al. (2014) present, that the most important occurence of tetrahedrite was described from Kliment gallery, at which mouth was built in the past the little Podlipa miner village. Other ore minerals are represented by hematite (specularite). The oxidation and cementation zone was very well developed. This zones were in the past rich in kuprite and in native copper. Characteristic is also the wide association of secondary Cu-minerals: libethenite, pseudo-malachite, olivenite, euchroite and farmako-siderite (Andráš et al., 2014).

Cu-deposit **Libiola** is situated in northern Apenines in Liguria near Sestri Levante in valley of Gromolo stream. It had in the past great importance. Even Strabon in 1. century B.C. mentioned the deposit in its writings (Ferrario, 1973). The total longitude of the galleries exceed 30 km and the extent of the ore-field is 4 km^2 (Klemm & Wagner, 1982). The ore was exploted also by quarries (Fig. 2). Since 1962 is the mine abandoned.

Figure 2. The Libiola surface mining area

The mineralization is of stratiform character and is associated with volcano-sedimentary massiv sulphidic ores (Terenzi, 1988). These ores are genetically connected with geodynamic evolution of Northern Apenines. The ores form massive lenses which are concordant with basaltoide rocks of pillow-lavas type and with ophiolites of internal Ligurian Val di Vara series and small sulphide aggregates fil the cavities and fissures in rock complex (Zaccarini & Garuti, 2008). Ferrario & Garuti (1980) distinguish massive pyrite-chalcopyrite ores in basalts, economically not important pyrite-chalcopyrite stockwork mineralization in pillow-lavas and disseminated pyrite mineralization in serpentinites and in basalts.

From galleries outflow two types of mining water: typical acid mine water (AMD/ARD) of orange colour (pH 2.4 – 3.5) and close neutral blue water (pH 6.5 - 6.7; Dinelli et al., 2001).

Tuscan **Caporciano** deposit in Montecatini Val di Cecina belonged during the 19. century to the most important European Cu-deposits. Already in 10th and 11th centuries B.C. was mined by Etruscs (Riparbelli, 1980; Schneider, 1890). The deposit is situated on western slopes of Monte di Caporciano. During the period from 1830 tu 1907 was here exploited 30 000 tons of copper and in 1855 even 2700 tons of copper (Orlandi, 2006). The experiments to exploit the deposit in 1950, 1955, 1957 and 1959 were not succesful and therefore the mine was in 1963closed (De Michele & Ostroman, 1987).

The magmatic rocks are considered to be the source of the ore mineralization. Mesothermal mineralization situated in ophiolites - efusive basaltic rocks was formed by remobilization of ores (Klemm & Wagner, 1982). Economically most important minerals were chalcopyrite, bornite and chalcocite (Mazzuoli, 1883;

Lotti, 1884). In the surrounding of the galleries are numerous dumps (Fig. 3).

Figure 3. The dump-field Caporciano at Montecatini Val di Cecina

Figure 4. The abandoned São Domingos mining area with massive production of acid drainage water along the downstream valley, with metalophyts in the surrounding of the mine wastes.

São Domingos is a Iberian Pyrite Belt Cu sulphide-deposit located in Baixo Alentejo Portuguese province, aproximatelly 60 km in SE direction from Beja. It was mined even in pre-Roman time. The Romans exploited in the surrounding of São Domingos gold and silver as well as base metals for sulphur production (Alvez, 1997). This deposit belongs even in present to the most important deposits of metallogenetic province of massive base-metal ores (VMS) of the Iberian Pyrite Belt, which ore resources are estimated in 1700 Mt (Sáez et al., 1999). Chalcopyrite-pyrite ores were exploited mainly during 19th century and in the first half on 20th century. Durig the period from 1867 to 1966 were here exploited 25 Mt of ore by Mason and Barry Company, including 9,9 Mt of Cu-bearing pyrite for sulphur production. 3445533 tons of copper was exploited from 1913 to 1932 (Matos et al., 2006, 2008). The mining was realised predominantly by surface mining (Fig. 4). The most important exploitation was realized in the surrounding of Achada do Gamo locality; nearby was situated the ore processing factory.

2. MATERIAL AND METHODS

The presented study of the plant PTE bioaccumulation potential for phytoremediation application was performed for *Pinus* spp. And *Quercus* spp. (*Pinus sylvestris* and *Quercus petraea* in Ľubietová, *Pinus pinaster* and *Quercus rotundifolia* at other deposits with exception of Libiola, where was found only kde *Pinus pinaster*). At all mentioned copper deposits were collected in 2012 – 2015 samples (Figs. 5 - 8) from several individuals (roots, branches and needles/leaves) and soil samples from the rootage to deep of about 40 cm. The same sampling was realized also at the reference areas (with exception of locality São Domingos.

Dry soil and plant (root, branch and needles/leaves) samples were analysed in ACME Laboratory (Vancouver, Kanada) by ICP-MS using weight of 2 g. The samples were steamed off on sand-bath in H_2O-HF-$HClO_4$-HNO_3 solution prepared in rate: 2 : 2 : 1 : 1. After adding of 10 ml 50 % HCl was the sample heated on the water-bash. The coolled solution was analyzed by ICP-MS.

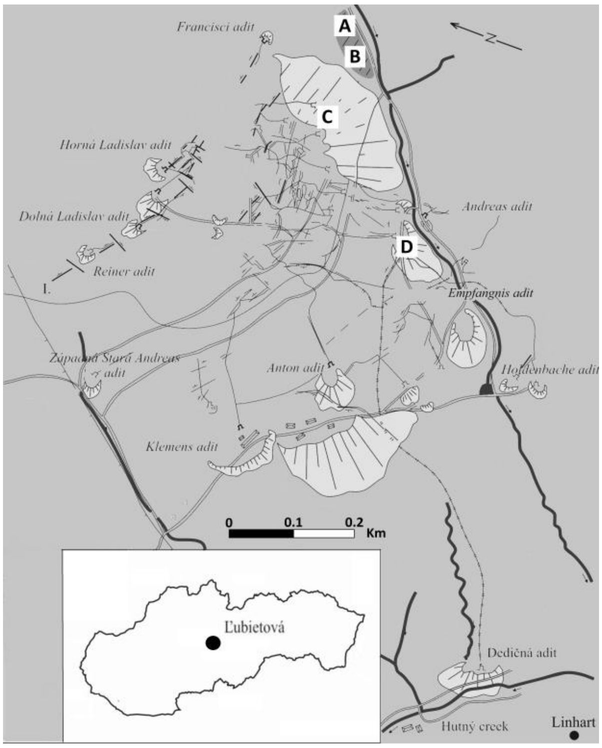

Figure 5. Samples localization at Ľubietová Podlipa dump-field

Bioconcentration factor (BCF) reflect the rate of the PTE content in shoot (in case of woody plants in leaves/needles) vs. PTE content in soil (Zhang et al., 2011). The calculation of BCF in *Pinus* spp. and *Quercus* spp. was realized using the data of PTE content in soil vs. plant assimilations organs. Baker (1981) distinguish according the BCF value the next plant strategies:

- **excluders** accumulate PTE (metals) from soil into roots and immobilize them in such a way that they are no table entry to their shoots (aerial parts). The BCF value is < 1 (Sheoran et al., 2011).

- **indicators** (BCF = 1) accumulate PTE in the shoots and reflect the PTE content in the soil (Sheoran et al., 2011).

- **accumulators and hyperaccumulators** (BCF > 1) are plants which are able accumulate PTE in their shoots (leaves and other aerial parts), preferentially in leaf-vacuolas (Memon & Schroder, 2009). The criteria for hyperaccumulation of PTE is that the plant is able accumulate 100- to 1000-times higher content of metals in shoots in comparison with their content in soil (Baker & Brooks, 1989).

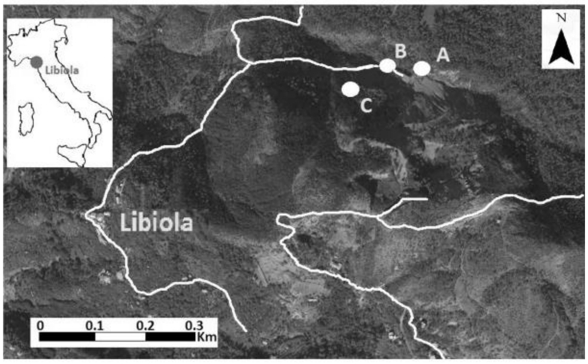

Figure 6. Samples localization at Libiola mining area

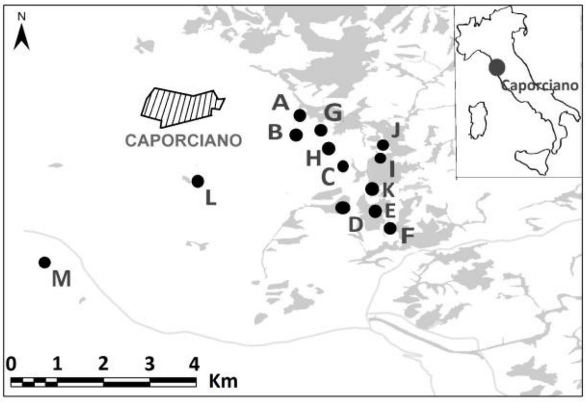

Figure 7. Samples localization at Caporciano (Montecatini Val di Cecina) study area

Translocation factor (TF) indicates the efficiency of the plant to translocate PTE to individual plant organs (Singh et al., 2010) It reflects rate of the chemical concentration of PTE in needles/leaves (or in case of weeds in shoot) vs. their content in roots (Zhang et al., 2011). The plant species with TF and BCF >1 are suitable for phytoextraction aplication (Yoon et al., 2006).

Enrichment factor (**EF**) was calculated as a PTE fraction in soil/plant from the contaminated site divided by PTE content from the reference area (Salomons & Förstner, 1984). In our research we calculated the EF as a fraction of PTE in soil from the dump-field vs. PTE in soil from reference area. Some problem was caused by the not totally identical set of analysed PTE from all studied localities.

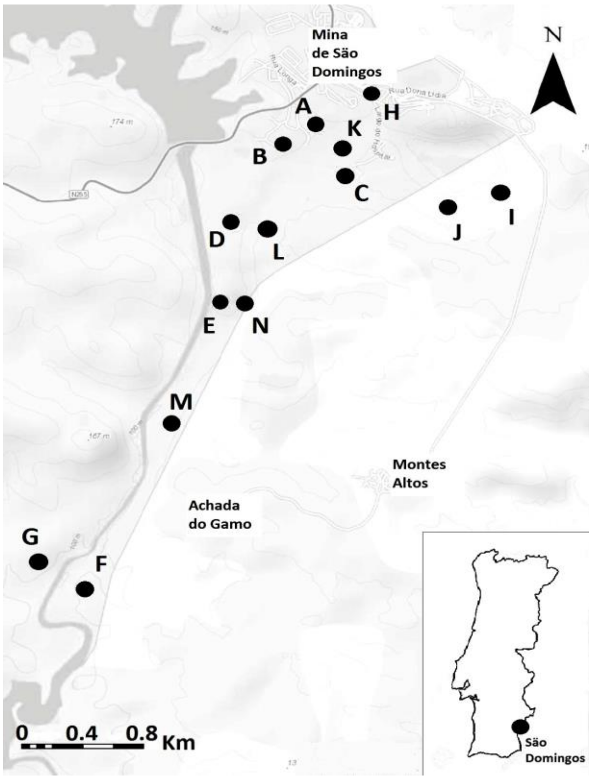

Figure 8. Samples localization at São Domingos mining area

3 RESULTS

The metal contents in soil from Ľubietová - Podlipa are presented in table 1. The highest average PTE at the dump-field show Cu (x = 3653.5 mg·kg^{-1}), As (x = 223.5 mg·kg^{-1}), Co (x = 44.25 mg·kg^{-1}), Sb (x = 32.8 mg·kg^{-1}), Fe (x = 2.415 %), Ni (x = 28.7mg·kg^{-1}), Pb (x = 20.9 mg·kg^{-1}), Zn (x = 19.5 mg·kg^{-1}), Ag (x = 1.15 mg·kg^{-1}) and Cd (x=0.1 mg·kg^{-1}). In table 2 are presented the data for *Pinus sylvestris* and *Quercus petrea*. The highest metal contents were described both in *Pinus sylvestris* and *Quercus petrea* in case of Fe (x = 150.05 and 204.88%). In *Pinus sylvestris* follow: Cu (x = 28.53 mg·kg^{-1}) > Pb (x = 26.95 mg·kg^{-1}) > Zn (x = 24.32 mg·kg^{-1}) >Ag > Ni > Co > As > Sb > Cd and in *Quercus petraea* Zn (x = 33.77 mg·kg^{-1}) > Pb (x = 28.33 mg·kg^{-1}) > Ag (x = 22.01 mg·kg^{-1}) > Ni (x = 5.73 mg·kg^{-1}), Cu (x = 4.90 mg·kg^{-1}) > Co > As > Sb > Cd.

Table 1. ICP-MS soil analyses from dump-field Ľubietová – Podlipa (A, B) and from reference area (C, D)

Localization	Fe	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	Sb
	%	$mg \cdot kg^{-1}$								
A	2.58	541	20	24.1	1.6	0.1	31.6	53.6	294	39.2
B	2.25	6766	19	17.7	0.7	0.1	25.8	34.9	153	26.4
x	2.42	3654	20	20.9	1.15	0.1	28.7	44.25	224	32.8
C	1.38	25	39	16.1	0.1	0.1	8.5	5.1	7	10.4
D	1.12	390	36	13.6	0.3	0.1	7.8	7.1	32	17.5
x	1.25	208	38	14.4	0.2	0.1	8.2	6.1	19.5	14.0

Table 2. Potentially toxic elements contents in *Pinus sylvestris* and *Quercus petrea* from dump-field Ľubietová – Podlipa and from reference area

Sample	Site	Part of the plant	Fe	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	Sb
			%	$mg \cdot kg^{-1}$								
Dump-field												
Pinus sylvestris	**A**	**a**	156.8	28.10	15.00	14.50	0.70	0.03	2.70	2.30	0.42	0.50
		b	164.6	2.90	15.70	32.20	3.04	0.03	2.50	1.30	0.56	0.13
		c	148.5	59.90	44.30	38.30	8.00	0.10	4.90	2.50	0.15	0.04
	B	**a**	148.0	25.40	15.00	10.30	0.55	0.02	2.33	1.98	0.22	0.32
		b	179.2	2.50	15.70	28.10	2.84	0.02	2.41	1.00	0.36	0.10
		c	103.2	52.40	40.20	38.30	6.04	0.09	5.22	3.10	0.11	0.02
	x A,B	**x a**	152.4	26.75	15.00	12.40	0.63	0.03	2.52	2.14	0.32	0.41
		x b	171.9	2.70	15.70	30.15	2.94	0.03	2.46	1.15	0.46	0.12
		x c	125.9	56.15	42.25	38.30	7.02	0.10	5.06	2.80	0.13	0.03
		∑ x	150.1	28.53	24.32	26.95	3.53	0.05	3.34	2.03	0.30	0.19
Quercus petraea	**A**	**a**	274.6	9.20	59.00	57.10	40.10	0.10	11.8	3.50	0.50	0.25
		b	204.1	0.00	41.70	4.70	2.04	0.10	4.70	1.00	0.64	0.09
		c	85.2	8.10	10.30	28.60	30.30	0.06	3.70	1.00	0.77	0.11
	B	**a**	305.0	6.40	48.10	54.10	32.47	0.07	9.82	2.75	0.30	0.19
		b	254.9	0.00	35.66	3.10	1.74	0.08	2.63	0.70	0.37	0.07
		c	105.5	5.70	7.87	22.40	25.39	0.03	1.74	0.82	0.68	0.10
	x A,B	**x a**	289.8	7.80	53.55	55.60	36.29	0.09	10.81	3.13	0.40	0.22
		x b	229.5	0.00	38.68	3.90	1.89	0.09	3.67	0.85	0.51	0.08
		x c	95.4	6.90	9.09	25.50	27.85	0.05	2.72	0.91	0.73	0.11
		∑ x	204.9	4.90	33.77	28.33	22.01	0.07	5.73	1.63	0.54	0.14
Reference area												
Pinus sylvestris	**C**	**a**	0.015	10.89	21.50	1.59	23.90	0.06	1.80	1.40	0.31	0.15
		b	0.009	2.12	32.30	1.23	19.50	0.02	1.30	1.62	0.80	0.19
		c	0.009	4.08	27.10	1.51	24.00	0.06	1.00	2.27	0.40	0.59
	D	**a**	0.021	9.87	18.40	1.40	19.70	0.05	1.60	1.20	0.20	0.04
		b	0.015	1.14	22.20	1.21	14.70	0.01	1.00	1.44	0.71	0.08
		c	0.015	3.1.5	26.30	1.61	24.00	0.04	0.90	2.03	0.30	0.05
	x C,D	**x a**	0.020	10.38	19.95	1.50	21.80	0.05	1.70	1.30	0.25	0.10
		x b	0.010	1.63	27.25	1.22	17.10	0.01	1.15	1.53	0.75	0.14
		x c	0.010	3.62	26.70	1.56	24.00	0.05	0.95	2.15	0.35	0.52
		∑ x	0.010	5.21	24.63	1.43	20.97	0.04	1.27	1.66	0.45	0.25
Quercus petraea	**C**	**a**	0.011	3.33	35.20	3.33	29.50	0.03	1.10	7.52	0.39	0.12
		b	0.006	0.72	26.80	0.76	1.40	0.04	0.70	0.63	0.10	0.12
		c	0.019	0.97	37.20	1.82	4.10	0.02	6.00	0.56	0.30	0.03
	D	**a**	0.007	4.11	41.20	4.23	36.70	0.05	2.30	8.12	1.11	0.25
		b	0.004	1.03	29.70	1.13	4.20	0.02	1.50	0.75	0.30	0.21
		c	0.015	1.26	44.11	2.62	9.80	0.04	7.90	0.66	0.69	0.13
	x C,D	**x a**	0.010	3.72	38.20	3.78	33.10	0.04	1.70	7.82	0.75	0.19
		x b	0.010	0.88	28.25	0.95	2.80	0.02	1.10	0.69	0.20	0.16
		x c	0.020	1.11	40.65	2.22	6.95	0.03	6.95	0.61	0.50	0.08
		∑ x	0.010	1.90	35.70	2.32	14.28	0.03	3.25	3.04	0.48	0.14

Explanations to tables. 2, 4, 6, 8a, 8b: a – root, b – branch, c – needles, ∑ x – average concentration of potentially toxic element in whole plant

The highest Cu, Zn, Pb, Ag, Cd, Ni, Co contents in *Pinus sylvestris* were found in needles, whereas in *Quercus petraea* in roots. Only Ag show the highest contents in leaves. The Fe contents are at reference area in five ranks and the Pb contents in one rank lower as at the dump-field.

Contents of PTE at Libiola are shown in table 3. The highest average contents at the dump-field were ascertained for Fe (x = 13.75 %), Cu (x = 6226 mg·kg^{-1}), Mn (x = 1812 mg·kg^{-1}), Ni (x = 717 mg·kg^{-1}), Zn (x = 439 mg·kg^{-1}), Co (x = 212 mg·kg^{-1}), Pb (x = 56 mg·kg^{-1}), As (x = 11 mg·kg^{-1}) and Sb (x = 3.4 mg·kg^{-1}).

Table 3. ICP-MS soil analyses from Libiola dump-field (A, B) and from reference area (C)

Site	Fe	Mn	Cu	Pb	Zn	Ni	Co	As	Sb
	%	mg·kg^{-1}							
A	15.90	960	946	75	411	81	34	11	4.0
B	19.08	750	3 239	114	265	668	82	15	7.7
x	**13.75**	**1 812**	**6226**	**56**	**439**	**717**	**212**	**11**	**3.4**
C	9.87	0.122	1628	18	952	65	22	7	1.5

Table 4. Potentially toxic elements contents in *Pinus pinaster* from dump-field Libiola and from reference area

Site	Part of the plant	Fe	Mn	Cu	Pb	Zn
		%	mg·kg^{-1}			
A	a	2540	32	69	3.1	32
	b	250	13	18	0.7	28
	c	480	15	19	0.6	38
B	a	1320	140	224	45.1	363
	b	560	148	56	12.3	331
	c	190	216	18	4.3	337
x	**a**	**1930**	**86**	**147**	**24.1**	**198**
	b	**405**	**81**	**37**	**6.5**	**180**
	c	**335**	**116**	**19**	**2.5**	**188**
x	**Σ**	**890**	**94**	**68**	**11.0**	**189**
C	a	760	21	24	2.8	22
	b	68	8	20	0.5	19
	c	113	11	14	0.4	24
x	**Σ**	**314**	**13**	**19**	**1.2**	**22**

Table 5. Results of the ICP-MS analyses of soil from dump-field Caporciano (A-L) and from reference area (M)

Site	Fe	Mn	Cu	Pb	Zn	Ni	Co	As	Sb
	%	mg·kg^{-1}							
Dump-field									
A	6.02	810	6 389	13	767	111	34	3	0.5
B	5.90	790	8 291	28	698	113	32	4	0.5
C	6.34	800	6 664	13	541	159	36	2	0.7
D	6.27	700	9 326	27	939	131	36	2	0.5
E	6.08	670	9 247	22	89	124	34	3	0.5
F	6.40	830	6 360	17	102	112	35	3	0.5
G	5.31	730	6 379	25	718	97	27	1	0.5
H	5.65	800	5 137	13	675	106	30	0.9	0.4
I	4.68	1250	5 021	27	589	145	32	3	0.6
J	5.72	820	8 451	23	883	97	30	2	0.4
K	6.43	890	11 324	24	1064	107	33	3	0.5
L	6.02	860	5 985	12	784	112	31	2	0.4
x	**5.79**	**809**	**7 300**	**24**	**582**	**115**	**32**	**3**	**0.5**
Reference area									
M	3.11	0.055	876	14	53	54	20	< 1	0.1

Table 6. ICP-MS analyses of *Pinus pinaster* and *Quercus rotundifolia* from Caporciano

Plant	Site	Part of the plant	Fe	Mn	Mg	Al	Cu	Pb	Zn	Cd
			mg·kg^{-1}							
Dump-field										
Pinus pinaster	A	a	280	10	1070	200	138	0.2	50	2.87
		b	350	23	1480	200	163	0.9	93	8.82
		c	120	52	2020	70	23	0.2	122	2.75
	F	a	770	25	1570	600	435	0.7	80	2.29
		b	360	28	1360	200	122	0.7	86	3.36
		c	580	59	2220	400	81	0.6	119	0.88
	G	a	910	17	2050	700	265	0.6	52	2.35
		b	510	18	1480	300	184	0.6	77	6.53
		c	300	55	2020	200	44	0.6	143	2.54
	L	a	620	22	1560	400	347	0.5	26	0.23
		b	280	71	1670	100	60	1.5	66	0.36
		c	520	137	3930	300	80	1.5	73	0.06
		x a	**645**	**19**	**1563**	**475**	**296**	**0.5**	**52**	**1.94**
		x b	**375**	**35**	**1498**	**200**	**132**	**0.9**	**81**	**4.77**
		x c	**380**	**76**	**2548**	**243**	**57**	**0.7**	**114**	**1.56**
		Σ x	**467**	**43**	**1869**	**306**	**162**	**0.7**	**82**	**2.75**
Quercus rotundifolia	B	a	967	28	1879	753	217	0.4	51	1.23
		b	470	55	1640	200	22	0.9	61	0.19
		c	120	99	2390	75	19	0.3	45	0.12
	C	a	1270	44	2790	1100	511	1.5	48	0.49
		b	840	71	2310	600	174	2.1	148	0.46
		c	560	121	3520	500	78	1.5	43	0.17
	D	a	12400	225	18710	9900	3288	7.8	545	9.18
		b	870	57	4040	700	181	0.6	87	4.56
		c	490	133	8220	300	80	0.3	81	1.09
	H	a	2100	59	3840	150	1446	2.1	92	0.86
		b	300	71	2000	100	37	1.1	77	0.22
		c	280	135	3020	100	17	0.8	75	0.08
	I	a	150	19	790	75	33	1.0	23	0.43
		b	130	26	1070	70	9	0.6	36	0.59
		c	130	130	1590	70	6	0.3	63	0.23
	J	a	690	96	3830	300	95	1.0	32	0.62
		b	240	166	2340	69	11	0.8	55	0.43
		c	260	431	3500	50	8	1.1	39	0.08
	K	a	620	22	1560	400	347	0.5	26	0.23
		b	280	71	10	100	60	1.5	66	0.36
		c	520	137	1670	300	80	1.5	73	0.06
		x a	**2599**	**70**	**4771**	**1811**	**848**	**2.0**	**117**	**1.86**
		x b	**447**	**74**	**1915**	**248**	**71**	**1.1**	**76**	**0.97**
		x c	**337**	**169**	**3416**	**199**	**41**	**0.9**	**60**	**0.30**
Quercus rotundifolia		Σ x	**1128**	**104**	**3367**	**753**	**320**	**1.3**	**84**	**1.03**
Reference area										
Pinus pinaster	M	A	98	10	420	40	20	0.3	20	0.10
		B	100	15	510	50	20	0.8	41	0.09
		C	40	24	780	61	10	1.0	52	0.04
Pinus pinaster		Σ x	**79**	**16**	**570**	**50**	**17**	**0.7**	**38**	**0.08**
Quercus rotundifolia	M	a	98	10	280	76	48	0.2	21	0.09
		b	78	16	11	52	7	0.4	28	0.28
		c	56	21	426	48	5	0.1	36	0.22
Quercus rotundifolia		Σ x	**77**	**16**	**239**	**59**	**20**	**0.2**	**28**	**0.20**

Metal contents in *Pinus pinaster* are presented in table 4. These contents decrease in range: Fe (x = 890 mg·kg^{-1}) > Zn (x = 189 mg·kg^{-1}) > Mn (x = 94 mg·kg^{-1}) > Cu (x = 68 mg·kg^{-1}) > Pb (x = 11,0 mg·kg^{-1}). The highest contents of Fe, Zn, Cu and Pb were described in roots with exception of Mn which content is the highest in needles.

The content of PTE in soil at Caporciano is presented in table 5. The highest metal contents are: Fe (x = 5,79 %), Cu (x = 7300 mg·kg^{-1}), Mn (x = 809 mg·kg^{-1}), Zn (x = 582 mg·kg^{-1}) and Ni (x = 115 mg·kg^{-1}).

The metal contents in *Pinus pinaster* and in *Quercus rotundifolia* in general decrease in range: Mg (x = 1869 and 3367 mg·kg^{-1}) >Fe (x = 467 and 1128 mg·kg^{-1}) >Al (x = 306 and 753 mg·kg^{-1}) >Cu (x = 162 and 320 mg·kg^{-1}). In *Pinus* sp. show the next highest concentrations Zn (x = 82 mg·kg^{-1}) >Mn (x = 43 mg·kg^{-1}) >Cd (x = 2,75 mg·kg^{-1}) > Pb (x = 0.7 mg·kg^{-1}). In *Quercus rotundifolia* is the sequence of the Mn content vs. Zn and Pb vs. Cd reverse: Mn (x = 104 mg·kg^{-1}) > Zn (x = 84 mg·kg^{-1}) >Pb (x = 1.3 mg·kg^{-1}) >Cd (x = 1.03 mg·kg^{-1}). The highest metal contents were found in roots. The Mg content in *Pinus pinaster* represents an exception. In this plant are the Mg contents higher in needles as in roots: 2548 vs. 1563 mg·kg^{-1}. The metal contents in soil at reference area are substantially lower. Also the sequence of concentrations partially differ. Here were described the highest contents of Mg (570 and 239 mg·kg^{-1}; table 6).

Table 7. Results of the ICP-MS analyses of soil from São Domingos

Site	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**Co**	**Mn**	**As**	**Sb**	**Bi**
	%	**mg·kg^{-1}**								
A	20.57	1207.7	1516.0	4162	16.0	73.9	268	507	48.7	11.2
B	9.30	347.1	2995.4	648	15.5	10.9	130	1474	62.8	32.1
C	10.15	546.4	6712.0	217	15.2	8.2	220	2631	102.9	54.3
D	8.76	229.9	572.5	168	8.3	3.4	59	1647	57.4	96.4
E	7.33	263.3	1789.7	102	9.4	3.6	139	780	48.9	13.8
F	4.68	147.9	136.5	97	52.5	18.1	1164	76	8.7	2.8
G	6.62	112.6	360.0	88	34.6	6.6	298	628	34.1	8.4
H	16.64	216.4	9407.3	85	4.9	2.5	92	3906	225.0	63.8
I	10.25	6204.7	1501.0	312	23.0	98.9	1386	343	50.4	12.5
J	6.25	1283.6	714.5	1463	62.3	36.7	1878	273	43.9	6.1
K	21.37	728.9	2008.1	574	75.4	23.7	547	922	74.5	22.9
L	7.82	233.7	718.9	169	8.4	7.9	150	1187	65.0	35.4
M	13.46	757.1	2122.6	2533	9.0	44.4	165	439	156.4	17.6
N	5.33	186.9	510.7	94	33.5	9.2	346	189	19.4	5.4
x	**9.84**	**890.44**	**2218.94**	**765.14**	**26.28**	**24.85**	**488.71**	**1071.57**	**71.29**	**27.33**

Table 8a. ICP-MS Analyses of *Pinus pinaster* from dump-field São Domingos

Plant	**Site**	**Part of the plant**	**Fe**	**Cu**	**Pb**	**Zn**	**Ni**	**Co**	**Mn**	**As**	**Sb**	**Ag**
			%	**mg·kg^{-1}**								
Pinus pinaster	**A**	a	0.261	44	47	61	2.5	6.2	72	22	1.29	366
		b	0.011	6	5	14	0.4	3.7	32	1	0.09	81
		c	0.024	4	5	36	0.7	1.9	159	14	0.14	176
	B	a	0.358	23	112	63	7.5	48.5	138	56	2.28	543
		b	0.045	4	16	186	7.1	2.7	533	17	0.28	430
		c	0.043	7	17	278	4.5	8.8	825	8	0.35	522
	C	a	0.281	106	230	41	3.0	2.8	66	100	2.83	1301
		b	0.026	7	10	67	2.1	2.6	86	10	0.12	723
		c	0.024	4	9	135	4.3	217.9	407	11	0.18	1555
	D	a	0.396	24	42	20	2.9	0.7	34	93	3.50	161
		b	0.025	6	5	11	1.9	1.0	58	9	0.08	1512
		c	0.027	5	5	22	1.6	1.2	118	12	0.20	94
	E	a	0.183	35	76	25	4.4	1.3	240	17	1.88	186
		b	0.025	8	12	44	3.0	1.4	681	2	0.20	366
		c	0.027	3	9	75	3.5	1.2	1965	3	0.20	81
		x a	**2.969**	**46**	**101**	**42**	**4**	**12**	**110**	**58**	**2.36**	**511**
		x b	**0.026**	**6**	**10**	**64**	**3**	**2**	**278**	**8**	**0.15**	**622**
		x c	**0.029**	**5**	**9**	**109**	**3**	**46**	**695**	**10**	**0.21**	**486**
		Σ x	**0.117**	**19**	**40**	**72**	**3**	**20**	**361**	**25**	**0.91**	**540**

Table 8b. ICP-MS Analyses of *Quercus rotundifolia* from dump-field São Domingos

Plant	Site	Part of the plant	Fe	Cu	Pb	Zn	Ni	Co	Mn	As	Sb	Ag
			%					mg·kg^{-1}				
Quercus rotundi-folia	F	a	0.095	22	8	19	5.4	10.8	509	2.2	0.58	29
		b	0.038	4	6	21	4.5	0.9	847	1.1	0.37	75
		c	0.018	3	6	28	3.1	0.5	1825	1.2	0.28	26
	G	a	0.104	9	15	51	6.4	4.8	1735	8.7	0.97	122
		b	0.016	6	6	49	6.8	1.8	2029	1.3	0.27	57
		c	0.019	4	5	59	3.8	1.1	2987	1.5	0.25	60
	H	a	0.136	17	57	43	4.6	0.6	81	18.5	1.39	147
		b	0.048	10	18	40	3.1	0.7	140	5.7	0.44	132
		c	0.054	5	25	72	2.1	0.6	497	8.5	0.49	68
	I	a	0.057	147	13	12	1.7	1.5	55	2.4	0.51	71
		b	0.017	9	3	27	1.9	1.6	328	1.0	0.12	77
		c	0.025	5	4	25	1.3	0.9	514	1.6	0.15	37
	J	a	0.168	79	51	223	4.3	1.7	131	21.4	4.88	169
		b	0.029	9	7	57	3.1	0.8	112	2.5	0.20	127
		c	0.030	5	7	68	18.0	0.6	213	3.0	0.31	54
	K	a	0.344	53	82	74	5.2	1.6	60	31.2	2.29	362
		b	0.022	5	5	13	0.4	3.6	08	1.0	0.15	133
		c	0.228	19	38	136	2.4	0.9	561	16.1	1.70	203
	L	a	0.178	103	45	136	2.7	3.9	70	26.2	2.66	1082
		b	0.023	28	6	105	2.5	3.8	110	1.7	0.19	650
		c	0.036	15	11	175	2.0	2.5	371	3.0	0.39	168
	M	a	0.168	25	45	82	1.7	1.8	120	8.6	1.62	196
		b	0.012	9	8	35	5.7	3.0	111	1.8	0.16	98
		c	0.025	4	6	115	0.9	1.1	664	1.8	0.20	112
	N	a	0.100	25	61	42	6.3	2.5	320	5.3	0.93	273
		b	0.021	9	8	35	5.9	3.1	1068	1.1	0.17	103
		c	0.029	5	7	42	3.7	1.4	2496	1.1	0.24	21
		x a	**0.150**	**53**	**42**	**76**	**4.3**	**3.2**	**342**	**13.8**	**1.76**	**272**
		x b	**0.025**	**10**	**7**	**42**	**3.8**	**2.1**	**528**	**1.9**	**0.23**	**161**
		x c	**0.052**	**7**	**12**	**80**	**4.1**	**1.1**	**1125**	**4.2**	**0.45**	**83**
		Σ x	**0.076**	**23**	**20**	**66**	**4.1**	**2.2**	**665**	**6.6**	**0.81**	**172**

The contents of PTE in antrosoil at São Domingos are shown in table 7. The highest contents show Pb (x = 2218.94 mg·kg^{-1}) and As (x = 1071.57 mg·kg^{-1}), than follow Cu (x = 890.44 mg·kg^{-1}) >Zn (x = 765.14 mg·kg^{-1}) >Mn (x = 488.71 mg·kg^{-1}) >Sb (x = 71.29 mg·kg^{-1}) >Bi (x = 27.33 mg·kg^{-1}) >Ni (x = 26.28 mg·kg^{-1}) >Co (x = 24.85 mg·kg^{-1}) >Fe (x = 9.84 %).

Table 8a show content of PTE in *Pinus pinaster* at dump-field São Domingos. The highest metal contents were ascertained for Fe (x = 0.117 %) and Ag (x = 540 mg·kg^{-1}). The contents of next metals were lower: Mn (x = 361 mg·kg^{-1}) > Zn (x = 72 mg·kg^{-1}) > Pb (x = 40 mg·kg^{-1}) >As (x = 25 mg·kg^{-1}) >Co (x = 20 mg·kg^{-1}) >Cu (x = 19 mg·kg^{-1}) >Ni (x = 3 mg·kg^{-1}) >Sb (x = 0.91 mg·kg^{-1}). The highest contents of Fe, Cu, Pb, Ni, As and Sb are in roots, whereas the highest contents of Ag are in branches and the highest accumulations of Zn, Co and Mn in needles.

Table 8b document content of PTE in *Quercus rotundifolia* from dump-field at São Domingos. The PTE contents decrease in range: Fe (x = 0.076 %) > Mn (x = 665 mg·kg^{-1}) > Ag (x = 172 mg·kg^{-1}) > Zn (x = 66 mg·kg^{-1}) > Cu (x = 23 mg·kg^{-1}) > Pb (x = 20 mg·kg^{-1}) > As > Ni > Co > Sb. The high concentrations of the metals with exception of Zn and Mn were in *Quercus rotundifolia* described in roots. Zinc and manganese were preferentially accumulated in leaves.

The contents of PTE in soil at São Domingos are presented in table 7. The highest average metal contents at the dump-field show Fe (x = 9.84 %), Pb (x = 2218.94 mg·kg^{-1}), As (x = 1071.57 mg·kg^{-1}), Cu (x = 890.44 mg·kg^{-1}), Zn (x = 765.14 mg·kg^{-1}), Mn (x = 488.71 mg·kg^{-1}), Sb (x = 71.29 mg·kg^{-1}), Bi (x = 27.33 mg·kg^{-1}), Ni (x = 26.28 mg·kg^{-1}) and Co (x = 24.85 mg·kg^{-1}).

The investigation confirmed relatively important differencies in *Pinus* and *Quercus* ability at individual deposits to accumulate metals in their tissues (Table 9). Calculated BCF values in studied plant species indicate, that with exception of Ag and

Cd in *Pinus* are the plants excluders (BCF<1). Representatives of both species are accumulators of Ag. At dump-field Podlipa (Ľubietová) is *Pinus* sylvestris also Zn and Pb accumulator. The same trend was confirmed also in the area of abandoned Cu-deposit São Domingos for *Pinus rotundifolia*, which is Mn, Ag, Cd and Co accumulator. Bioaccumulation and translocation trends at Libiola and Caporciano deposits are shown in table 9.

In most cases the TF values indicate. that in studied plant species *Pinus* and *Quercus* are the metals accumulated mainly in roots. Only in rare cases are the PTE preferentially translocated from soil to leaves or needles. The most massive accumulation of metals in needles was recognized in *Pinus* sp. from dump-field Podlipa (Ľubietová) and at Caporciano. Increased translocation factor values (TF>1) were described also in *Quercus* sp. at Caporciano. The highest contents of TF in general were found for Mn. Zn. Ni and Co. In comparison with BCF differ TF values mainly by the data for Ag. which don't show general trend of increas of BCF and TF values (Table 9).

4. DISCUSSION

The best comparison of bioaccumulation of PTE in plants enable the same species present at all studied deposits (in our case *Pinus* spp. and *Quercus* spp.). The low BCF values at all localities and in both plant genus species indicate that for all harmful metals (Fe, Cu, Pb, Zn, Cd, As, Sb, Ni and Co) are *Pinus* spp. and *Quercus* spp. excluders. Silver is the only important excess: the BCF both for *Pinus* spp. and *Quercus* spp. are >1 (they vary in range 5.00 – 73.75), so the studied plants are accumulators of Ag. At Caporciano and São Domingos in *Pinus pinaster* are the BCF values higher than in *Quercus* sp. at Ľubietová and Libiola.

At Ľubietová and São Domingos are the values of BCF>1 also for Zn. Pb and Cd (Ľubietová) and for Mn. Cd and Co (São Domingos). so these plants are here also accumulators of the mentioned PTE.

TF values, which reflect the ability of the plant translocate contaminants from roots into shoots. are mostly low. The value 1 is usually exceeded only in case of Mn, Zn, Ni and Co (Table 9). The increased TF values were ascertained in *Pinus pinaster* and *Quercus rotundifolia* at Caporciano deposit in general but the highest TF value was calculated for Co in *Pinus pinaster* at São Domingos deposit (Table 9). In most plants are the PTE imput accumulated preferentially in roots (cf. Baker, 1981) and only in several few cases are able transport the pollutants to shoots or to needles/leaves.

Table 9. BCF and TF calculated for Pinus sp. and Quercus sp. at studied deposits

Deposit	Plant	Fe	Mn	Cu	Zn	Pb	Ag	Cd	Ni	Co	As	Sb
Bioconcentration factor – BCF												
Ľubietová	*Pinus sylvestris*	0.010	0.11	0.27	**2.22**	**1.60**	**5.00**	**1.00**	0.00	0.05	0.00	0.00
	Quercus petrea	0.000	0.17	0.16	0.51	**1.19**	**18.93**	0.60	0.12	0.02	0.00	0.00
Libiola	*Pinus pinaster*	0.002	0.12	0.01	0.68	0.02	**66.36**	0.69	0.01	0.04	0.01	0.02
Caporciano	*Pinus pinaster*	0.002	0.07	0.01	0.29	0.04	**73.75**	0.45	0.01	0.02	0.05	0.01
	Quercus rotundifolia	0.006	0.14	0.01	0.08	0.05	**66.59**	0.07	0.03	0.15	0.52	0.34
S. Domingos	*Pinus pinaster*	0.003	**4.97**	0.01	0.42	0.01	**57.51**	**1.85**	0.24	**5.62**	0.01	0.00
	Quercus rotundifolia	0.004	**3.54**	0.24	0.41	0.01	**43.79**	0.27	0.16	0.11	0.01	0.01
Translocation factor – TF												
Ľubietová	*Pinus sylvestris*	0.940	**1.1**	**2.14**	**2.95**	0.18	**11.43**	**3.33**	**1.81**	**1.9**	**0.36**	0.08
	Quercus rotundifolia	0.770	0.99	0.87	0.50	0.50	0.75	0.60	0.31	0.29	**1.54**	0.44
Libiola	*Pinus pinaster*	0.170	**1.1**	0.18	**1.6**	0.14	0.23	0.20	**3.75**	0.31	0.09	0.06
Caporciano	*Pinus pinaster*	0.590	**4.26**	0.19	**2.37**	**1.46**	**1.59**	0.67	**1.00**	**1.75**	**1.00**	0.36
	Quercus rotundifolia	0.400	**3.82**	0.11	**1.36**	0.94	**2.29**	0.23	**1.27**	**3.60**	**1.00**	**1.94**
S. Domingos	*Pinus pinaster*	0.103	**5.20**	0.14	**2.49**	0.11	0.45	0.70	0.67	**16.4**	0.23	0.30
	Quercus rotundifolia	0.300	**5.56**	0.21	**1.36**	0.32	0.45	0.41	0.99	0.51	0.45	0.10
Enrichment factor – EF												
Ľubietová	*Pinus sylvestris*	8467		0.26	0.75	8.29	0.00	0.05	1.48	1.65	1.28	0.42
	Quercus petraea	32200		0.21	1.40	14.71	0.11	0.21	6.36	0.40	0.53	0.12
Libiola	*Pinus pinaster*	1.72	7008	1.28	0.36	5.25			5.76	2.64	1.86	3.90
Caporciano	*Pinus pinaster*	2.54	4.10	6.13	9.00	8.61						
	Quercus rotundifolia	26.52	7.00	17.67	5.57	10.00		20.67				

Explanations: BCF >1 and TF >1 is marked by bolt

There is available only not complet data set of enrichment factors data (Kisku et al., 2000; Singh et al., 2010). which indicetes important differences in soil and plants contamination from reference area vs. soil from contaminated localities. The greatest differences were recognised in Fe, Mn, Cu and Pb contents (Table 9).

The studied plants are not suitable for fytoextraction. The contaminants are accum-mulated mainly in roots. In areas with very high PTE contents, e.g. at dump-fields or at setting pits is often to use plants for phytostabilization (Ali et al., 2013), it means a management strategy which controll spreading of the PTE to the country components (Vangronsveld et al., 2009). In such a territories would be necessary to applicate phytoextraction sometimes even for several thousand years. The plants stabilize during phytostabilization polutants by the help of redox reactions. This process cause gradual change of PTE to not-soluble forms and incorporate them into their organs (Kaduková et al., 2006; Bálintová et al., 2012). Migration of contaminants in soil is controlled by absorption and accumulation (incorporation) of polutants into roots, eventually by adsorption on rootage, precipitation. formation of complex compounds and by reduction (Privetz, 2001). Significant role in the PTE transport control plays also organic matter (Gaiero et al., 1997). Phytostabilization is applicated as a last step of remediation management at areas cleaned up by various methods (Zhang. et al., 2011). For this type of remediation are used usually plants with low ability to accumulate PTE in their shoots (El Zahrani & El Saied, 2011; Ruchita et al., 2015). This strategy was confirmed also our study for predominant part of PTE in studied tree species. The studied plant species at selected Cu-deposits Ľubietová, Libiola, Caporciano and São Domingos are suitable only for phytostabilization to immobilize the contaminants in soil by direct influence of chemical, biological and physical conditions in substrate.

5. CONCLUSIONS

The highest Fe contents in soil were described at Libiola. For this deposit are typical high Cu, Ni and Co contents. Similary high Cu contents are confirmed in Caporciane. The soils at deposit São Domingos show extraordinary high Pb, Zn, As and Sb contents.

The contents of PTE in plants from the dump-fields and those from reference areas substantially differ: the mining areas are in comparison with reference areas much more contaminated by metals. Althought at individual deposits show the plants different relations the bioavailability of metals is relatively limited in general. Most of the metals is accumulated in roots. thus the *Pinus* spp. and *Quercus* spp. are excluders (BCF<1) and they are not suitable for phytoextraction (for removing of metals from soil). The only exception represents several metals which are not dangerous from the viewpoint of the environmental risk (e.g. Ag). The studied wood species show at all localities vital and numerous populations (with exception of singular *Quercus petraea* occurrence at Ľubietová) and are suitable only for phytostabilization purposes.

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REFERENCES

Ali, H., Khan, E. & Sajad., M. A., 2013. *Phytoremediation of heavy metals - Concepts and applications*. Chemosphere, 91, 7, ISSN 00456535, 869-881.

Alvez, H., 1997. *S. Domingos mine. example of specific industrial mine.* Arquivo de Beja, 4/3, 7-17 (in Portuguese).

Andráš, P., Dadová, J. & Dirner, V., 2014. Environmental study at abandoned Cu-Ag deposit Ľubietová. Technická univerzita v Košiciach, ISBN 978-80-553-1799-1, 112 p.

Anithamary, I., Ramkumar, T., Venkatramanan, S. & Vasudevan, S., 2012. *Assesment of heavy metal concentrations in surface sediments of Coleroon Estuary of Tamil-nadu. East coast of India*. Carpathian Journal of Earth and Environmental Sciences, 8, 1, ISSN 1842-4090, 39-46.

Baker, A. J. M., 1981. *Accumulators and excluders – strategies in the response of plant to heavy metals*. Journal of Plant Nutrition, 3, 1-4, ISSN 0190-4167, 643-654.

Baker, A. J. M. & Brooks, R. R., 1989. *Terrestrial higher plants which hyperaccumulate metallic elements. A review of their distribution. ecology and phytochemistry*. Biorecovery, 1, ISSN 0269-7572, 81-126.

Bálintová, M., Petrilaková, A. & Singovszká, E., 2012. *Study of metals distribution between water and sediment in the Smolnik Creek (Slovakia) contaminated by acid mine drainage.* Chemical Engineering Transactions, 28, ISSN 978-88-95608-27-3, 73-78.

Bizo, M. L., Levei, E. A., Kothe, E., Senilá, K., Modoi, C. O. & Ozunu, A., 2015. *Chemical assesment of soil quality for ecological remediation strategies.* Carpthian Journal of Earth and Environmental Sciences, 10, 4, ISSN 1842-4090, 195-202.

Dadová, J.,. Krnáč, J. & Kupka, J., 2014. *Environmental study in territory of closed ore deposits.* Technical

University Press. Košice, ISBN 978-80-553-1772-4, 106 p.

De Michele, V. & Ostroman, A., 1987. *Mineral processing at Montecatini deposit from 1888 to 1938. Milano*: Museo Civico Storia Naturale, 1-38.

Dinelli, E., Lucchini, F., Fabbri, M. & Cortecci, G., 2001. *Metal distribution and environmental problems related to sulfide oxidation in the Libiola copper mine area (Ligurian Apennines, Italy).* Journal of Geochemical Exploration, 74, 1-3, ISSN 0375-674, 141-152.

El Zahrani, H. A. & El Saied, Al., 2011. *Bioremediation of heavy metal toxicity from factory effluents by transconjugants bacteria.* Journal of Egyptian Society of Parasitology, 41, 3, ISSN 1110-0583, 641-650.

Ferrario A. 1973. *Copper-bearing pillowlavas of Liguria Orientale.* Rendiconti della Societa Italiana di Mineralogia e Petrologia. XXIX. Pavia, 485-495 (in Italian).

Ferrario A. & Garuti. G., 1980. *Copper deposits in the basal breccias and volcano-sedimentary sequences of the Eastern Ligurian Ophiolites (Italy).* Mineralium Deposita, 15, 3, ISSN 1432-1866, 291-303.

Gaiero, D. M., Ross, **G. R., Depetris**, **P. J. & Kempe, S.,** 1997. *Spatial and temporal variability of total nonresidual heavy metals content in stream sediments from the Suquia river system. Cordoba. Argentina*. Water Air & Soil Pollution, 93, 1, ISSN 0049-6979, 303-319.

Kaduková, J., Miškufová, A. & Štofko, M., 2006. *Utilization of plants for stabilization and cleaning up of metal contaminated soil and water.* Acta Montanistica Slovaca, 11, 2, ISSN 1335-1788, 130-136.

Kisku, G. C., Barman, S. C. & Bhargava, **S. K.,** 2000. *Contamination of soil and plants with potentially toxic elements irrigated with mixed industrial effluent and its impact on the environment*. Water. Air and Soil Pollution, 120, 1-2, ISSN 0049-6979, 121-137.

Klemm, D. D. & Wagner, J., 1982. *Copper deposit in ophiolites of Southern Tuscany.* Ofioliti, 7, 2-3, ISSN 0391-2612, 331-336.

Koděra, M., Andrusovová-Vlčeková, G., Belešová, O., Briatková, **D., Dávidová, Š., Fejdiová, V., Hurai, V., Chovan, M., Nelišerivá**, **V., Ženiš, P., Fejdi, P., Gregorová, Z., Greguš, J., Határ, J., Hvožďara, P., Chovanová, M., Judinová, V., Karolusová, E., Ondrušová, S., Šamajová, E.** & **Varčeková, A.,** 1990. *Topographic mineralogy 2.* Bratislava. Veda, SAV, 518 p. (in Slovak).

Lăcătuşu, R., Lăcătuşu, A. R., Stanciu-Burileanu, M. M., Virginia, C., Lazăr, R., Lungu, M. & Rizea, N., 2012. *Phytoremediation of a sludge deposit proceeded from a city wastewater treatment plant.* Carpathian Journal of Earth and Environmental Sciences, 7, 1, ISSN 1842-4090, 71-79.

Lacková, E., Stalmachová, B., Polanská, J. & Čmielová, L. 2011. *The functional potential assessment of the landscape affected by the extraction of raw materials*. 11th International Multidisciplinary Scientific GeoConference SGEM 2011, 1.-3, STEF92 Technology Ltd.. ISSN 1314-2704, ISBN 0-000-00000-0, 693-700.

Lacková, E., Kupec, P., Polanská, J. & Stalmachová, B., 2012a. *Social forest functions of reclaimed spoil heaps in the Ostrava-Karvina district.* Journal of Forest Science. Institute of Agricultural and Food Information, 58, 5, ISSN 1212-4834, 203-212.

Lacková, E., Žampachová, D., Čmielová, L., Polanská, J. & Stalmachová, B., 2012b. *Effect of Forest Reclamation on the Křivý Důl Spoil Heap (Upper Silesia. Czech Republic).* Carpathian Journal of Earth and Environmental Sciences, 7, 1, ISSN 1842-4090, 205-212.

Lichnovský, J., Kupka, J., Štěrbová, V., Dadová, J. & Herzogová, K., 2015. *Selected groups of terrestrial invertebrates as bioindicators of changes in mining landscape (Paskov mine. Czech republic).* International Multidisciplinary Scientific GeoCon-ference Surveying Geology and Mining Ecology Management, 2, 5, ISSN 1314-2704, 447-454.

Lotti, B., 1884. *Montecatini mine in Val di Cecina***.** Bollettino del Reale Comitato Geologico d'Italia. 15, ISSN 1338-3523, 359-394 (in Italian).

Lone, M. I., He, Z.-Li, Stoffella, P. J. & Yang, X., 2008. *Phytoremediation of heavy metal polluted soils and water: Progresses and perspectives.* Journal of Zheyjang University Science B., 9, 3, ISSN 1673-1581, 210-220.

Marin, C., Tudorache, A., Moldovan, O. T., Povară, I. & Rajka, G., 2010. *Assessing the contents of arsenic and of some heavy metals in surface flows and in the hyporheic zone of the Arieş stream catchment area. Romania.* Carpathian Journal of Earth and Environmental Sciences, 5, 1, ISSN 1842-4090, 13-24.

Matos, J. X., Pereira, Z., Oliveira, V. & Oliveira, J. T., 2006. *The geological setting of the São Domingos pyrite orebody. Iberian Pyrite Belt.* VII Cong. Nac. Geologia. Estremoz. Un. Évora. Portugal, 283-286.

Matos, J. X., Martins, A., Rego, M., Mateus, A., Pinto, A., Figueiras, J. & Silva, E., 2008. *Roman Slag Distribution in The Portuguese Sector of the Iberian Pyrite Belt*; in V Congreso Internacional sobre Minería y Metalurgia Históricas, Leon, 563-573.

Mazzuoli, L., 1883. *Geological features of copper mineralization at Montecatini*. Reale Comitato Geologico d'Italia, Bollettino, 9, 10, 44-52 (in Italian).

Memon, A. R. & Schroder, P., 2009. *Implications of metal accumulation mechanisms to phytoremediation.* Environmental Science and Pollution Research, 16, 2, ISSN 0944-1344, 162-175.

Orlandi, **P.,** 2006. *Localities of interesting mines and mineralogical sites in territory of Pisa province.* Piano Territoriale di Coordinamento approvato con Deliberazione di Consiglio Provinciale n. 100 del 27/07/2006 (in Italian).

Polák, M., Filo, I., **Havrila, M., Bezák, V., Kohút, M., Kováč, P., Vozár, J., Mello, J., Maglay, J., Elečko, M., Olšavský, M., Pristaš, J., Siman, P., Buček, S., Hók, J., Rakús, M., Lexa, J. & Šimon, L.,** 2003. *Explanations to geological map Starohorské Mts. Čierťaže and northern part of Zvolenská fold. 1 : 50 000. Štátny* geologický ústav Dionýza Štúra, Bratislava, 218 p.

Privetz, B. E., 2001. Phytoremediatzion of contamined soil and ground water at hazardous waste sites. EPA/540/S-01/500.

Riparbelli, A., 1980. *History of Montecatini Val di Cecina and of its mine. Firenze*: Tipografia Giuntina, 31 tabs, OCLC 11563375, 187 p.

Ruchita, D. W., Deepti, M., Kuppusamy, P., Udai, B. S., Asha, S., Renu, S., Bhanu, P. S., Jai, P. R., Pawan, K. S., Harshad, L. & Diby, P., 2015. *Bioremediation of heavy metals from soil and aquatic environment: An overview of principles and criteria of fundamental processes.* Sustainability 7, 2, ISSN 2071-1050, 2189-2212.

Sáez, R., Pascual, E., Toscano, M. & Almodovar, G. R., 1999. *The Iberian type of volcano-sedimentary massive sulphide deposits*. Mineralium Deposita, 34, 5, ISSN 0026-4598, 549-570.

Salomons, W. & Förstner, U., 1984. *Metals in the hydrocycle*. Springer. Berlin Heidelberg Tokyo, ISBN 978-3-642-69327-4, 349 p.

Sheoran, **V., Sheoran**, **A. & Poonia**, **P.,** 2011. *Role of hyperaccumulators in phytoextraction of metals from contaminated mining sites: a review*. Critical Reviews in Environmental Science and Techno-logy, 41, 2, ISSN 1064-3389, 168-214.

Singh, R., Singh, D.P., Kumar, N., Bhargava, **S. K. & Barman, S. C.,** 2010. *Accumulation and translocation of heavy metals in soil and plants from fly ash contaminated area.* Journal of Environmental Biology, 31, 4, ISSN 0254-8704, 421-430.

Schneider, A., 1890. La miniera cuprifera di Monte-catini V.C. Firenze: Tipografia G. Barbera, 52 p.

Švehláková, H. & Kupka, J., 2014. *The mining landscape of Teschen silesia region – structure and developłment.* International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, 1, 5, ISSN 1314-2704, 751-754.

Terenzi, A., 1988. *La miniera cuprifera di Montecatini in Val di Cecina (PI).* Rivista Mineralogica Italiana, 12, 1, ISSN 0391-9641, 19-26.

Vangronsveld, J., Herzig, R., Weyens, N., Boulet, J., Adriaensen, K., Ruttens, A., Thewys, T., Vassilev, A., Meers, **E., Nehnevajova, E., Van der Lelie, D. & Mench, M.,** 2009. *Phytoremediation of contaminated soils and groundwater: lessons from the field*. Environmental Science and Pollution Research, 16, 7, ISSN 1614-7499, 765-794.

Yoon, J., Caoy, **X., Zhou, Q. & Ma, L. Q.,** 2006. *Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site*. Science of the Total Environment, 368, 2-3, ISSN 0048-9697, 456–464.

Zaccarini, F. & Garuti, G., 2008. *Mineralogy and chemical composition of VMS deposits of northern Apennine ophiolites, Italy: evidence for the influence of country rock type on ore composition*. Mineralogy and Petrology, 94, 1, ISSN 0930-07, 61-83.

Zhang, D. Q., Zhang, H., He, P. J. & Shao, L. M., 2011. *Effect of biostabilization on the release potential and speciation of heavy metals in municipal solid waste*. Waste Management and Research, 29, 4, ISSN 0734-242X, 406-413.

Urbancová, L., Lacková, E., Kvíčala, M., Čecháková, L., Čechák, J. & Stalmachová, B., 2014. *Plant communities on brownfield sites in upper Silesia (Czech Republic).* Carpathian Journal of Earth and Environmental Sciences, 9, 2, ISSN 1842-4090, 171-177.

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