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COMPARISON OF SOIL CONTAMINATION AT THE SELECTED EUROPEAN COPPER MINES

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Abstract: This article reports the results of a study concerning contamination of the dump-fields by potentially toxic elements at five abandoned copper mines: Ľubietová, Špania Dolina (Slovakia), Libiola, Caporciano (Italy) and São Domingos (Portugal). This paper offers an updated description of soil contamination at the individual deposits and indicates a possible solution of the derived environmental problems. Contamination of technosoils by PTEs at the dump-fields shows an irregular spatial distribution of Fe, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sb and Pb. Contents of PTEs often exceed both national and EU law limits. Whereas at Ľubietová, Špania Dolina and Caporciano the environmental risk is limited, at Libiola and São Domingos it seems to be very heavy. The technosoil (slag) of the dump-fields is not well aerated and the soil colloids have (except for Špania Dolina) negative surface charge, so they are suitable for PTEs sorption. The main environmental risk in the mining area of Sao Domingos district is the long time formation of acid mine drainage water and the high Zn, As and Pb contents. The release of PTEs to the environmental components may be limited by phytostabilization and immobilization of metals, by suitable admixtures into the technosoil/slag. The environmental situation at Caporciano is not so compromised as at São Domingos mining area. Phytostabilization will be able to stop erosion, and installation of wetlands under the dump will stop the release of Cu to the environment.

Key words: abandoned Cu mines; potentially toxic elements; dump-fields; technosoil; environmental risk

1. INTRODUCTION

Slovakia, Italy and Portugal are known in Europe for their mining tradition. In all three countries, in fact, heavy environmental problems have derived from mining, treatment and processing activities. The pre-sented article is focused on comparison of the poten-tially toxic elements (PTEs) contamination of the dump-fields at the selected five abandoned Cu-deposits (Ľubietová, Špania Dolina, Caporciano, Libiola, and São Domingos; (Fig. 1), with respect to their environmental risk.

Ľubietová is located in the central part of the Western Carpathians. It was one of the most important copper mining districts in the past. The volcano-sedimentary Cu-(Ag-) mineralization is genetically connected with the basic, intermediate and acid Permian volcanism. There, metals were mobilized by granite intrusion during the Alpine orogeny. The main ore minerals are chalcopyrite, tetrahedrite (often Ag-bearing) and pyrite (Andráš et al., 2008; 2009). The mine was closed in 1915. The dump-field material on the steep slope consists of mixture of strongly weathered greywacke fragments with coarse-grained sandy gravel, which contain rests of the ore minerals.

The landscape relief at Špania Dolina is significant-ly changed by mining activity since Bronze age up to the 20th century. The extractive activities affected a total area of 4 x 1.5 km^2. The most important pyrite mineralization of Triassic age is rich with chalcopyrite, tetrahedrite, ankerite, Cu-sulphides and Cu-carbonates, as malachite and azurite. These minerals are still present in the dump-material. Among the large heap-fields, the most important one from the viewpoint of the environmental risk is the Maximilian heap, immediately above Špania Dolina village. It consists of the coarse-grained rock-fragments and sandy gravel (Nagyová et al., 2013). The exploitation of ore in Špania Dolina finished in 1888.

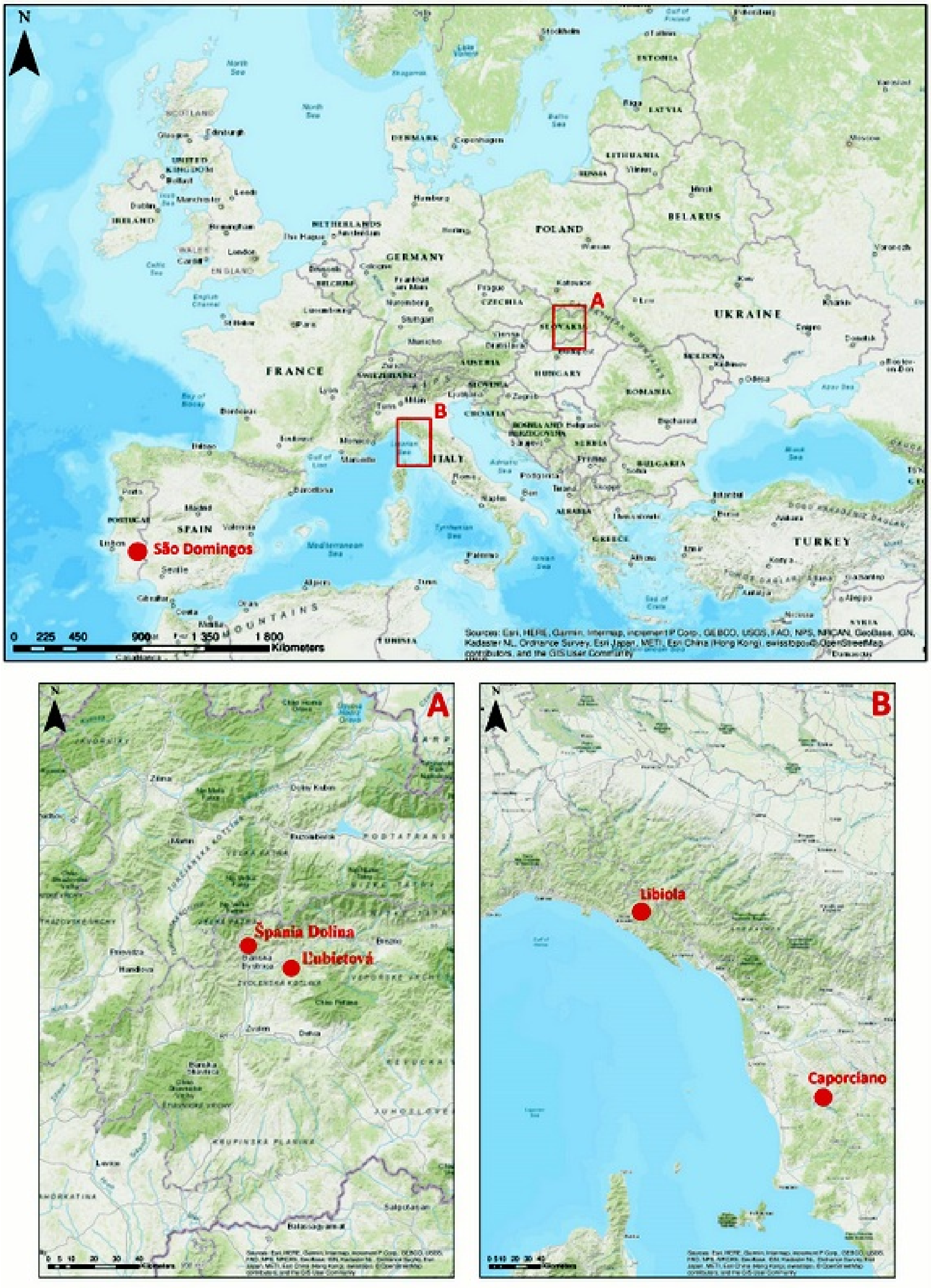

Figure 1. Localization of the studied abandoned Cu-deposits (Processed in ArcGIS 10.5)

Libiola deposit may be classified as a strata-bound volcanic-associated massive sulphide deposit (VMS), where sulphide mineralization is mainly associated to pillow basalts and basaltic breccias and, subordinately, to serpentinitic rocks of ophiolites of Internal Ligurian Units (Ferrario et al., 1980). The deposit was exploited both by the system of numerous galleries and in the open-pit mine on the top of the mountain range. The stratified dump-field material, covering an area of 0.5 km^2, is heterogeneous in its grain size and lithology of the rocks (mixture of ultramafic and Fe-rich phases; Dinelli et al., 2001). The dumped material contains significant amounts of chalcopyrite and pyrite ore waste (Marescotti et al., 2010). The end of mining activity at Libiola is dated to 1961 (Galli & Penco, 1966).

Caporciano deposit, near Montecatini Val di Cecina, was the most important Cu deposit in Europe in the 19th century (Riparbelli, 1980). In 1963, the mine was definitively closed. Caporciano mine may be considered as a remobilization deposit, showing features of medium temperature hydrothermal origin, whose mining importance is connected to the extraction of three sulphides: chalcopyrite, bornite and chalcocite (De Michele et al., 1987). The deposit was divided into two different mines: the large open-pit mine and underground galleries whose total longitude exceeded 30 km (Klemm et al., 1982). The spoil-heap consists of grey sandy material and, because of the steep slope of its surface and limited plant cover, it is strongly affected by erosion (Buccheri et al., 2014a).

São Domingos belongs to the most important Cu-mineralizations of a metallogenetic province in the Iberian Pyrite Belt (Sáez et al., 1999; Álvarez-Valero et al., 2008). It was exploited since Roman Age. As the demand for copper grew in the 19th century, the exploitation was renewed after the assignation of the mining concession to the English company Mason & Barry in 1859. The massive pyrite-chalcopyrite ore body forms the top parts of the Volcano-Sedimentary Complex, consisting of felsic, intermediate to basic volcanic rocks, and black shales (Matos et al., 2006a, 2008). The main economically important ores were: pyrite, sphalerite, chalco-pyrite, galena, arsenopyrite and sulfosalts (Matos et al., 2006b; Webb, 1958). Spacious areas without any or with poor vegetation cover reflect the strong negative impact of the long-term mining activities. The slag and technosoil contain high PTEs content (Álvarez-Valero et al., 2008; Mateus, et al. 2011; Carvalho, 1971). All the country is markedly affected by acid mine drainage water (Abreu et al., 2010). The great open-pit mine was closed in 1966 due to mineral depletion (Matos et al., 2006a).

For our study, we selected a set of PTEs which are typical for all five studied deposits: Fe, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sb and Pb.

2. MATERIAL AND METHODS

Sampling procedure involves sample collection and sample reduction. The soil material was collected according to a regular 20x20 m network in such a way that each final representative sample consists of 5 original samples, which were mixed together and subsequently homogenized. 33 samples from the dump-fields and 3 samples from the reference area were taken at Ľubietová, and 40 dump-samples were collected at Špania Dolina. For the research, we also collected further 36 and 12 dump samples, as well as 3 and 2 samples from reference areas at Libiola and Caporciano. The set of samples was completed by 30 samples from São Domingos mining area and by 5 samples from its reference area. The samples were then dried at laboratory temperature.

The rinse pH and Eh were measured according to Sobek et al., (1978) in water. The paste pH and Eh were measured in 1M KCl lixivium, using pH-metre EUTECH Instruments. The determined pH and Eh values were calculated for standard hydrogen electrode.

For comparison of Eh values at different pH, the rH_2 factor was used, defined by Richter et al. (2003) as it follows: $rH_2 = Eh/30 + 2pH$. Well aerated soils are characterized by rH_2 factor ranging between 28 and 34, whereas not aerated soils, are characterized by rH_2 factor <20.

The D_{pH} factor is defined as $pH_{H2O} – pH_{KCl}$ difference (McNeill, 1992). Positive values of the D_{pH} factor indicate presence of soil colloids with negative surface charge and, vice versa, negative values of the D_{pH} factor reflect colloids with positive charge.

The technosoil samples were homogenized and dried at laboratory temperature and consequently analysed for Fe, Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Sb and Pb, using ICP-MS method, in ACME Laboratory (Vancouver, Canada).

2 g of technosoil powder was wetted with a distilled H_2O and subsequently digested to dry vapour in H_2O-HF-$HClO_4$-HNO_3 mixture. 10 ml of 50% HCl was added to the samples and the solutions were heated on water bath. The well homogenized and limpid solution was refilled by HCl to exact volume and analysed by ICP-MS in ACME laboratories (Vancouver, Canada).

3. RESULTS

At all investigated deposits, the results demonstrate high concentrations, except for Fe, mainly of Cr, Mn, Ni, Cu, Zn, As, Sb and Pb on the dump-fields (Table 1, Fig. 2). The most contaminated technosoil is at **São Domingos** mining area, where the average concentrations of Zn, As and Pb are, respectively, 960 $mg \cdot kg^{-1}$, 1 191 $mg \cdot kg^{-1}$ and 3 122 $mg \cdot kg^{-1}$ (Tables 1; 2).

The dump-field contamination is also very high at Libiola. The average PTEs contents are 16.54 % as for Fe, 633 $mg \cdot kg^{-1}$ as for Cr, 91 $mg \cdot kg^{-1}$ as for Co and 451 $mg \cdot kg^{-1}$ as for Ni (Tables 1; 3), whereas the highest Sb contents (on average 366.2 $mg \cdot kg^{-1}$) were described at **Špania Dolina** deposit, where the most important source of Sb is tetrahedrite (Tables 1; 4).

Caporciano dump-field is firstly characterized by the most high Cu contents (on average 7 302 $mg \cdot kg^{-1}$), as well as by high Mn and Cd contents (on average 827 $mg \cdot kg^{-1}$ and 3.4 $mg \cdot kg^{-1}$, respectively; Tables 1; 5).

The metal contents at the dump-fields substantially exceed the background PTEs contents at the reference areas (Tables 2 – 6).

Table 1. Average metal contents at the studied dump-fields

Deposit	Fe	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
	%	mg·kg^{-1}									
Ľubietová	2.16	17	365	28	31	3 662	23	179	0.1	31.8	30
Špania Dolina	1.56	16	235	22	23	1 500	38	234	0.1	**366.2**	26
Libiola	**16.54**	**633**	639	**91**	**451**	3 543	364	20	1.5	4.8	68
Caporciano	2.70	136	**827**	32	115	**7 302**	765	2	**3.4**	<3.0	20
São Domingos	10.06	64	393	21	23	656	**960**	**1 191**	0.9	144.1	**3 122**

Table 2. ICP-MS analyses of technogenic soil from São Domingos mining area.

Sample	Fe	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
	%	mg·kg^{-1}									
dump-field area											
S-1	11.80	69	292	25.9	25.4	370	414	1004	0.4	125	2 737
S-2	7.45	89	722	21.7	49.1	27	69	100	0.6	20	726
S-3	6.70	94	565	11.4	32.8	265	153	551	1.1	279	6 695
S-4	9.59	54	174	11.4	14.4	793	772	1 742	2.6	667	13 500
S-5	8.22	49	125	12.7	13.2	874	1 470	1965	3.8	1095	12 000
S-6	20.43	35	426	66.3	12.1	1 481	8 760	916	3.9	388	8 499
S-7	4.68	95	1164	18.1	52.5	148	97	76	0.2	9	137
S-8	6.62	103	298	6.6	34.6	113	88	628	0.2	34	360
S-9	9.41	36	16	0.6	1.1	57	16	1751	0.1	18	3 194
S-10	8.44	31	101	3.9	8.6	257	74	1540	0.3	57	2 305
S-11	16.64	73	92	2.5	4.9	216	85	3906	0.3	225	9 407
S-12	25.24	66	182	49.2	6.5	1 665	4 503	1768	1.6	197	6 255
S-13	10.25	50	1386	98.9	23.0	6 205	312	343	0.8	50	1 501
S-14	6.25	43	1878	36.7	62.3	1 284	1 463	273	2.6	44	715
S-15	20.57	64	268	73.9	16.0	1 208	4 162	507	0.8	48.7	1 516
S-16	9.30	67	130	10.9	15.5	347	648	1 474	0.4	62.8	2 995
S-17	21.37	69	547	23.7	75.4	729	574	922	1.0	74.5	2 008
S-18	10.15	70	220	8.2	15.2	546	217	2 631	0.8	102.9	6 712
S-19	14.78	20	56	9.2	2.9	279	815	2 405	0.4	112.1	4 025
S-20	8.76	98	59	3.4	8.3	230	168	1 647	0.1	57.4	573
S-21	7.82	65	150	7.9	8.4	234	169	1 187	0.4	65.0	719
S-22	3.29	58	126	4.0	15.6	335	75	362	0.1	43.0	516
S-23	13.46	59	165	44.4	9.0	757	2 533	439	0.5	156.4	2 123
S-24	5.43	55	170	3.6	12.7	82	68	1 865	0.2	63.4	293
S-25	5.88	81	858	18.9	45.7	190	386	247	1.3	14.0	322
S-26	5.47	84	463	16.6	43.4	227	245	65	0.3	6.5	80
S-27	6.73	52	112	3.5	9.3	149	102	4 366	0.9	234.1	1 295
S-28	4.59	65	553	13.7	31.2	162	159	86	0.2	8.5	162
S-29	7.33	57	139	3.6	9.4	263	102	780	0.0	48.9	1 790
S-30	5.33	66	346	9.2	33.5	187	94	189	0.1	19.4	511
reference area											
S-1R	3.41	51	813	14.2	25.1	28.4	53	26	0.3	4.2	52
S-2R	1.78	26	513	5.9	13.7	24.5	43	8	0.3	3.7	18
S-3R	4.84	75	2 001	25.1	44.9	39.2	137	68	0.6	2.9	67
S-4R	5.23	75	1 497	27.0	47.3	39.1	139	84	0.6	4.4	70
S-5R	4.90	105	2 403	27.2	55.2	48.3	128	17	0.8	4.0	48

Table 3. ICP-MS analyses of technosoil from Libiola deposit

Sample	Fe	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
	%	$mg \cdot kg^{-1}$									
dump-field area											
LB-1	15.89	222	960	33	80	945	410	10	1.0	4.0	74
LB-2	14.22	702	600	61	509	2 991	228	6	9.4	2.3	16
LB-3	11.89	1 118	3 380	461	1 022	11 000	606	7	2.2	3.1	48
LB-4	15.09	830	4 610	539	907	12 400	691	14	2.7	3.1	69
LB-5	9.28	1 158	1 380	195	1 104	7 345	436	11	1.3	2.8	30
LB-6	10.82	1 374	1 010	108	713	5 638	435	8	3.6	4.8	33
LB-7	19.08	1 145	750	81	667	3 238	265	14	0.5	7.7	113
LB-8	7.75	961	1 232	85	982	1 794	374	5	0.9	2.2	44
LB-9	6.38	752	1.068	73	732	1 624	328	5	0.8	1.9	47
LB-10	10.02	989	952	101	1 115	1 765	402	4	1.1	2.5	27
LB-11	15.50	444	683	87	574	11 800	2 851	3	5.3	1.8	14
LB-12	19.25	86	18	21	9	323	22	10	0.7	2.0	137
LB-13	41.00	117	40	9	18	3 343	219	110	1.0	1.7	40
LB-14	42.00	1 121	385	34	308	12 050	354	266	0.3	84.0	476
LB-15	21.13	190	198	10	32	1 383	113	12	0.8	2.2	38
LB-16	35.23	114	112	28	29	2 870	85	11	0.4	1.9	18
LB-17	15.70	386	417	38	250	2 328	225	8	1.3	2.6	67
LB-18	16.98	641	469	71	645	4 652	248	4	1.1	1.8	19
LB-19	16.91	529	477	79	433	4 868	214	3	0.6	2.0	25
LB-20	23.88	763	233	87	437	6 680	242	3	0.3	1.6	25
LB-21	15.43	267	800	59	154	2 287	168	6	0.2	2.0	14
LB-22	15.82	238	738	40	89	1 535	175	10	0.4	1.8	365
LB-23	23.70	69	27	4	8	1 193	45	60	0.4	2.6	54
LB-24	24.34	423	330	31	191	3 737	150	36	0.9	2.5	196
LB-25	22.54	348	573	59	160	4 961	241	10	0.9	2.9	44
LB-26	14.09	516	770	66	433	2 950	442	8	1.4	2.7	122
LB-27	14.88	593	544	81	661	4 266	234	4	1.4	2.2	25
LB-28	17.67	575	485	76	496	4 762	286	5	2.1	1.9	34
LB-29	18.74	481	485	81	356	5 990	308	6	2.5	2.5	23
LB-30	20.48	656	452	94	471	6 880	286	5	2.3	1.3	32
LB-31	11.80	1 225	1 202	114	717	1 884	345	5	1.5	1.0	19
LB-32	14.21	245	846	35	127	2 291	247	5	0.6	2.7	21
LB-33	15.93	303	1 177	153	224	5 347	579	8	1.8	2.2	16
LB-34	14.00	559	614	83	619	4 108	227	5	0.6	2.2	26
LB-35	18.83	376	354	42	231	3 065	195	10	0.6	2.0	29
LB-36	14.80	734	481	59	724	6 337	420	11	3.0	2.0	72
reference area											
LB-1R	9.86	111	627	132	483	18	7	6	1.1	0.1	17
LB-2R	12.97	269	509	68	284	2 543	148	3	0.4	2.0	15
LB-3R	5.15	455	603	38	435	448	189	6	0.3	1.0	32

The soil reaction is mainly characterized by pH and Eh. The pH and Eh range and average values are shown in Table 7. The results show that the most acid conditions are at São Domingos (average $pH_{(H2O)}$ = 4.29; $pH_{(KCl)}$ = 3.95) and Ľubietová (average $pH_{(H2O)}$ = 4.74; $pH_{(KCl)}$ = 4.94) deposits. At Caporciano deposit. it was found that conditions are the closest to the neutral values (average $pH_{(H2O)}$ = 6.56; $pH_{(KCl)}$ = 5.99).

The average redox potential $Eh_{(H2O)}$ ranges from 100.64 (at Ľubietová). to 62.85 (at Špania Dolina). to 67.71 (at Libiola) to 15.01 (Caporciano). up to 153.32 (at São Domingos). $Eh_{(KCl)}$ ranges from 58.00 (at Caporciano) to 173.90 (at São Domingos). Both the $Eh_{(KCL)}$ values and the D_{ph} and rH_2 factors are presented in Table 8.

4. DISCUSSION

Basic informative data about the contamination of the dump-fields by PTEs at selected deposits were

Table 4. ICP-MS analyses of samples from Maximilian dump-field (Špania Dolina)

Sample	Fe	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
	%	$mg \cdot kg^{-1}$									
dump-field area											
MX-1	1.67	16	262	22.6	23.2	2 713	51	347	0.2	533	43.9
MX-2	1.58	16	200	20.5	24.6	1 541	31	277	0.1	451	20.8
MX-3	1.32	15	102	13.7	22.1	1 241	27	174	0.1	311	15.4
MX-4	1.67	19	275	23.9	23.0	1 065	32	204	0.2	330	25.3
MX-5	1.53	16	244	34.5	30.2	2 057	46	272	0.2	417	15.3
MX-6	1.77	15	250	14.5	17.0	603	35	116	0.1	167	16.7
MX-7	1.81	15	313	15.2	17.8	741	31	230	0.1	410	23.4
MX-8	2.01	16	359	16.1	15.8	559	38	94	0.1	144	18.0
MX-9	1.80	15	351	18.2	18.0	981	32	130	0.1	208	16.6
MX-10	1.83	15	361	33.3	30.3	1 859	51	229	0.2	367	18.8
MX-11	1.91	17	352	35.4	33.8	2 377	55	297	0.2	477	17.2
MX-12	1.29	15	164	21.7	23.2	722	27	138	0.1	195	22.2
MX-13	1.31	17	146	13.1	19.2	855	32	124	0.1	402	27.2
MX-14	1.43	17	162	11.3	18.5	639	28	105	0.2	168	37.1
MX-15	1.49	17	223	22.0	21.6	716	34	195	0.1	259	32.2
MX-16	1.86	18	427	31.9	20.4	1 035	44	235	0.2	340	34.7
MX-17	1.47	14	256	29.7	23.3	1 157	38	192	0.1	287	21.9
MX-18	1.25	14	164	20.7	19.3	948	34	258	0.1	382	31.0
MX-19	1.63	13	336	30.4	24.8	2 126	51	217	0.2	387	15.9
MX-20	1.75	20	355	23.3	18.8	1 031	47	119	0.3	163	64.8
MX-21	1.73	20	331	21.1	20.9	823	38	115	0.1	175	51.8
MX-22	1.97	15	225	28.8	24.4	8 502	99	983	0.4	1 403	72.0
MX-23	1.29	13	62	9.6	27.4	1 083	18	300	0.1	539	15.4
MX-24	1.73	20	194	27.1	31.6	2 039	36	316	0.1	476	23.2
MX-25	1.71	19	174	18.2	27.6	1 582	27	377	0.0	588	28.2
MX-26	1.15	10	156	15.5	13.9	1 319	26	185	0.0	306	16.6
MX-27	1.36	13	108	11.6	23.6	926	24	239	0.0	443	18.3
MX-28	1.94	17	366	30.2	26.4	1 840	43	270	0.2	441	17.8
MX-29	1.46	15	186	20.7	19.9	820	29	225	0.1	324	23.6
MX-30	1.44	18	218	26.3	22.4	989	33	160	0.1	229	29.7
MX-31	1.69	18	302	30.8	21.9	1 030	36	201	0.0	288	26.4
MX-32	1.29	16	179	22.9	22.1	1 068	52	229	0.2	298	24.3
MX-33	1.12	15	91	12.1	19.0	605	32	168	0.1	229	22.0
MX-34	1.40	17	248	19.1	19.8	1 064	38	213	0.2	266	21.2
MX-35	1.15	16	143	17.7	21.2	840	32	252	0.0	340	23.4
MX-36	1.19	17	169	28.7	26.2	2 705	48	333	0.2	444	16.8
reference area											
MX-1R	1.16	8	112	4.9	1 0	96	22	44	0.0	111	8.8
MX-2R	1.14	4	98	3.2	0 8	111	10	38	0.0	98	7.6
MX-3R	1.11	6	122	5.5	0 9	87	9	18	0 0	88	10.1

Table 5. ICP-MS analyses of technosoil from Caporciano deposit

Sample	Fe	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
	%	mg·kg^{-1}									
dump-field area											
MC-1	5.30	147	799	34	111	6 388	766	2	3.1	<3	12
MC-3	5.64	148	775	32	113	8 290	697	3	3.2	<3	27
MC-3	4.69	206	785	36	159	6 663	540	<1	2.4	<3	12
MC-4	5.71	175	813	36	131	9 337	947	2	4.0	<3	27
MC-5	6.42	142	819	35	112	8 619	797	3	3.0	<3	23
MC-7	0.30	102	730	27	97	6 379	718	1	3.7	<3	13
MC-8	0.33	104	800	30	106	5 137	675	1	2.7	<3	27
MC-9	0.27	105	1 250	32	145	5 021	589	3	3.7	<3	23
MC-10	0.33	132	820	30	97	8 451	883	2	4.5	<3	24
MC-11	0.38	112	890	33	107	11 324	1 064	3	4.1	<3	12
MC-12	0.32	101	860	31	112	5 985	784	2	2.5	<3	25
MC-13	0 30	8	68	20	54	876	53	0 7	1.4	<3	9
MC-14	0 34	7	102	18	44	549	166	1 2	2 8	<3	11

Table 6 (part 1) ICP-MS analyses of samples from Podlipa at Ľubietová

Sample	Fe	Cr	Mn	Co	Ni	Cu	Zn	As	Cd	Sb	Pb
	%	mg·kg^{-1}									
dump-field area											
P-1	2.01	12	264	27	29	2 228	18	141	0.05	51.2	17.2
P-2	2.27	15	508	68	44	3 784	19	140	0.05	53.1	16.1
P-3	1.73	13	207	18	28	1 288	16	140	0.01	52.5	31.5
P-4	1.98	11	231	30	32	1 757	11	163	0.07	37.6	22.6
P-5	2.36	15	173	29	42	2 216	14	207	0.10	61.5	72.4
P-6	2.68	19	225	11	30	1 179	16	176	0.10	55.6	29.4
P-7	2.81	20	108	11	37	1 128	15	252	0.07	47.2	31.9
P-8	2.08	12	150	16	38	2 136	15	290	0.08	32.4	22.8
P-9	1.72	15	378	32	28	4 056	22	102	0.09	13.6	13.9
P-10	1.67	15	238	23	24	4 927	17	162	0.08	20.9	25.3
P-11	1.81	13	357	44	36	6.740	16	234	0.07	20.0	16.7
P-12	2.20	13	203	30	32	9 032	15	256	0.08	27.2	15.3
P-13	2.14	13	199	29	43	6 190	15	361	0.06	31.9	16.5
P-14	2.62	18	372	44	43	10 196	21	304	0.08	27.3	19.3
P-15	2.21	15	223	38	36	9 278	18	269	0.08	23.1	14.7
P-16	2.23	18	34	8	23	2 736	10	338	0.09	34.2	21.1
P-17	2.90	25	225	35	33	4 113	15	300	0.08	42.5	29.8
P-18	2.60	22	245	30	32	4 270	17	231	0.07	38.4	22.0
P-19	2.76	22	385	41	43	6 346	18	261	0.10	31.4	24.7
P-20	2.77	25	671	37	35	4 584	26	160	0.10	29.6	26.8
P-21	2.28	24	474	19	31	3 580	17	170	0.10	44.1	24.1
P-22	2.69	22	534	36	33	6 216	25	205	0.10	35.5	30.3

Table 6 (part 2) ICP-MS analyses of samples from Podlipa at Ľubietová

P-23	2.29	31	366	19	21	2 312	20	105	0.08	20.0	24.7
P-24	2.26	29	381	23	23	2 402	20	121	0.09	22.1	28.2
P-25	1.76	17	768	24	33	1 754	47	175	0.40	44.4	75.7
P-26	2.37	24	1 500	44	31	1 729	90	41	0.31	27.4	76.8
P-27	2.29	19	981	46	44	3 648	121	182	0.60	38.1	105.3
P-28	1.76	18	198	14	23	2 523	17	118	0.08	26.2	55.4
P-29	1.76	10	282	16	18	2 258	15	84	0.09	17.8	10.1
P-30	1.56	11	268	15	18	1 949	13	70	0.08	16.4	9.0
P-31	1.60	13	280	20	19	1 477	15	70	0.07	17.8	15.5
P-32	1.66	11	326	25	16	1 163	18	38	0.08	16.7	20.4
P-33	1.41	11	301	15	16	1 645	13	57	0.06	14.3	9.1
reference area											
P-1R	1 22	13	47	2	6	29	20	11	0.10	13.4	20 8
P-2R	1 32	12	67	5	7	55	18	10	0.11	14.2	19 1
P-3R	1 22	10	56	5	6	48	19	9	0.13	11.9	31 0

Table 7. pH and Eh range and average values of technosoil from dump-fields

Deposit	**pH($_{H2O}$)**			**Eh($_{H2O}$) (mV)**			**pH($_{KCl}$)**			**Eh($_{KCl}$) (mV)**		
			$\bar{x}$			$\bar{x}$			$\bar{x}$			$\bar{x}$
Ľubietová	3.75	6.32	4.64	-5	156	100.64	3.82	5.96	4.86	-16	159	90.60
Š Dolina	4.32	6.91	5.29	-42	127	62.85	4.26	6.75	5.30	-36	130	62.63
Libiola	4.01	6.07	5.21	12	146	67.71	3.95	6.18	5.16	4	147	69.29
Caporciano	5.99	7.13	6.56	-12	42	15.01	4.93	7.00	5.99	-4	111	58.00
S Domingos	2.74	7.10	4.29	-10.7	243.4	153.32	2.69	246.5	3.95	-5.6	166.4	173.90

Table 8. D_{ph} and rH_2 factors range and average values in technosoil from dump-fields

Deposit	**D_{ph} values range**		**$\bar{x}$**	**rH_2 values range**		**$\bar{x}$**
Ľubietová	-9.59	0.84	0.22	13.22	13.93	13.58
Špania Dolina	-0.42	0.45	-0.01	9.75	12.83	12.33
Libiola	-0.27	0.31	0.04	12.47	12.80	12.63
Caporciano	0.01	1.19	0.58	13.44	19.29	14.21
São Domingos	0.05	0.60	0.32	11.66	14.72	13.61

published by many authors. For example the first information about the PTEs content in technosoil at **Ľubietová** and **Špania Dolina** was presented by Andráš et al., (2008; 2009) and Nagyová et al., (2013) Some information about waste-heaps at **Libiola** and **Caporciano** was presented by Marescotti et al (2010) and Buccheri et al., (2014a). Most available information was published about **São Domingos** deposit by Matos et al., (2006a) According to Mateus et al., (2011) the reddish clay-rich slag contains up to 30-40% Fe up to 1 7% Zn 0 9% Pb and 0 5% Cu. The present research (Table 2) confirmed these data. The extraordinarily high Zn As and Pb contents at the dump-field of **São Domingos** mining area are caused by the presence of the main ore minerals in the technosoil: pyrite sphalerite chalcopyrite galena arsenopyrite and different sulfosalts (Matos et al. 2006b).

The sandy–gravelly sediments at **Libiola** contain high amounts of chalcopyrite- and pyrite-rich material. The mixture of secondary Fe-oxydes and Fe-oxyhydroxides influences the high Fe content whereas the main source of Cr Co and Ni is pyrite (Marescotti et al., 2010). The source of the highest Sb content described at **Špania Dolina** deposit is tetrahedrite.

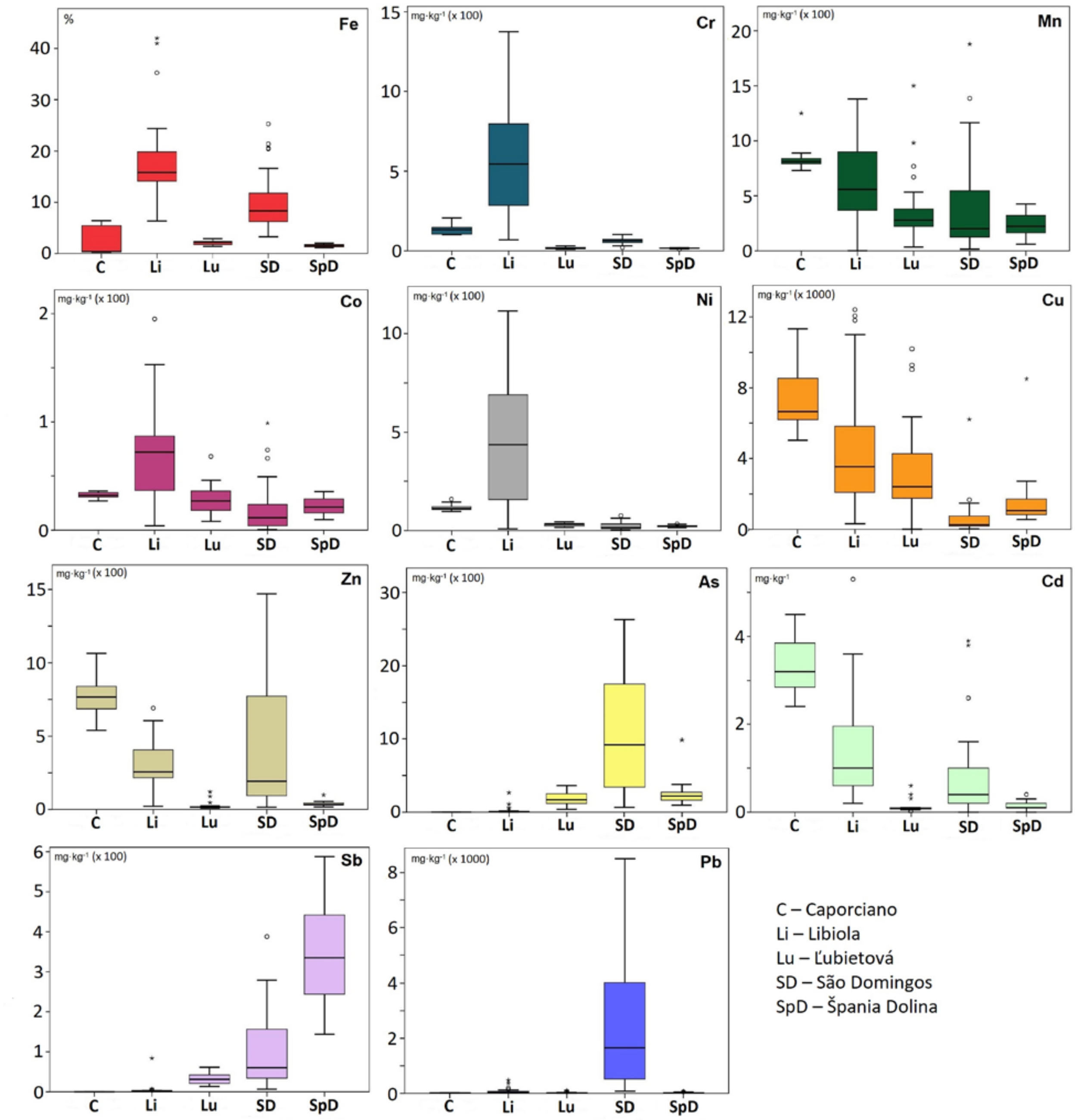

Figure 2. Box-and-whisker plots, showing the difference of PTEs distribution among the investigated study areas. The outlayers describing the extremest values were excluded in order to improve the transparency of graphic outputs.

Caporciano dump-field is firstly characterized by the highest Cu Mn and Cd contents (on average 7302 mg·kg^{-1} 827 mg·kg^{-1} and 3.4 mg·kg^{-1} respectively).

The red and brown colours at **São Domingos** and **Libiola** dump-fields indicate oxic conditions but the technosoil is not sufficiently aerated and the range of the Eh values (-10 7 to 243 4; Table 7) is typical for anoxic soils (Alloway 1992). The rH_2 factor < 20 (Richter et al., 2003) also confirms the same conclusions. According to McNeill (1992) the mostly positive D_{pH} values at all deposits except for Špania Dolina (Table 8) indicate presence of soil colloids with negative charge so they have suitable sorption ability for metal cations. Data about the free sorption capacity of clay minerals at **Ľubietová** deposit was also published by Andráš et al., (2009).

Results of analyses show that contents of heavy metals are irregular and in most cases exceed national law limits as well as EU limits for soils according to the Council Directive 86/78/EEC.

Repeated sampling at **Ľubietová** and **Špania Dolina** revealed great chemical variations and irregularities particularly in the dump-field area depending on weathering process PTEs migration ability formation of secondary minerals and sorption capacity of some minerals. The waste shows some self-cleaning ability a great part of PTEs is fixed in porous material in Fe-hydroxides and in clay minerals still showing an important free sorption capacity. For this reason it is not effective to interfere with dump materials (Andráš et al., 2008; 2012; Nagyová et al., 2013). The main environmental risk at Ľubietová is represented by contamination of groundwater by PTEs mainly by the very toxic forms As^{3+} and Sb^{3+} (Franková et al., 2012). In order to eliminate this risk a Fe^0-barrier was installed in the valley under the dump-field (Kupka et al., 2015). The dam system was installed to prevent the erosion caused by heavy rain and inappropriate technical interventions in the early 90s.

Similar conditions can be described for Špania Dolina. As presented by Franková et al., (2012), the main risk is caused by contamination of grounwater by As^{3+} and Sb^{3+} from the Cu-ores. No effective measures have been performed until now.

At **Libiola** the significant contents of Fe Cu Cr Co Ni as well as of Zn As and Mn in the technosoil from the dump-field are released during the weathering process into the acid mine drainage water which is mixed with the slightly alkaline surface water (*Gromolo* river) with pH 8 (Dinelli et al., 2001; Buccheri et al., 2014a) in the valley near the inhabited area. The pH change and the precipitation of the amorphous Fe-phases (e g ferrihydrite schwertmannite) enable sorption of PTEs on their surface so that water shows acceptable quality in the inhabited area. Remobilization of PTEs should not be expected (Dinelli et al., 2001). It should be important to stabilize the slope (under the open-pit mine) on which the waste material is situated either by technical means or by suitable vegetation cover in order to limit PTEs release to the country components.

The main environmental risk at **Caporciano** is due to the heavy erosion of the heap that is situated in a terrain depression. The several pioneer plant species (dwarf species of *Pinus* spp. and *Quercus* spp.) are not able to stabilize the dump-material (Buccheri et al., 2014b). The deposit is situated high on the mountains and the nearest populated area is relatively far (about 2 km) thus the relatively mobile Cu influences only the vineyards under the dump-field slope. There is neither creek nor river in the surrounding area thus the environmental risk due to diffusion of PTEs is limited. On the other hand a little marsh under the dump is saturated by sewage water from the hotel above the dump-field which drains the waste material. Adaptation of this marsh to anaerobic and aerobic wetland system could substantially eliminate the Cu-release to the country.

The most important environmental risk at **São Domingos** is due to the massive formation of acid drainage water. The greatest part of this water is collected in the flooded mine open pit. The rest is drained to the distant stream by >14 km long channels. One part of the water is evaporated and the less substantial part of it reaches the creek and is diluted in nearby lake. Small dams store a significant volume of acid water. The enormous extent of the mining area does not enable simple solutions of the contaminated country remediation. One of the possible procedures how to reduce the negative impact of PTEs on the country components is phytostabilization of metals in the contaminated area using autochthon and pioneer plant species (Abreu et al., 2012; Andráš et al., 2018). Currently several admixtures are tested which can immobilize PTEs in the waste material.

5 CONCLUSIONS

The distribution of PTEs content in the dump material (technosoil and slag) of the individual studied abandoned Cu-deposits is different and, within each deposit, irregular. The highest Zn, As and Pb contents were described in São Domingos mining area, whereas the dump-field material from Libiola is rich with Fe, Cr, Co, Ni and the dump-field material from Caporciano is rich with Cu, Mn and Cd. The highest Sb content was found in the waste material from Špania Dolina deposit. The dump-field at Ľubietová is contaminated by PTEs less than the dump-fields at the remaining four deposits.

The common features of the technosoil from these dump-fields are their limited aeration and anoxic conditions. The soil colloids are characterized (except for Špania Dolina) by negative charge and have suitable sorption ability for metal (PTEs) cations. Most of the PTEs contents exceed the EU law limits for the soil.

At Ľubietová and Špania Dolina deposits, the main risk is represented by the intoxication of the groundwater by As and Sb. Libiola and Caporciano deposits are situated far from the inhabited areas. At Libiola, the main risk is caused by formation of acid drainage water with high Cr, Co, Ni (and Cu) content, but this water is consequently neutralised and the PTEs precipitate, so that the river in the closest villages has close to neutral pH values and contain acceptable amount of PTEs. At Caporciano, it would be suitable to stop the waste erosion by covering the dump-field with vegetation cover. The contamination of the slope under the dump by Cu could be limited by installation of a wetland system in the depression beneath the dump.

The most contaminated mining area is São Domingos. The main hazard for the environment is represented by the enormous amount of acid mine drainage water and by very high PTEs contents in the technosoil and slag, first of all by Zn, As and Pb. One of the possible remediation techniques, which could be able to limit the PTEs release to country components (soil, water, plants) is phytostabilization, by using pioneer plant species; another possible remediation technique is the application of various admixtures to immobilize PTEs in the technosoil and slag.

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