

HEAVY METAL CONTAMINATION AND ITS IMPACT ON PLANTS AT CAPORCIANO Cu-MINE (MONTECATINI VAL DI CECINA, ITALY)

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Abstract: This article reports an environmental study concerning the abandoned Caporciano copper mine in Montecatini Val di Cecina. The environmental matrices (water, soil, dump sediments, plants) of the studied mining sites were investigated in order to evaluate its environmental status. The heavy metals mobilization can cause contamination of country components. Our attention was focused on heavy metal content in the studied environmental matrices. Concentration values which we found out by laboratory analyses were also compared with concentration limits provided by Italian law (L.D. 152/06) as far as soil and water are concerned. Acidification potential of dump sediments and soils from the dump was also studied. The acidification risk seems to be negligible. The bioconcentration factor (BIF <1) and translocation factor (TF in average 4.063 for *Pinus* sp. and 3.340 for *Quercus* sp.) of the heavy metals in the studied plants indicate that the plants are excluders. Also the enrichment factor (EF) is not very high. The highest EF value was calculated for Cd in *Pinus* sp. (in average 42.59), while for Mn, Pb and Cu in *Quercus* sp. (EF = 8.10, 8,00, 8.23 in average). The lowest EF shows Cd in *Quercus* sp. (1.19 in average).

Key words: contamination, dump-field, heavy metals, soil, plants, biocaccumulation factor, translocation factor, enrichment factor

1. INTRODUCTION

In Italy, mines and quarries represent an important sector of National economy and, even when they are ruled, serious environmental problems derive from extraction activities. Besides temporary impacts (noise, powder, pollution, etc.), they also cause deep and changes to landscape, soils degradation, pollution of groundwater and lot of problems about use destination of abandoned areas.

Mining activity in Italy had an increasing trend till the mid of the 20th century. Nowadays, it is residual and it mainly concerns extraction of marls for concrete, ceramic and industrial minerals. Progressive decrease in extraction activities, particularly the ones concerning metals (whose refuses present high pollution), has surely relieved territories of mining impact. Nevertheless, structural and healthy problems remain because many abandoned mines also have their tailings and their washers, which have not been restored, yet.

In spite of its distribution all in the National territory, mining activity must be differentiated both for concentration and for type of extracted minerals. About copper, Italy is not particularly rich, and its small or medium mines are enough widespread through the National territory, usually as thin veins whose extracted minerals did not contain a big amount of copper.

Our environmental study concerned the abandoned Caporciano copper mine, located in the territory of Montecatini Val di Cecina (Fig. 1), in the middle of the territory belonging to Pisa Province and at the orographic right of the low Cecina River Valley. The square of this mining area is 449 meters above sea level, and the main entrance to the extraction well „Alfredo” is just about 25 meters upper, at the southern slope of Monte Caporciano (Terenzi, 1988). Within this mining area, the total extent of wells is 4.105 m, total extent of chimneys and galleries is 6.000 m, and total extent of galleries is 35.350 m. The overall extent is therefore 45.555 m.



Figure 1. Caporciano in Montecatini Val di Cecina:
Pinus sp. vegetation on the dump-field

Included in the orogenic context of the northern Apennine, which was corrugated starting from upper Cretaceous, Caporciano mine was exploited at a not continuous way (at first for Cu and then also for Fe and Pb) from Etruscan times (10th – 11th centuries B.C.) to 1907 (De Michele & Ostroman 1987; Riparbelli, 1980; Schneider, 1890). During the 19th century, it was the largest copper mine in Europe. Between 1827 (year of reactivation after closure because of pestilence in 1630) and the end of the 19th century, over 50.000 tons of metallic copper were there exploited, with a peak in production of 2700 t in 1855 (Orlandi, 2006). Caporciano mine was definitively closed in 1963, after negative results of the last researches between 1950 and 1963 and after some attempts in order to excavate new segments of tunnels (Marrucci, 2000). It is nowadays used as a mining museum as well as a document center.

The hydrothermal mineralization, later remobilized, is situated in a mass of ophiolitic rocks (Klemm & Wagner, 1982) which are dislocated within the zone itself and which show themselves as two outcrops (each one is about 1 km²), separated one from another by a thin barrier formed by sedimentary (calcareous-clayey) rocks (Terenzi, 1988). The outcropping ophiolitic complex (Eocene) is there formed by an effusive basaltic component

(present both as a mass and as pillows, more or less transformed) and by two more terms, gabbros and serpentinites, which can be only observed at higher depth. Intense tectonics interested ophiolites and, because of friction between igneous and sedimentary rocks, some clayey pockets in effusive rocks were thus transformed and became place of most of cupriferous mineralization there.

The deposit is divided into two main areas: the older one is located at the southern side of Monte Massi, whereas the second one is totally separated from the other one and it is situated at higher depth on the southern slope of Poggio la Croce. According to a traditional division, we can distinguish two mineralized bodies: a „red vein” and a „white vein”, both wedging out downward at the point where the underlying sedimentary rocks begin (Beck, 1905). Characterized by a thickness of 5 meters, the vertical red vein was formed by a reddish clayey mass (with nodules and small amounts of minerals). Derived by alteration of deeper gabbros and formed by a steatitic whitish clay having thickness between 30 and 100 meters, the white vein was the richest side of the mining area: from the lower side of the deposit, it passed upwards into the red vein (Bertolani & Rivalenti, 1973).

Economic importance of Caporciano mining area is related to exploitation of chalcopyrite (present in form of nodules or small masses, some cm in size), bornite and chalcocite (Mazzuoli, 1883; Lotti, 1884). Covelline and secondary native copper had only secondary importance (Terenzi, 1988).

2. MATERIALS AND METHODS

13 plant samples (5 *Pinus* sp. and 8 *Quercus* sp.) of roots, branches and leaves from the same places (Fig. 2) were collected: 12 from the dump-field (MTC-1 to MTC-12) and 2 from reference area (MTC-13) 1 *Quercus* sp. and 1 *Pinus* sp. Also root ball soil samples of each plant from the heap and reference site were obtained. Sampled were the mixed representative A and B horizons (within 2 samples were distinguished A, B and C soil horizons).

Samples of soil and of dump sediments were collected in August 2013 when all above-ground organs of individuals were fully developed. The samples were dried at laboratory temperature. Rinse and paste pH was measured according to Sobek et al., (1978).

Rinse pH was determined in water suspension, and paste pH in 1M KCl (64 g KCl/1000 ml H₂O) lixivium. To 5 g of sample in glass bake was added 15 ml of distilled water or 1M solution of KCl and after two hours mixing of this suspension

by electromagnetic stirrers, both pH and Eh were measured in laboratories of Geological Institute of Slovak Academy of Science in Banská Bystrica using pH-metre EUTECH Instruments. The determined Eh values were calculated for standard hydrogen electrode according to Pitter (2009).

pH measured in water suspension is known as rinse pH whereas pH in KCl-soil (NaCl-soil) suspension is known as paste pH. Paste pH represents not only the balance between the concentration of hydrogen (H⁺) and hydroxyl (OH⁻) ions in solution but it also reflects the function of adsorbed Al³⁺ ions in colloidal complexes of soil. Al³⁺ ions could be released into soil solution by activity of hydrolytically neutral salts (NaCl, KCl, CaCl₂). Because the Eh is dependant also on pH of 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 not altered soils, rH₂ value is <20 (Richter & Hlušek, 2003).

Paste pH_(KCl) of soil/technosoil enables to determine ionic composition of soil sorption complex and the cation exchange capacity (McNeill, 1992; Čurlík

and Šefčík, 1999; Čurík, 2003). The pH_{H₂O} – pH_{KCl} difference is expressed by D_{pH} value. Positive value is equal to the occurrence of soil colloides with negative charge, and negative value reflects the occurrence of colloids with positive charge.

ICP-MS analyses of soil/technosoil samples were realised in ACME Laboratory (Vancouver, Canada) from samples of 50 g in weight. Samples were homogenized and dried at laboratory temperature. The grinding in agate mill was realized in laboratory of Geological Institute of Slovak Academy of Science in Banská Bystrica.

2 g of rock powder was wetted with a few drops of water and then digested to dry vapour in H₂O-HF-HClO₄-HNO₃ mixture with rate: 2 : 2 : 1 : 1. After adding 10 ml of 50 % HCl, the samples were slowly heated on water bath under continual mixing. Cooled solution was refilled by HCl to exact volume and ICP-MS analysed.

The concentration values that we found out by laboratory analyses were finally compared with concentration limits provided by Italian law (Law Decree 152/06) as far as soil and water are concerned, in order to check whether the studied environmental matrices are polluted.

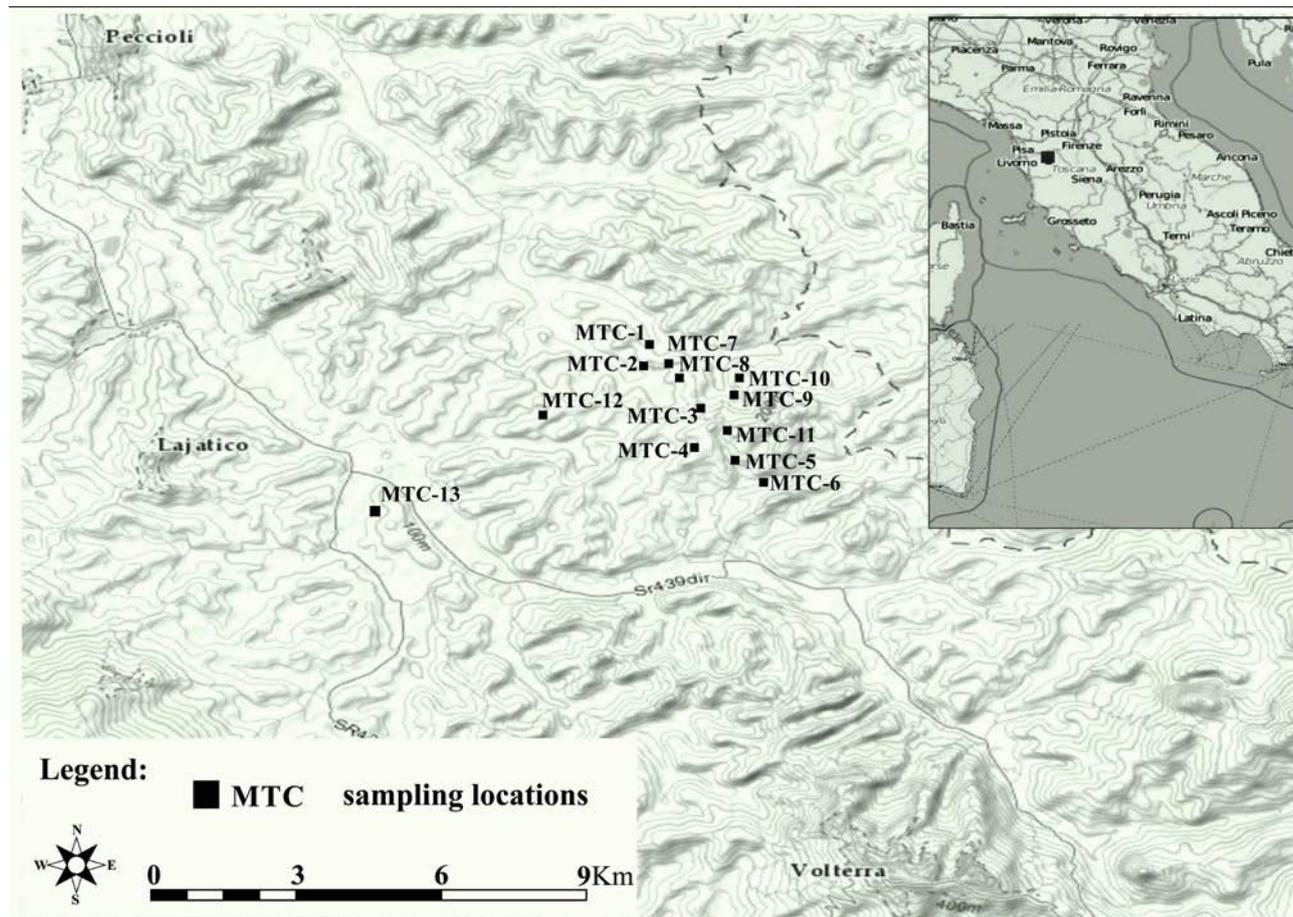


Figure 2. Map of the sampling localities in Caporciano at Montecatini Val di Cecina.

For the bioaccumulation calculation, two parameters are important: the bioconcentration factor (BCF) and the translocation factor (TF). These factors are determined from analytical data about the heavy metals content in soil from root age system, underground part of the plant and elevated part of the plant.

We calculated the BCF value as a metal content in leaves/ metal content in soil (Mehes-Smith et al., 2013). If the $BCF < 1$, the plant is excluder,

if $BCF = 1$, the plant is indicator,
if the $BCF > 1$, the plant is accumulator to hyperaccumulator (Baker, 1981).

Translocation factor (TF) reflects the rate of chemical concentration of contaminant in leaves vs. concentration of contaminant in roots. This parameter shows in which part of the plant is the contaminant (in our case individual heavy metal) preferentially accumulated.

Table 1. ICP-MS analyses of soil/technosoil

Sample	Soil horizon	Fe	Mn	Cu	Pb	Zn	As	Sb	Mo	
		%		mg·kg ⁻¹						
		dump-field								
MTC-1	A/B	6.01	0.080	6388	12	766	2	0.4	2.7	
MTC-2	A/B	5.89	0.078	8290	27	697	3	0.4	3.5	
MTC-3	A/B	6.33	0.079	6663	12	540	1	0.6	1.9	
MTC-4	A/B	6.38	0.081	9337	28	947	2	0.5	2.7	
MTC-5	A/B	6.10	0.078	9258	23	91	3	0.6	2.7	
MTC-6	A	4.09	0.064	5022	71	174	3	1.0	3.3	
	B	6.39	0.082	6359	16	101	3	0.4	3.6	
	C	6.29	0.082	8619	18	118	3	0.4	3.2	
MTC-7	A/B	5.30	0.072	6378	24	717	1	0.5	1.8	
MTC-8	A/B	5.64	0.079	5135	12	674	< 1	0.4	1.9	
MTC-9	A	4.69	0.124	5020	26	588	3	0.6	1.8	
	B	5.30	0.145	6123	11	417	3	0.6	2.4	
	C	5.22	0.951	8222	13	425	3	0.2	1.7	
MTC-10	A/B	5.71	0.081	8449	22	882	2	0.4	2.8	
MTC-11	A/B	6.42	0.088	12 100	23	1063	2	0.5	2.5	
MTC-12	A/B	6.01	0.084	5984	11	783	2	0.4	2.8	
		reference area								
MTC-13	A/B	5.10	0.055	876	14	53	< 1	0.1	1.1	

Table 1. (continuation) ICP-MS analyses of soil/technosoil

Sample	Soil horizon	Ni	Co	Th	U	Cd	Bi	V	Ag	
		mg·kg ⁻¹								
		dump-field								
MTC-1	A/B	110	33	0.4	2.5	3.1	1.1	145	1.6	
MTC-2	A/B	112	31	0.3	2.6	3.1	0.9	142	2.2	
MTC-3	A/B	159	35	0.8	1.9	2.4	0.5	153	1.6	
MTC-4	A/B	130	35	0.6	3.1	4.0	1.1	143	2.3	
MTC-5	A/B	123	33	0.8	2.8	4.1	0.9	147	2.4	
MTC-6	A	81	25	1.0	2.0	4.0	0.6	86	1.4	
	B	110	34	0.3	3.1	2.7	0.6	143	2.2	
	C	116	35	0.3	3.1	3.3	0.8	148	2.3	
MTC-7	A/B	96	27	0.4	2.1	3.7	0.6	150	1.7	
MTC-8	A/B	105	30	0.2	2.0	2.7	0.5	160	1.4	
MTC-9	A	144	31	2.8	2.0	3.7	0.4	118	2.5	
	B	154	37	1.1	3.3	1.8	0.4	226	2.7	
	C	177	40	1.0	3.3	2.6	0.9	231	3.1	
MTC-10	A/B	97	30	0.3	2.4	4.4	0.7	169	2.2	
MTC-11	A/B	106	33	0.3	2.6	4.1	1.0	164	3.2	
MTC-12	A/B	111	30	0.4	2.6	2.5	0.4	164	1.7	
		reference area								
MTC-13	A/B	54	20	0.3	2.1	0.8	0.2	38	0.9	

In order to determine the risk of the studied site contamination, it is necessary to calculate the enrichment factor (EF): content of contaminant in soil or in part of plant from contaminated site/ contaminant in soil or in part of plant from not contaminated site. We calculated EF according to the rate: heavy metal content in leaves of contaminated plants from the dump-field/ heavy metal content in leaves of not contaminated plants from reference area (Kisku et al., 2000).

About samples MTC-6 and MTC-9 we used for calculation the average value of individual heavy metal in A and B horizons.

3. RESULTS AND DISCUSSION

3.1 Heavy metals content in soils

The analysis of heavy metals in soil/technosoil at the dump-field area proved high Fe (4.09 – 6.42 %), Cu (5020 – >10000 mg.kg⁻¹), Zn (91 – 1063 mg.kg⁻¹), V (86 -169 mg.kg⁻¹) and Ni (81 – 159 mg.kg⁻¹) contents. By comparing the soil horizons, we found out that the highest Pb, Zn and Cd contamination is in A horizon whereas the highest Fe, Mo and U contents were found in B horizon. The highest Cu, Mn, Ni, Co, Bi, V and Ag contents were found in C horizon. Mn, As, Sb, U and Th contents are the highest both in B and C horizons (Table 1).

The less strict limits (for industrial/commercial sites) of the National Law 152/06 are exceeded only by Cu, but if we accept the comparison with more strict limits of this law (for public green sites), then Zn, Sn, Ni, Co, Cd, V and Cr contents exceed also the allowed limits (Tables 1 and 2).

Table 2. Limit values (mg.kg⁻¹) for soils concerning public green, private and residential sites (A), and industrial/commercial sites (B), provided by Italian Law Decree 152/2006

Element	mg.kg ⁻¹	
	A	B
Cu	120	600
Pb	100	1000
Zn	150	1500
Ni	120	500
Co	20	250
Cd	2	15

Element	mg.kg ⁻¹	
	A	B
As	20	50
Sb	10	30
V	90	250
Cr	150	800
Sn	1	350
Be	2	10

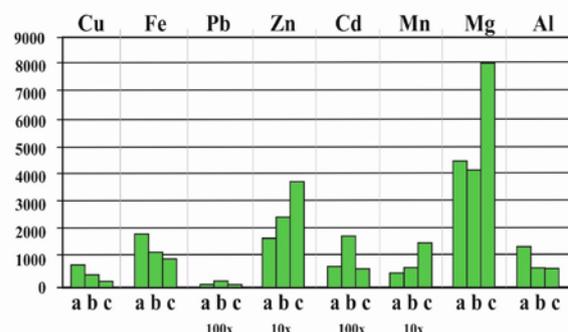
The rinse pH_(H₂O) of the soil samples is close to neutral conditions. It ranges from 5.99 to 7.13 (average pH_(H₂O) value is 6.66). The average paste pH_(KCl) is 5.87 (Table 3). These pH values are not very favourable for massive heavy metal mobilization. The average rH₂ factor calculated from paste Eh is 13.86. This values indicates not well aerated soils. The positive D_{pH} values (0.13 to 1.19,

average 0.597; Table 3) indicate occurrence of soil colloids with negative charge.

Table 3. Characteristics of soil/technosoil from the dump-field

Sample	H ₂ O		KCl		D _{pH}
	pH	Eh (mV)	pH	Eh (mV)	
MTC 1	6.84	8	6.24	46	0.60
MTC 2	7.13	-4	6.72	38	0.41
MTC 3	5.99	24	5.49	89	0.50
MTC 4	6.17	39	5.13	97	1.04
MTC 5	6.22	27	5.46	85	0.76
MTC 6A	6.36	19	6.15	74	0.21
MTC 6B	6.66	8	6.72	22	0.06
MTC 6C	6.87	-5	7.00	-4	-0.13
MTC 7	6.72	7	6.04	46	0.68
MTC 8	7.04	-12	6.12	41	0.92
MTC 9A	6.34	29	5.28	91	1.06
MTC 9B	6.72	11	6.62	31	0.10
MTC 9C	7.00	-1	6.99	-3	0.01
MTC 10	6.12	42	4.93	111	1.19
MTC 11	6.36	28	5.40	83	0.96
MTC 12	6.48	21	5.55	75	0.93
MTC-13	7,02	2	6,98	22	0.04

Pinus sp.



Quercus sp.

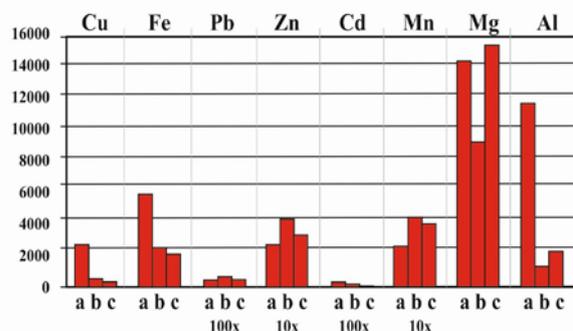


Figure 3. Cumulative heavy metal concentrations in plant genuses from Caporciano (Montecatini Val di Cecina) dump-fields; a-roots b-branches/stem, stalk c-leaves/needles

The results show similar situation as it was described at another mining dump-fields, mentioned e.g. by Marschalko et al., (2012), Kempa et al., (2013) or Andráš et al., (2007).

3.2 Heavy metals in plants

Many authors study contamination of plants by

heavy metals at contaminated sites (e.g. Banášová et al., 2006; Horn et al., 2012; Turisová et al., 2013; Füleky & Barna, 2008). The floristic composition on Cu-dumps is usually poor (e.g. Banášová et al., 2006; Aschenbrenner et al., 2011; Turisová et al., 2013) but it is possible to see some morphometric differences between the species from metalliferous and non-metalliferous sites (Štrba et al., 2013).

Table 4. Analyses of plants from Caporciano mine dump-field (a - roots, b – steems/branches, c – leaves/needles)

Sample	Plant species	Part of plant	Fe	Mn	Mg	Al	Cu	Pb	Zn	Cd
			mg·kg ⁻¹							
dump-field										
MTC-1	<i>Pinus</i> sp.	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
MTC-6		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
MTC-7		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
MTC-12		a	290	11	1102	180	140	0.2	48	2.68
		b	355	25	1465	203	171	1.0	88	9.11
	c	119	60	2080	82	22	0.3	124	2.47	
MTC-2	<i>Quercus</i> sp.	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
MTC-3		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
MTC-4		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
MTC-8		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	
MTC-9	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	
MTC-10	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	
MTC-11	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	
reference area										
MTC-13	<i>Pinus</i> sp.	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
MTC-13	<i>Quercus</i> sp.	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

The heavy metal contents in individual parts of the two dominant plant genera (*Pinus* sp. and *Quercus* sp.) are presented in table 4. The most important contaminants are Mg > Fe > Al > Cu > Zn > Mn and Cd. The highest Fe, Cu and Al contents in *Pinus* sp. (Fig. 3) are in roots and the highest Zn, Mg and Mn contents in leaves, whereas the highest Pb and Cd contents were found in branches. In *Quercus* sp., the highest Fe, Cu, Al and Cd contents are in roots and the highest Mn and Zn contents in branches. Only Mg shows the highest contents are in branches and leaves. This very complex situation is very similar as at Slovak Cu deposits Ľubietová, Špania Dolina and Staré Hory (Andráš et al., 2007, 2012, 2014).

The BCF and the TF are the most important indicators of heavy metals acceptance by plants and of their accumulation in plant tissues (Hemond &

Fechner-Levy, 2000). BCF value is for all studied plants at Caporciano dump-field <1, so all these plants are excluders. In excluders is the heavy metal content immobilized in roots, and in elevated parts of plants it is relatively low (Baker, 1981).

The TF indicates in which part of plant are the heavy metals preferentially accumulated. The TF values (Table 5) are the highest for Mn in *Pinus* sp. (in average 4.063) and for *Quercus* sp. (in average 3.340). The lowest values were described for Cd (in average 0.120) in *Pinus* sp. and for Cu (in average 0.110) in *Quercus* sp. These low TF values correspond with some data from Slovak Cu deposits (Banášová et al., 2006; Tomaškin & Tomaškinová, 2012, Turisová et al., 2013 or Štrba et al., 2013) and they reflect the predominant accumulation of metals in roots.

Table 5. Bioconcentration factor (BCF) and translocation factor (TF)

Sample	Plant	BCF					TF				
		Cu	Pb	Zn	Mn	Cd	Cu	Pb	Zn	Mn	Cd
dump-field											
MTC-1	<i>Pinus</i> sp.	0.011	0.017	0.159	0.001	0.887	0.167	1.000	2.440	5.200	0.958
MTC-6		0.014	0.014	0.862	0.081	0.259	0.186	0.186	1.488	2.360	0.384
MTC-7		0.007	0.025	0.199	0.076	0.686	0.166	0.166	2.750	3.235	1.081
MTC-12		0.020	0.027	0.158	0.071	0.988	0.157	1.500	2.583	5.455	0.922
x		0.013	0.021	0.345	0.057	0.705	0.169	0.713	2.315	4.063	0.836
MTC-2	<i>Quercus</i> sp.	0.002	0.011	0.065	0.127	0.039	0.088	0.750	0.882	3.536	0.098
MTC-3		0.012	0.125	0.080	0.153	0.071	0.153	1.000	0.896	0.275	0.347
MTC-4		0.009	0.010	0.086	0.164	0.273	0.024	0.024	0.149	0.591	0.119
MTC-8		0.003	0.067	0.111	0.171	0.030	0.012	0.012	0.765	2.288	0.093
MTC-9		0.013	0.017	0.126	0.096	0.082	0.182	0.182	2.739	6.842	0.535
MTC-10		0.001	0.050	0.044	0.532	0.018	0.084	0.084	1.219	4.489	0.129
MTC-11		0.007	0.065	0.069	0.163	0.015	0.230	3.000	2.808	6.227	0.822
x		0.006	0.043	0.128	0.176	0.066	0.966	0.646	1.182	3.340	0.829
reference area											
MTC-13	<i>Pinus</i> sp.	0.011	0.714	0.981	0.002	0.050	0.500	3.333	2.500	2.400	0.200
MTC-13	<i>Quercus</i> sp.	0.006	0.007	0.679	0.038	0.275	0.104	0.500	1.714	2.100	2.444

Table 6. Enrichment factor (EF)

Sample	Plant species	EF				
		Cu	Pb	Zn	Mn	Cd
dump-field						
MTC-1	<i>Pinus</i> sp.	2.3	2.0	2.34	2.16	23.09
MTC-6		8.1	6.0	2.29	2.45	22.00
MTC-7		4.4	6.0	2.75	2.29	63.50
MTC-12		1.7	3.0	2.38	2.50	61.75
x		4.1	4.2	2.44	2.35	42.59
MTC-2	<i>Quercus</i> sp.	3.8	3.0	1.25	4.71	0.55
MTC-3		15.6	15.0	1.19	5.76	0.77
MTC-4		16.0	3.0	2.25	6.33	4.95
MTC-8		3.4	8.0	2.08	6.43	0.36
MTC-9		1.2	3.0	1.75	6.42	1.05
MTC-10		1.6	1.1	1.08	20.52	0.36
MTC-11		16.0	1.5	2.02	6.52	0.27
x		8.23	8.0	1.66	8.10	1.19

In order to determine the risk of the individual site contamination the enrichment factor (EF) is used. The obtained data from Caporciano mine (Table 6) show that the leaves of plant from contaminated sites (dump-field) are several times more contaminated than the leaves from reference area. The highest EF was determined for Cd in *Pinus* sp. (in average 42.59) and for Mn, Pb and Cu in *Quercus* sp. (EF = 8.10, 8.00, 8.23 in average). The lowest EF was calculated for Cd in *Quercus* sp. (1.19 in average).

4. CONCLUSIONS

The contents of the heavy metals in plant tissues decrease in the following rank: Fe, Mn, Cu, Zn and Ni. Most of these metals exceed the concentration limits provided by the Italian law Decree 152/06 for public green sites. The pH of the soils/technosols is close to neutral values.

At the dump-fields only two dominant plant species are present: *Pinus* sp. and *Quercus* sp.

The comparison of additive concentrations of heavy metals in individual types of plant tissues (roots, branches/stems and leaves/needles) showed that the highest concentrations of Cu, Fe and Al are in root system whereas the highest Zn, Mg content is determined in leaves and needles. The BIF values identify all these plants as excluders. Also the TF and EF values are relatively low. A little bit higher TF values are only for Mn in *Pinus* sp. and in *Quercus* sp. In spite of heavy metal contamination in the plants, the latter are not suitable to be used for phytoremediation.

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