Environmental Risk Due to Heavy Metal Contamination Caused by Old Copper Mining Activity at Ľubietová Deposit, Slovakia

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Abstract

The more than 200 years old dump-fields at closed Cu (Ag) deposit Ľubietová are situated near the village settlement. Heavy metal space distribution is controlled by geochemical behaviour of the elements, depend on their content, solubility, migration and sorption ability. The major sources of metals to the country components (soil, technogenous sediments, groundwater, surface water, plants…) may be classified according to expected solubility of primary minerals. The content of heavy metals in sediments and soils at the studied dump-field shows irregular distribution. Also the heavy metal contamination of the surface water and groundwater was studied both in the rainy as well as during the dry periods. The speciation of As and Sb proved in the water presence both of As^{3+} and Sb^{3+} as well as the less toxic As^{5+} and Sb^{5+} species. In the soil and sediments prevail As^{5+} and Sb^{5+} species while in the water is often dominant the As^{3+} and Sb^{3+} form. The article also presents some results of the plant tissue degradation study under heavy metal contaminated conditions at dump-fields. The dump sediments and the primitive soil formed locally on the surface of the technogenous sediments show only limited acidification potential. The Fe^0-barrier installation at bottom of the down part of the valley seems to be a good solution for the groundwater decontamination.

Keywords: acidification, heavy metal contamination, dump-field, impact on flora, remediation

1. Introduction

The Ľubietová deposit was exploited since the time of the Bronze Age and in the 16th and 17th centuries it was one of the most important and most extensively exploited Cu-mines of Europe. The Cu-ore was in the 18. century exported to more than 50 countries (Bergfest, 1951). The Cu mineralisation with Ag admixture is developed within 4–5 km long and 1.5 km wide range of N-S direction. It is situated in a crystalline complex which consists of arcose greywackes, arcose schists and various conglomerates. The ore mineralisation was genetically connected with the basic, intermediate and acid Permian volcanism. It is characterised by a rather simple paragenesis represented by quartz, siderite, chalcopyrite, Ag-tetrahedrite, arsenopyrite, pyrite and rare galena. The deposit is famous also by the numerous secondary minerals as libethenite, annabergite, langite, azurite, brochantite, erithrine, evansite, euchroite, cuprite, malachite, olivenite, pseudomalachite, etc. (Koděra et al., 1990; Ebner et al., 2004). There are three great ore-fields at Ľubietová: Podlipa, Svätodušná and Kolba with admixture of Co/Ni-mineralisation. The Cu content in the ore ranged from 4–10% and the Ag content was about 70 g·t^{-1} (Bergfest, 1951).

Figure 1. Dump-field podlipa at abandoned Cu-deposit Ľubietová

The extent of the dump-field Podlipa (Figure 1) is about 2 km[2]. This ore-field was exploited by 18 adits. The Cu-ore mineralisation is situated mainly in the terrigene crystalline complex of Permian age which consists of arcose greywackes, arcose schists and various conglomerates. The most important tectonic structures are of NE-SW direction and the ore veins have E-W and N-S direction. They are 30–40 m thick.
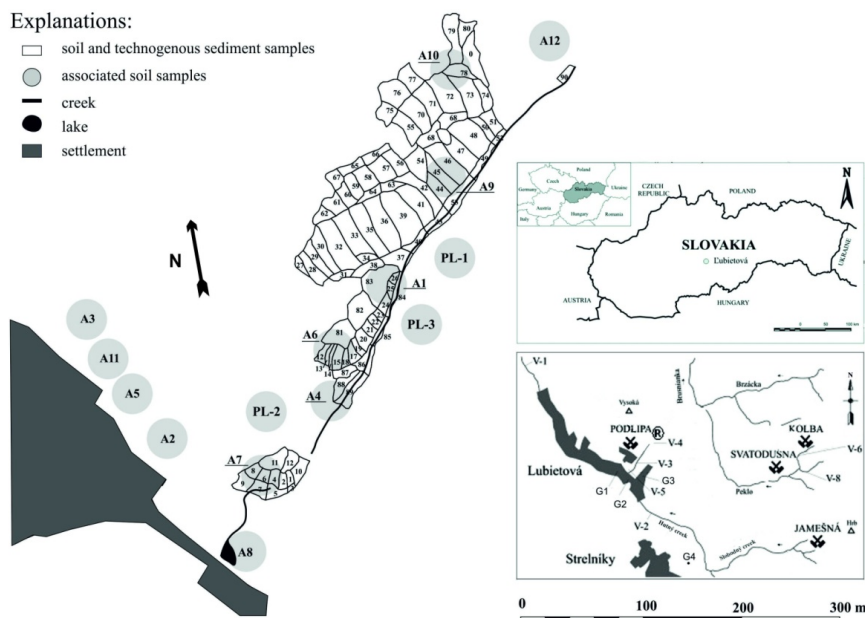

Figure 2. The Podlipa dump-field: localisation of the soil (samples A-1 to A-12 and 1–80) and water (samples V, CD and LH) sampling

The important mining stopped in the second half of the 19th century although the last little gallery near Haliar locality was exploited by Ernest Schtróbl only in April 1915.

2. Material and Methods

The technogenous sediment and soil samples (of about 10 kg weight; samples 1–80 and A-1 to A-12 from the Podlipa dump-field and soils from 15–20 cm depth (the sampling step was about 25 m[2]) were collected in order to characterize components of landscape contamination. Next three samples PL-1 to PL-3 are samples of soil horizons (A, B, C). To each surface water sample (stream water, drainage water-samples V-1 to V-6) and groundwater samples (G-1 to G-4; Figure 2) 10 ml of HCl was added to conserve them.

The reference site was located above the ore-field (Figure 2, sample A-12), outside of geochemical anomalies of heavy metals and represent graywakes of Permian age similar to material at the dump-field. Plant samples were collected both from reference area and from the dump-area.

The samples of technogenous sediments and soil from the dumps were dried and 0.25 g of sample was heated in HNO_3-$HClO_4$-HF to fuming and taken to dryness. The residue was dissolved in HCl. Solutions were analysed by ICP-MS analysis at the ACME Analytical Laboratories (Vancouver, Canada). The minerals in the clay fractions were determined by X-ray diffraction and the clay mineral samples were ICP-MS analysed, then macerated 14 days in natural drainage water of the studied locality containing heavy metals and analysed again. The pH of the sediments was determined from suspension both with distilled water and 1M KCl after 3 hours of maceration.

The sulphur, total carbon, organic carbon and inorganic carbon content in the sediments was IR analysed using furnace Ströhlein C-MAT 4000 at the laboratories of Geological Institute of Slovak Academy of Sciences. A static test of the total acid potential was realized according to Morin and Hutt (1997) and Sobek et al. (1978). The water samples were analysed using AAS in the National Water Reference Laboratory for Slovakia at the Water Research Institute in Bratislava. The speciation of As was performed on the basis of different reaction rate of As^{3+} and As^{5+} depending on pH and Eh. The experimental study on Cu precipitation on the surface of iron particles (testing of the Fe^0-barrier) mixed with dolomite was realized at the laboratory of the Comenius University in Bratislava by Dr. Bronislava Lalinská according to Bartzas (2006).

3. Results

3.1 Heavy Metal Contamination of Technogenous Sediments and Soil

The dump-field technogenous sediments are influenced by heavy metals (Table 1) from the hydrothermal ore mineralisation. The main contaminants are: Cu (up to 20 360 ppm), Fe (up to 2.58%), As (up to 457 ppm), Sb (up to 79.3 ppm) and Zn (up to 80 ppm) are accompanied also by U (up to 10 ppm) and Th (up to 35 ppm) from the Permian volcano-sedimentary metamorphosed rocks.

Table 1. ICP-MS analyses of technogenous sediments and soils from the dump-field

Sample	Cu	Pb	Zn	Ni	Co	As	Sb	Bi	U
					ppm				
A-1	2829	28.1	14	36.8	10.4	162	61.6	2.8	1.3
A-1c	1693	63.8	18	36.0	11.3	258	60.1	4.5	1.4
A-1c*	2345	229.1	95	71.8	18.3	628	153.2	14.6	3.3
A-2	198.8	13.0	21	9.8	5.9	10	7.1	0.2	1.4
A-2c	574.3	22.4	36	12.2	10.3	19	9.2	1.4	1.1
A-2c*	472.4	27.9	62	17.0	6.4	15	12.6	1.5	1.1
A-3	827.5	16.0	20	32.1	14.0	71	22.4	8.5	1.7
A-3c	624.2	23.1	25	28.3	17.0	110	24.0	7.2	1.8
A-3c*	857.4	37.4	47	30.4	11.0	105	28.0	12.1	1.9
A-4	4471	9.6	23	55.0	50.0	169	59.5	23.7	1.6
A-4c	3324	14.9	16	42.4	58.3	237	79.3	39.2	1.7
A-4c*	3112	37.8	27	64.4	32.1	300	129.8	90.9	2.2
A-5	3150	16.9	19	34.0	24.4	60	17.2	1.7	1.0
A-5c	3001	14.8	18	34.1	30.4	64	16.3	2.1	1.2
A-5c*	2078	21.9	45	55.4	29.6	105	30.3	3.2	1.4
A-6	4797	15.6	13	51.6	41.8	134	49.8	25.4	1.4
A-6c	2503	24.6	14	45.1	40.9	224	56.2	24.4	1.6
A-6c*	2918	72.3	65	61.7	32.0	305	92.3	51.7	2.2
A-7	755.8	16.8	26	10.4	10.2	16	11.5	0.9	1.1
A-7c	855.1	20.2	33	10.1	12.0	17	7.1	1.2	1.1
A-7c*	2026	73.7	176	26.0	15.5	33	17.4	3.6	2.3
A-8	716.0	6.5	7	58.0	89.9	61	17.9	0.5	2.6
A-8c	835.5	6.3	14	66.5	69.7	52	20.2	0.7	2.5
A-8c*	836.7	4.2	4	62.5	104.5	46	18.9	0.8	2.1
A-9	5903	29.5	24	39.8	36.0	244	37.0	15.1	2.7
A-10	7699	30.2	19	52.2	48.0	457	62.7	25.1	4.0
A-11	1563	24.8	37	19.0	8.7	16	14.9	4.8	1.7
A-12	113.1	39.4	29	8.9	8.6	16	5.6	0.7	1.4
A-17	14 440	8.4	59	51.7	73.4	289	43.2	7.2	2.3
A-17c	20 360	49.0	80	43.0	70.0	260	40.0	6.0	2.0

Explanations: A-1 to A-11 – technogenous sediments and soils from the dump-field, A-12 reference area, A-17 hydrogoethite, A-1c to A-17c clay fraction, A-1* to A-17* - clay fraction after 14 days maceration in drainage water, containing heavy metals.

The weathering processes of reactive minerals in surrounding and mainly acid rocks mobilise heavy metals and toxic elements (e.g. Cu, As) from the primary minerals (Figure 4), form secondary minerals (mainly Cu-oxides and arsenates – Figure 5, Fe hydroxides – Figure 6 and carbonates – Figure 7) and contaminate the landscape components.

The main Cu concentration was found to be near the Najvyššia Johan gallery collar, inclusive of the slope beneath the gallery. High Cu concentration is at the bottom of the valley (Figure 3a). The most important source of As and Fe are the galleries Najvyššia Johan, Horná Johan and Stredná Johan (Figures 3b, 3c). The highest Pb concentration was found in front of the Zollweiner Maria Empfängnis and Jakob galleries collars (Figure 3d). Th contamination is derived from Francisci and Bartolomej galleries (Figure 3e) and important Sb contamination was detected mainly at the dumps at Zollweiner Maria Empfängnis gallery (Figure 3f).
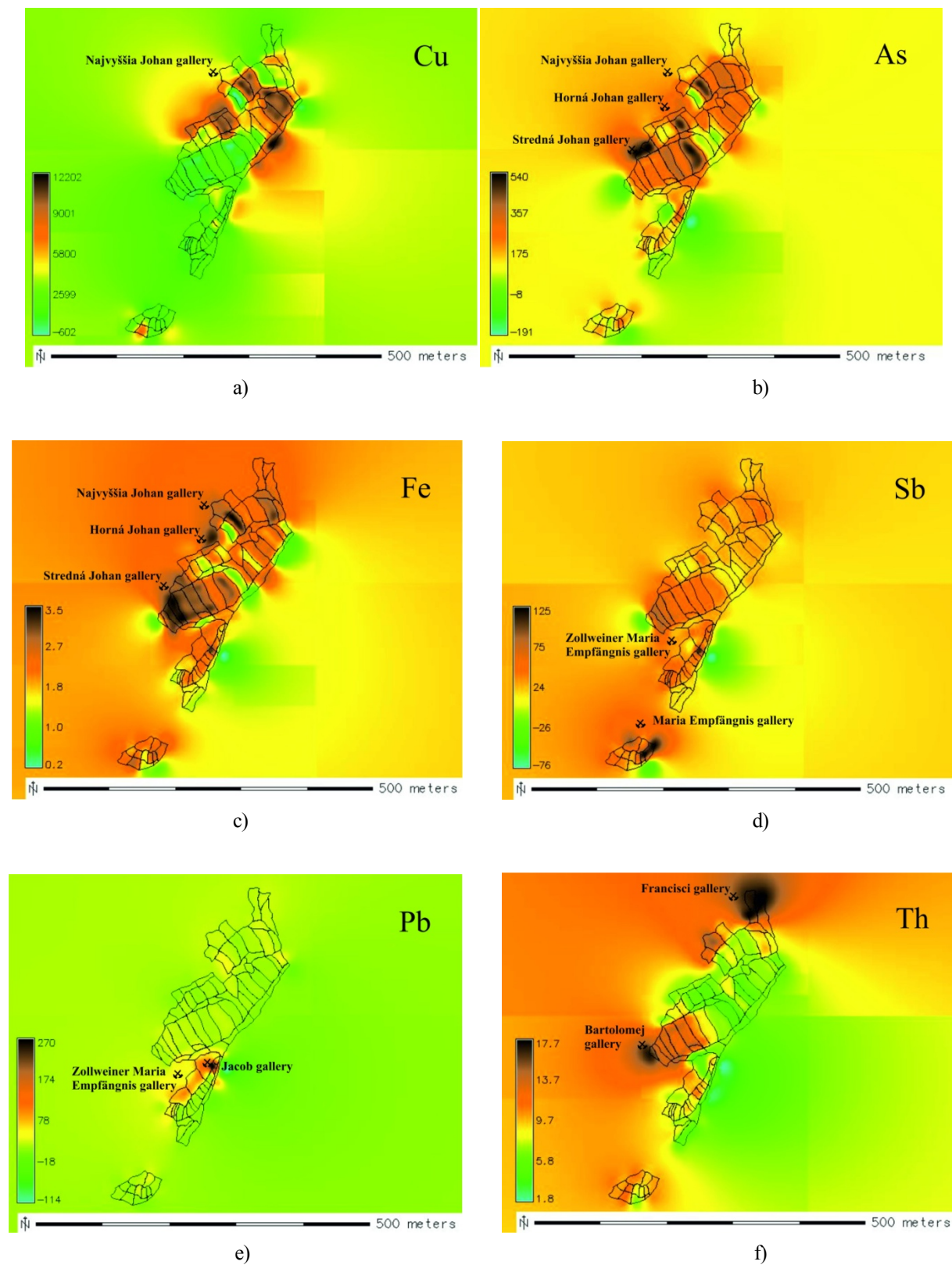
Figure 3. Distribution of heavy metals at the Podlipa dump-field: Cu, As, Fe, Pb, Th, Sb-distribution (numbers show the individual heavy metal content in ppm)

In mould horizon A are accumulated Ca, P, Pb, Zn, Cd, Cr and Th. In soil horizont B folowing elements: Cu, Ag, Ni and As are accumulated in clay minerals and sesquioxides. The C horizon is enriched in Ba (Table 2). The other analysed elements (e.g. Fe, Mg, Ti, Al, Na, K, Mo, Mn, U) show no unambiguous trend to be accumulated in some soil horizon. The Sb, Bi and Co concentrations in individual soil horizons show no unambiguous trends.

Table 2. ICP-MS analyses of individual soil horizons

Sample	Horizon	Fe	Ca	P	Mg	Ti	Al	Na	K
		%							
PL-1	A	2.48	0.40	0.093	0.62	0.155	5.98	0.328	3.02
	B	2.01	0.27	0.090	0.59	0.125	6.01	0.269	3.37
	C	2.05	0.17	0.067	0.50	0.146	6.41	0.344	3.74
PL-2	A	3.02	0.33	0.097	0.42	0.099	5.81	0.321	3.05
	B	2.49	0.22	0.058	0.45	0.084	6.06	0.496	3.43
	C	6.87	0.12	0.053	0.26	0.093	5.73	0.122	3.01
PL-3	A	1.32	0.49	0.092	0.56	0.083	4.45	0.052	2.24
	B	1.65	0.05	0.076	0.44	0.097	5.58	0.043	3.03
	C	2.01	0.11	0.077	0.66	0.154	4.73	0.022	4.01

Sample	Horizon	Cu	Pb	Zn	Ag	Ni	Cd	As	Sb
		ppm							
PL-1	A	5864	32.6	136	7.6	38	0.7	1010	2449
	B	9425	33.3	130	8.5	40.9	0.4	1081	2356
	C	3633	10.4	89	4.7	36.7	0.2	497	1159
PL-2	A	4462	33.9	133	5.3	27.5	1.1	553	1216
	B	8230	17.2	134	6.8	33.6	0.5	884	1539
	C	6059	8.1	142	10	33	0.3	565	1704
PL-3	A	3366	66	77	1.1	30.8	1.1	77	24
	B	8085	15.1	11	2.2	36.3	0.1	231	23
	C	5115	15.1	16	1.2	34.3	0.2	158	37

Sample	Horizon	Mo	Mn	Co	Bi	Cr	Ba	U	Th
		ppm							
PL-1	A	0.7	1033	46.5	122	31	607	5.4	9.2
	B	1.2	953	43.8	112.1	26	694	6.1	6.9
	C	0.7	765	26.5	42.9	19	705	3.3	7.3
PL-2	A	0.9	1123	32.8	49.4	22	620	3.2	7.5
	B	0.4	1171	49.2	70.3	13	841	3.2	6.3
	C	0.7	2220	20.1	37.4	20	1099	3.5	7.3
PL-3	A	3.3	352	35.2	3.3	18	218	1.4	4.9
	B	3.3	253	45.1	8.1	11	283	2.9	6.7
	C	0.3	351	48.8	8.6	13	303	3.3	7.7

The distribution of individual metals at the studied dump-field is uneven. It depends on the mineralogical composition of ores, on the original concentration of the mentioned metals in the technogenic sediments of the spoil dumps, and also on their migration abilities and sorption properties (Figure 3). At Podlipa were described only few correlations between metal couples (Ni/As, Fe/Ni, Pb/Cd, Co/Cu., Zn/Cd, Zn/Pb, Cd/Pb ant Th/U). This situation substantially differs from the dump-field Reiner, where we can distinguish high correalition ratio between four times more element couples as at Podlipa (Andráš et al., 2009). The main reasons of this separate geochemical behaviour of the same elements at the two neighbour localities is the different rock-surrounding (homogenous rock-surrounding at Reiner locality built by greywakes vs. grauwakes - arcose schists rock composition at Podlipa, which form different quantity of natural sorbents as clay minerals; Andráš et al. (2009). The distribution of elements can be controlled also by formation of various metastable, secondary phases, which depend on pH and Eh, eventually on ionic radius of elements.
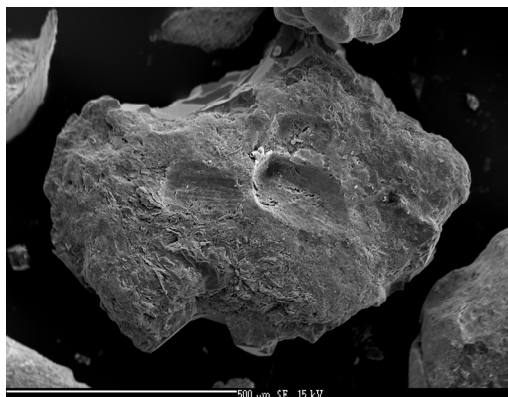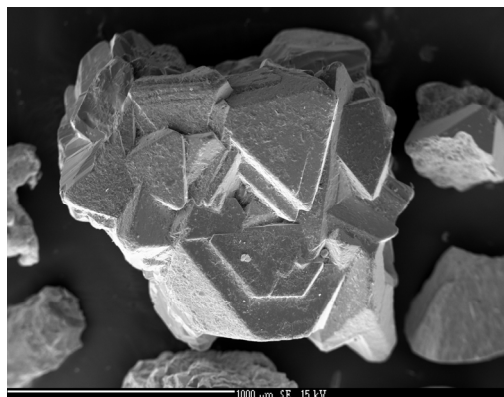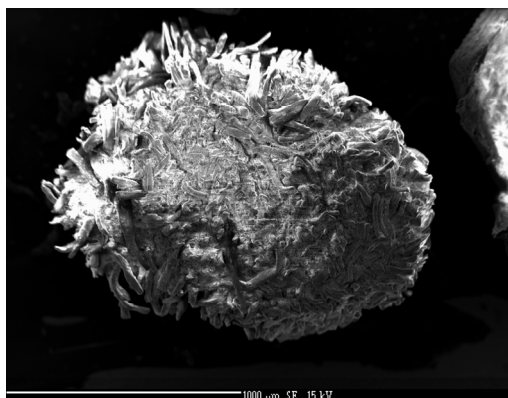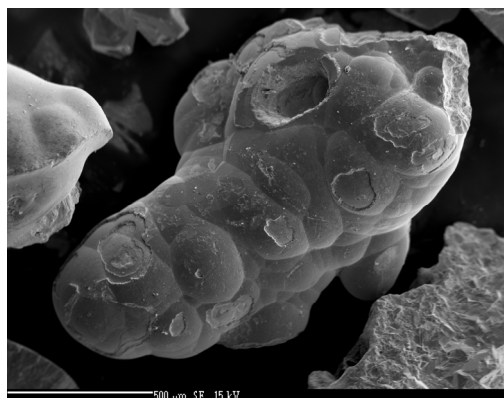
Figure 4. Grain of native copper

Figure 5. Euchoite ($Cu_2(AsO_4)(OH) \cdot 3H_2O$) aggregate

Figure 6. Lepidocrocite (γ-FeO(OH)) aggregat

Figure 7. Malachite ($Cu_2CO_3(OH)_2$) aggregate

3.2 Heavy Metals in Water

The surface water in the creek draining the valley bottom along the dump-field is gradually contaminated by heavy metals leached from the technogenous sediments of the mining dumps. This surface water contains high Cu (up to 2060 $\mu g \cdot L^{-1}$), Fe (up to 584 $\mu g \cdot L^{-1}$), Zn (up to 35 $\mu g \cdot L^{-1}$) and sometimes also Co (up to 10 $\mu g \cdot L^{-1}$) and Pb (up to 5 $\mu g \cdot L^{-1}$) concentrations. The highest As concentration is 6.11 $\mu g \cdot L^{-1}$ (Table 3).

Table 3. Atom absorption spectrometric analyses of surface water

Sample	pH	Eh	Mn	Zn	Cd	Co	Cu	Fe	Ni	Pb	Sb	As
		(mV)					$\mu g.l^{-1}$					
V-1a	6.5	-6	<1	<10	0.04	1.1	2.2	26	4.1	4.2	0.74	<1.0
V-1b	7.5	-58	<1	<10	0.05	2.2	2.7	73	5.9	4.3	<1.00	<1.0
V-1c	6.5	-8	11	<10	<0.05	<1.0	5.1	94	1.2	<1.0	1.03	<1.0
V-2b	6.7	-14	<1	<10	0.13	<1.0	42.1	584	2.1	3	<1.00	1.69
V-2c	6.9	-21	<1	<10	0.09	<1.0	38.2	580	1.6	2.9	<1.00	1.54
V-3a	6.7	-12	<1	30	0.04	7	1 810	86	3.2	2.2	1.12	<1.00
V-3b	6.1	14	<1	40	0.05	9.6	2 060	101	4.9	2.8	1.88	3.41
V-3c	6.5	0	21	<10	<.05	7.6	1 980	45	8.5	2.8	2.35	1.14
V-4a	6.7	-14	<1	<10	0.06	3.1	22.2	263	2.1	4.2	1.72	<1.0
V-4b	6.2	14	<1	<10	0.06	8.1	1 850	274	5.6	3.6	1.57	1.21
V-5a	6.2	-11	<1	<10	0.06	5.5	6	170	6	4.8	1.66	2.79
V5b	6.3	-8	7	20	0.08	8.3	7.9	210	7.1	5.1	2.21	3.21
V-5d	6.2	-7	4	30	0.07	6.6	8.1	160	8.1	1	2	1.08
V-6a	7.6	-62	<1	30	0.07	1.9	30.4	270	4.3	3.2	2	6.02
V-6b	7.1	-62	<1	32	0.07	2.2	34.8	263	5	3.4	2.01	6.11

Explanations: Samples marked by index "a" - rainy period (June 14th, 2006), samples marked by index "b" - dry period (February 25th, 2007), samples marked by index "c" - rainy period (March 31st 2008), samples marked by index "d" - dry period (May 27th, 2008).

The heavy metals content in the water is in most cases higher during dry periods than during rainy periods. On the other hand, the As content both in the surface (and drainage) water as well as in the groundwater is not high (6.11 µg·L^{-1}; Table 3). The presence of *Acidithiobacteria* species or of sulphate reducing bacteria was not proved. The pH both of the surface and of groundwater is close to neutral values (pH 6.4–7.6).

The most contaminated is the mineral water from the spring Linhart (sample G-4; Figure 2). Its total radioactivity is 6,498 Bq·L^{-1} and the Fe (380 µg·L^{-1}), Cu (181 µg·L^{-1}), Pb (1 µg·L^{-1}) and Cd (82.0 µg·L^{-1}) contents (Table 4) exceed the Slovak decrees No. 296/2005, No 354/2006 Coll.

Table 4. Atom absorption spectrometric analyses of groundwater (samples G-1,G-2 and G-3) and mineral water (sampleG-4)

Sample	pH	Eh	Fe	Ni	Mn	Zn	Cu	Cd	Pb	Bi	As	Sb
		(mV)					µg.l^{-1}					
G-1a	6.55	-4	11	1.1	<5	<10	22	<0.05	<1.1	1.36	<1	<1.0
G-1b	6.63	-10	17	1.2	<5	<10	1.3	<0.05	1.9	1.55	<1	<1.0
G-2a	6.72	-14	366	1.3	18	<10	3	<0.05	1.3	<1.00	<1	<1.0
G-2b	6.23	-16	210	1.5	8	<10	2.2	<0.05	<1.0	<1.00	<1	<1.0
G-3a	6.85	-21	146	<1.0	15	61	14	0.13	3.4	<1.00	5	1.42
G-3b	6.55	-23	120	<1.0	17	350	5.9	0.1	3.3	<1.00	1.52	1.21
G-4a	6.4	4	380	5	20	<10	30	0.5	<1.0	<1.00	1.98	<1.0
G-4b	6.48	-2	2 260	<1.0	55	<10	181	82	<1.0	<1.00	2.52	<1.0

Explanations: a - sampled on March 31st 2008 during the rainy period; b – sampled on May 27th 2008 during the dry period.

Table 5. Paste and rinse pH (H$_2$O and 1 M KCl), sulphur and carbon contents in samples of technogenous sediments and soils

Sample	pH$_{H20}$	Eh $_{H20}$	pH $_{KCl}$	Eh $_{KCl}$	S$_{tot.}$	S$_{SO4}$	S$_s$	C$_{tot.}$	C$_{org.}$	C$_{inorg.}$	CO$_2$	CaCO$_3$	TAP (kg.t^{-1})
A-1	5.14	77	4.61	109	0.25	0.1	0.15	0.74	0.2	0.54	1.97	4.48	7.813
A-2	5.89	34	5.4	63	0.02	0.01	0.01	0.86	0.38	0.48	1.75	3.99	0.625
A-3	4.87	94	4.21	131	0.1	0.03	0.07	0.62	0.34	0.28	1.02	2.32	3.125
A-4	5.46	59	5.33	66	0.33	0.13	0.01	0.34	0.26	0.08	0.29	0.66	10.313
A-5	5.77	42	5.37	64	0.05	0.01	0.05	0.78	0.35	0.43	1.57	3.57	1.563
A-6	5.17	74	5.06	83	0.42	0.15	0.27	0.4	0.27	0.13	0.47	1.08	13.125
A-7	7.93	-84	7.34	-58	0.03	0.02	0.01	1.63	0.1	1.53	5.61	12.71	0.938
A-8	5.42	36	5.22	42	0.01	0.01	0.01	0.45	0.13	0.32	1.17	2.66	0.313
A-9	5.03	83	5.01	85	0.03	0.03	0.01	0.4	0.37	tr.	tr.	tr.	0.938
A-10	5.25	71	5.14	78	0.04	0.02	0.02	0.48	0.46	tr.	tr.	tr.	1.25
A-11	6.11	22	5.95	30	0.11	0.04	0.07	4.31	4.18	0.13	0.47	1.08	3.438
A-12	4.21	133	3.47	173	0.02	0.01	0.02	4.05	4.03	tr.	tr.	tr.	0.625

In spite of the limited kinetics of the cementation process, the electron microprobe study proved that the cementation causes on the surface of iron particles gradual displacement of Fe^{2+} ions and precipitation of Cu^{2+} ions, both in form of Cu-oxides, Cu carbonates and in form of native copper. The cementation copper is of a high fineness (it contain up to 96.07 wt. %).

The pH-Eh stability diagram for Cu-Fe-S-H$_2$O system (Fairthorne et al., 1997) show that formation of insoluble Fe oxides/hydroxides is possible both at neutral or alkaline pH and at high Eh values also in acid conditions (Figure 8). According to Fairthorne et al. (1997) the decrease in the amount of metal ions present in solution when the pH is increased and when nitrogen is replaced with oxygen is due to the formation of iron and copper oxides/hydroxides at the mineral (chalcopyrite) surface creating a physical barrier for further metal dissolution. The Eh value measured in this study at pH 5 is very close to the separation line Fe^{2+}/Fe$_2$O$_3$ when the mineral is

conditioned in nitrogen but it moves away from this line in oxygen conditioning. The formation of insoluble cupric oxide/hydroxide is less thermo-dynamically favourable and only occurs at pH values larger than 6.

The Cu in soil and in technogenous sediments is present mostly in Cu^{2+} form, less as a Cu^{3+} (Cu_2O_3 - stability field) and only in 2 cases in the elementary form (Cu^0). Cu from the surface water occupies several stability fields: Cu_2O_3, Cu^0, Cu_2S, $CuFeS_2$ as well as CuS fields. Similar situation is in the case of the groundwater with exception of the Cu_2O_3 field (Figure 8). It means that the Cu in surface water is present in Cu^0, Cu^{2+} and Cu^{3+} forms while in groundwater only in Cu^0 and Cu^{2+} forms.
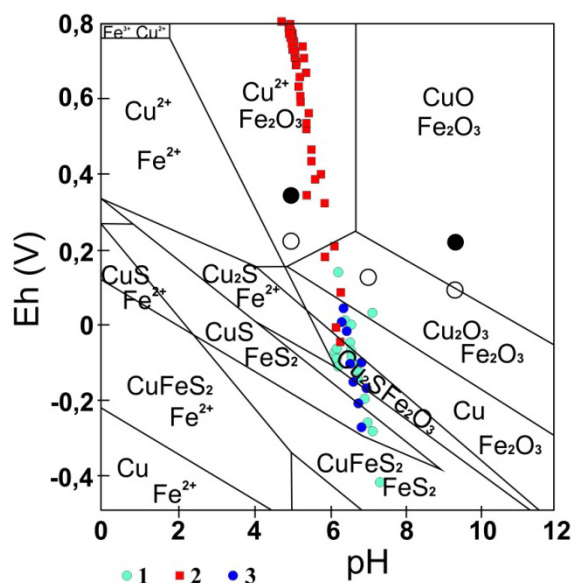
Figure 8. pH- Eh stability diagram for Cu-Fe-S-H_2O system (Fairthorne et al., 1997); (o) - the separation line Fe^{2+}/Fe_2O_3 in nitrogen conditions and ($\bullet$) - in oxygen conditions

The Fe in soil and in technogenous sediments is in the Eh-pH stability diagram for Cu-Fe-S-H_2O system (Fairthorne et al., 1997) situated only in the Fe_2O_3 stability field (Figure 8) or $Fe(OH)_3$ stability field (Figure 9), in consequence of this finding it is possible presume that the Fe is present in Fe^{3+} form. In groundwater and in surface water was described mostly Fe^{3+} but less often also Fe^{2+} form (Figure 8).

The speciation of As (Figure 9) and Sb (Figure 10) indicate that there are present both As^{3+}, Sb^{3+} and the less toxic As^{5+}, Sb^{5+} species. In the sediments prevail As^{5+} and Sb^{5+} species.

Migration of As and Sb in water may be realised in form of acidic or basic oxyions $H_2AsO_4^-$, $HAsO_4^{2-}$ and $HAsO_2^0$ or SbO_3^- and SbO_2^- under mildly oxidising conditions (Greenwood & Earnshaw, 1990; Manning & Goldberg, 2011). Under reducing, near-neutral to more alkaline conditions, transport of a sulphide complex such as $Sb_2S_4^{2-}$ is possible. By far the bulk of the stability field of water is covered by solid Sb-species (Sb_2S_3, $Sb(OH)_3$, Sb_2O_4, Sb_2O_5), thus suggesting that Sb transport must take place at moderately low Eh values.

At Ľubietová are in the water dominant the As^{3+} and Sb^{3+} forms (Figures 9, 10). As^{3+} is much more mobile than As^{5+} (Greenwood & Earnshaw, 1990; Manning & Goldberg, 2011) in weathering zone. The high As content in the water is controlled by tetrahedrite (and arsenopyrite) decomposition and by As sorption on amorphous Fe oxides and oxyhydroxides, on clay minerals and hydrogoethite (Andráš et al., 2007). Antimony is under supergenous conditions mobile and it has very similar behavior as arsenic Vink (1966). Determination of antimony speciation enables pH-Eh stability diagrams (Vink, 1966). Part of the anthropogenic sediment samples and soils are in the stability field of SbO_3^- water solution, the second part in senarmontite stability field (Figure 10).
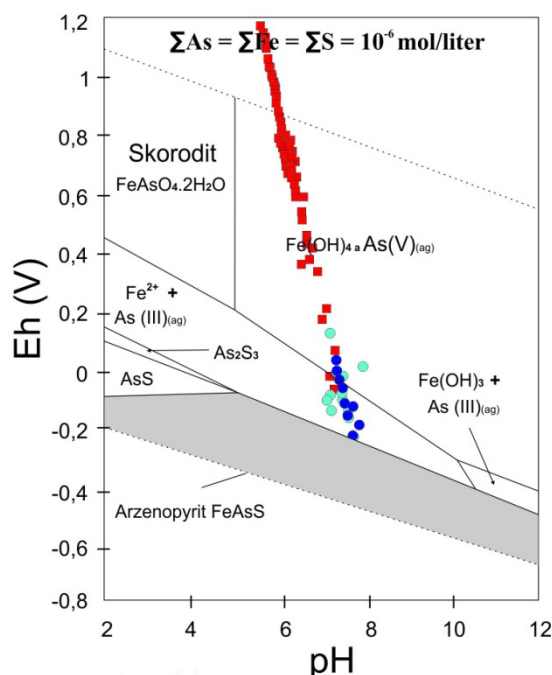
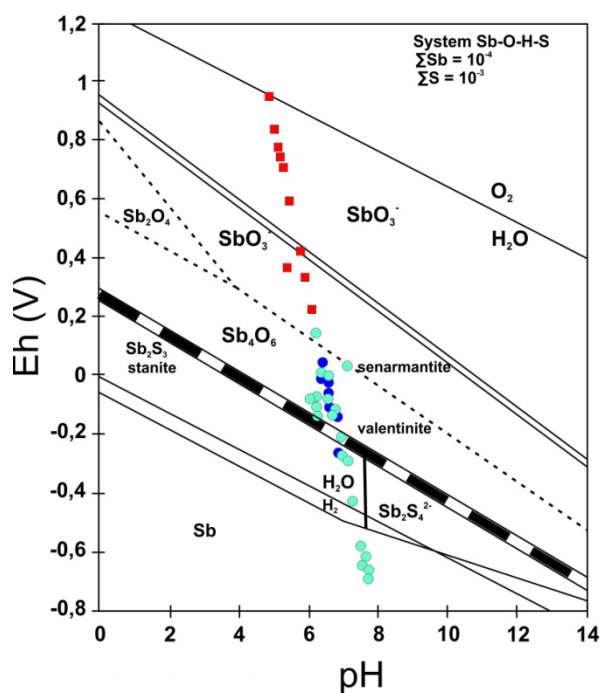Figure 9. pH-Eh stability diagram of Fe-As-H_2O-S system according to Ryu (2002)

Figure 10. pH-Eh stability diagram of Sb-H_2O-S system according to according to Vink (1966)

In groundwater, antimony is mainly present in the form Sb_4O_6. Only in one single sample we can find antimony in the form of elementary Sb^0 and Eh as well as pH values of one sample are at diagram on the border between water solution and stibnite – Sb_2S_3 (Figure 12). Also in surface water the dominant form of antimony is Sb_4O_6. Forms SbO_3^- and elementary Sb^0 are very rare (Figure 12).

3.3 Natural Sorbents

Transport of heavy metals in form of mobile nanoparticles is influenced by natural sorbents. As the most important natural sorbents at the studied locality were described clay minerals (X-ray diffraction analyse proved

presence of illite and muscovite mixture, caolinite but also minerals of smectite group and chlorite group) as well as hydrogoethite (Figure 11).
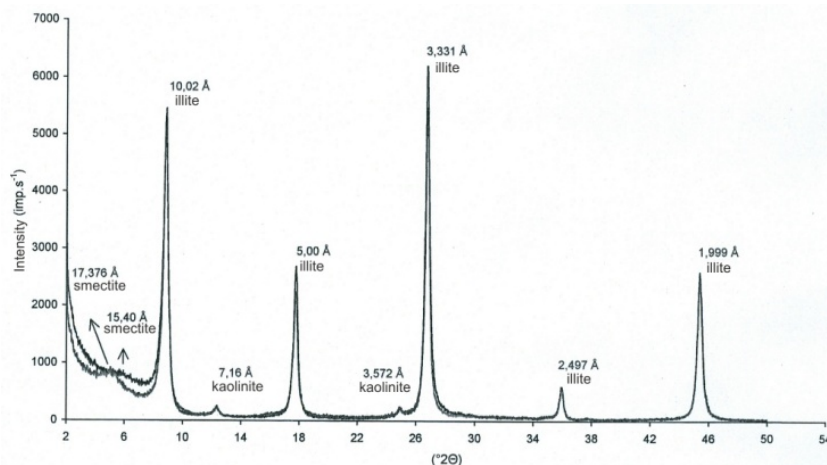

Figure 11. Rtg-diffraction diagram of clay mineral fraction from sample A-6

The best sorbent is hydrogoethite (Table 1, sample A-17). In most cases also the present clay minerals show good sorption capacity. These minerals generate in the dump-field material effective geochemical barrier which effect precipitation of metals and their fixation on the hydrogoethite and clay minerals surface.

Preferential sorption of Cr and Th on surface of clay minerals in comparison with hydroghoethite was described. On hydrogoethite surface are preferentially fixed Cu, Zn ($\pm$ Fe, Cd, Co).

Laboratory testing showed that most metals were sorpted on the clay minerals surface during 14 days maceration of the clay fraction in the drainage water percolating the dump-field material. This result indicates that the clay fraction still dispose by free sorption capacity.

Substantial differences in sorption capacity among various clay mineral mixtures were not certified, probably because of the matrix of all clay fraction consists predominantly of illite and muscovite. The variable quota of smectite, which has according to Andráš et al. (2007) higher sorption capacity as illite or muscovite, is not enough important to show substantially higher sorption efficiency.

3.4 The Total Acid Potential of the Dump-Field and the Posibility of Remediation

If distilled water is used in the measurement of paste or rinse pH of sediments or soils, its pH is usually around 5.3. pH values less than 5.0 indicates that the sample contains net acidity at the time of analyse (Sobek et al., 1978).

Values of paste pH between 5.0 and 10.0 can be considered near neutral at the time of the analysis. From the viewpoint of this study, only two samples (A-3 and A-12) account acid values (Table 5). It is surprising that one of these samples was taken from the reference area. The probable reason of such a behavior is the lack of carbonates (Table 5). The map of the soil and sediment acidity at the Podlipa dump-field is presented at Figure 12.

The measurement of the pH paste in the samples using solution of 1M KCl gives similar values. It means that only several few samples show markedly acid reaction (Table 5).

The very low total carbon ($C_{tot.}$) content (Table 5) reflects the lack of carbonates. The Figure 13 shows the $C_{tot.}$ distribution and enable comparison with the map of the acidity (Figure 12).

The total acid potential (TAP) was calculated according to Sobek et al. (1978):

$$TAP = \left(\% \, S_{tot.} \right) \times 31.25 \qquad (1)$$

where TAP is provided in any of three equivalent units: kg $CaCO_3$, equivalent/metric tone (t) of sample, t $CaCO_3$ equivalent/1000 t of sample, or parts per thousand (ppt) $CaCO_3$ equivalent.

The TAP values from the dump-field Podlipa range between 0.625 in samples A-12 (reference area) and A-2 to 13.125 in sample A-6 (Table 5).
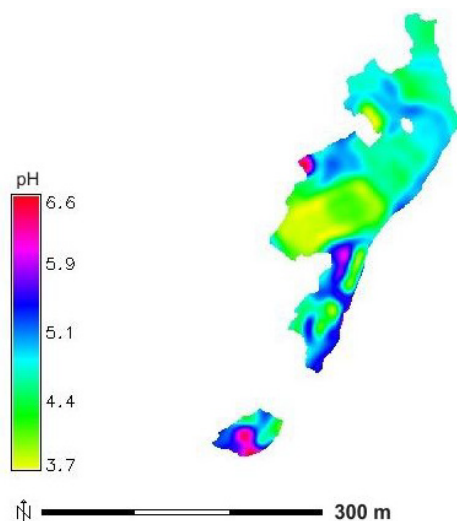

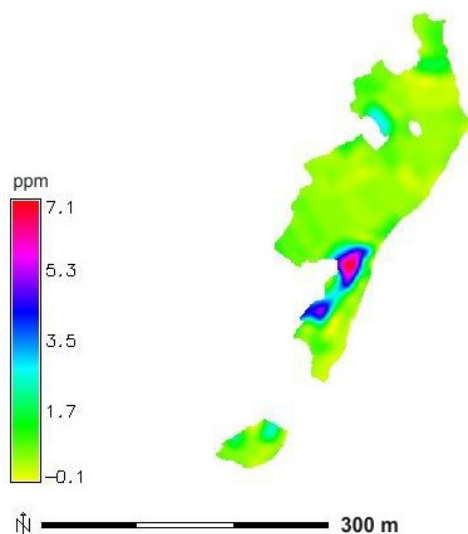Figure 12. Map of the sediments acidity at the Podlipa dump-field

Figure 13. Map of the Ctot, distribution in the sediments at the Podlipa dump-field

If we compare the highest TAP value for sample A-6 with the data about the sulphur content, we can demonstrate that both the highest sulphide and sulphate sulphur contents were described from this sample, which represents the sedimentary material from Zollweiner Maria Empfängnis adit. The highest TAP value is also the consequence of the relatively low carbon content.

The ability of drainage water to precipitate cementation copper on iron surfaces makes the realization of an Fe^0-barrier for elimination of heavy metals (Cu, As, Cd, Zn and others) from the contaminated water a possibility. Mixture of Fe chips with dolomite also allowed to eliminate the released Fe.

3.5 Changes in Plant Tissues

We studied in 2009 and 2010 the influence of the specific ecological conditions at dump-fields with high heavy metal content on selected plant species which represent tolerant ecotypes. The relatively common *Pinus sylvestris* show various defects of their tissues: exfoliation of summer tracheide cell-wall layers, formation of the traumatic resin channels in closeness to the calluses, absence of the cell-wall coarsening or presence of funguses
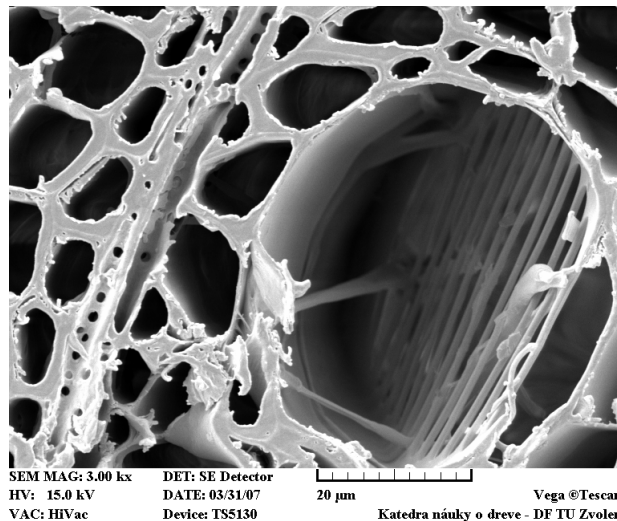
hyphaes in tracheae (Figure 14).

Figure 14. Funguses hyphaes in tracheae of Pinus sylvestris

Important chlorophyll insult causing even necrosis (mainly of leaves) was described in case of *Acetosella vulgaris*-plant which is considered to be so called „exclude-plants which use exclusion mechanisms by which uptake and/or root-to-shoot transport of heavy metals are restricted (Adams et al., 2011) or associated metal-tolerant species, which are moderately tolerant of heavy metals in soil, but not dependent on their presence (Baker et al., 2010). At 150 m long sectors from base of the dumps to their top we found 19 to 37 individuals of this species and at each plant were described on leaves violet to necrotic spots (Figure 15). Plants damage at individual sectors varied in range 88–100%.

Figure 15. Violet to necrotic spots on leaves of Acetosella vulgaris. a) initial damage; b) complete change of the original colour

Typical nanistic-pygmy forms, drying of branches, reduced organs (leaves, fruits), yellowing leaves, short annual shoot and dense age-bands were described on plants from the dump-field area (e.g. on *Picea abies*, *Pinus sylvestris*, *Larix decidua*, *Salix caprea*, *Betula pendula* etc.). Site influence was statistically tested on size of *Betula pendula* leaves. For statistical analysis the STATISTICA 7.0 statistical package was used (StatSoft Inc., 2004). ANOVA test enabled evaluate differences in width of leave bases among individual plants on dump-field surface with those from reference area. Measuring of 50 individuals was realised from each locality. For each individual plant were measured on 10 leaves leave-blade bases from 8 pieces of one year old branches. Main descriptive characteristics of investigated set of plants both from dump-field and from reference area are presented in Table 6.

Table 6. Main descriptive characteristics of investigated set of plants

	Dump-field Podlipa	Reference area
Sample size	400	400
Arithmetic mean	2.92	5.76
Median	2.87	5.74
Mode	2.61	5.71
Variance / dispersion	0.237	0.501
Standard deviation	0.487	0.708
Minimum	1.62	3.64
Maximum	5.23	11.05
Range	3.61	7.41

Result of Least Significant Difference (LSD) shows statistically significant difference between the wide of base of birch leaves (it means also total size of leaves) from individuals of Cu-dump field and reference locality with $p < 0.05$ (Table 7).

Table 7. Result of LSD with $p < 0.05$

Source	Sum of squares	Degrees of freedom	Mean square	F-ratio	p-value
Between groups	1618.82	1	1618.82	4386.38	0.000
Within groups	294.506	798	0.369		
Total	1913.32	799			

4. Discussion

Heavy metal distribution at the investigated dump-fields at Ľubietová reflect the geochemical behavior of the elements, depending on their content, solubility, migration potential and sorption properties (Cataldo & Wildung, 1978). Hydrolysable metals (e.g., Ni, Cd) or metals forming insoluble precipitates with S or P on entering the soil in soluble forms may be expected to be rapidly insolubilised at the near neutral pH of most soils due to hydrolysis on dilution and subsequent precipitation on, or reaction with particle surfaces. Certain elements (e.g. Fe) may also form precipitates with S or P (Routson & Wildung, 1969). The soil physicochemical parameters, most important in influencing the solubility of metals include: composition of solution, Eh, and pH; type and density of charge on soil colloids; and reactive surface area (Keeney & Wildung, 1977).

The main Cu sources at the dump-fields are sulphides (tetrahedrite and chalcopyrite) and secondary Cu-minerals (libethenite, langite, brochantite, pseudomalachite, malachite and azurite). Cu released to the solution during weathering processes, contaminates aqueous medium.

Mobility of the majority of heavy metals is in the nature mostly determined by their sorption on natural sorbents, which are mainly represented by clay minerals (Missana et al., 2008).

Kaolinite has been used as a good sorbent for most heavy metals (Wahba & Zaghloul, 2007). Cu, Pb, Zn and Cd show favourable sorption on smectite and Pb also on illite surface (Rybicka et al., 1995). The uptake of Pb and Cu on illite and smectite is usually very fast. Kinetics of Zn, Ni and Cd sorption on illite and smectite are not so efficient. Mg, Fe and Al sorption on clay minerals is more efficient at higher pH. It is caused by absence of free H^+ ions and by increase of negative charge on clay minerals surface (Kish & Hassan, 1973). $pH_{(H_2O)}$ of the technogenous sediments at Podlipa dump-fields ranges from 4,21 to 7,93 (pH$_{(KCl)}$ 4.00–7.34), thus conditions for Cu, Pb, Zn and Cd adsorption on clay minerals are not the best but also not inefficient.

Thorium contents in clay minerals are amazingly lower than in the dump-sediment. It means that the Th is during the maceration washed out from the clays. This trend is noticeable because U is generally considered to be more mobile as Th (Polanski & Smulikowski, 1978). The better mobility of U at the Ľubietová deposit caused that while the content of Th in soil is several times higher than the content of U, while in plants (Andráš et al., 2007) is the Th/U rate in consequence of better U mobility approximately identical (about 1 : 1).

Acidity is mainly up to the geochemical behavior (weathering) of particular minerals (mainly pyrite). The calculation of the acid mine drainage water (AMD) formation potential (neutralisation potential, total acidity production, net neutralisation potential) is also discussed. The value of the net neutralisation potential (NPP) and the NP : AP ratio show that the potential of the acid mine drainage water formation is very limited (NPP = 1,42; NP : AP = 1,72) and the environmental risk is negligible.

Lack of carbonates at Ľubietová deposit causes that in 5 cases among 12 studied samples, are the NNP values negative (neutralisation matter is entirely absent) and two values (samples A-3 and A-11) are very low (7.4 and 20.1; Table 4). NNP values from -20 to 20 (kg $CaCO_3 t^{-1}$ of dump material) are possible to account as a "*scale of uncertainty*" sensu US EPA methodics (Lintnerová & Majerčík, 2005) from viewpoint of the acidity production, because there is no unambiguous forecast if the AMD will be produced. In spite of this fact results of our study suggest that at Reiner and Podlipa is the assumption of AMD production very limited.

Mining dump surrounding is characterized by no or very poor and dry soil cover with lack of soil nutrinents, minimum of water combined with intensive evaporation, strong solifluction patterns and high heavy metal content. The plants growing at such as habitats are usually tolerant to a high metal content, characterized by high vitality and typical for xerothermic conditions.

As a symptom of heavy metal contamination is possible mention violet to red stigmas and necrosis on leaves and stems of vascular plants, nanic growth (Andráš et al., 2007; Chaves et al., 2011), reduction of roots (Banásová, 1976), chlorosis of leaves with green veining, growth stagnancy (Kopponen et al., 2001), drying of young branches and decrease of leaves size (Pulford & Watson, 2003), ultrastructural effects (Ouzounidou et al., 1992).

Toxicity symptoms in plants from mining dumps (tendency for mould diseases, growth decrease, deformations of cell organelles and plant tissues, chlorosis of leaves) show sometimes similar features as influence of lack of essential elements. If the soil contains very high content of copper, we can in the plants see lack of Fe as a consequence of immobilisation of Fe by Cu. As a result of Fe-lack we can see chlorosis of leaves, which could be caused also by superabundance of Zn (Kopponen et al., 2001). To state the unambiguous specification of toxicity reasons is necessary to have information about the heavy metal content in soil-plant system.

Betula pendula is the tree which represents the most important dynamic element on mining dumps and is considered as a focus of initial stages of vegetation due to litter formation, shadow and leeward (Banásová, 1976). *Betula pendula* is a suitable bioindicator of air pollution in urban areas (Samecka et al., 2009; Petrova, 2011) and it is used as a model organism in several studies focused on heavy metal influence on growth, annual additions and reproductive effort (Samecka et al., 2009; Franiel & Babczynska, 2011). Our study also confirmed decrease of birch leave blades caused by heavy metal content.

5. Conclusions

The soil and technogenous sediments contamination is very irregular. It depends on the mineralogical composition of ores, on the original concentration of the mentioned metals in the technogenic sediments of the spoil dumps, and also on their migration abilities and sorption properties. Bilateral correlation of metals seems to be influenced by incorporation of elements to various metastable phases as well as by present natural sorbents. This proces is controlled both by oxidation state and by ionic radius of elements.

The surface water (and drainage water) as well as the groundwater water are substantially contaminated predominantly by Cu, Fe, As and Sb. The content of the most dangerous contaminants: As^{3+}, As^{5+}, Sb^{3+} and Sb^{5+} don't pose acute risk. The only risk poses the spring of the mineral water Linhart because of the high radioactivity and high Fe, Cu, Cd and Pb contents.

The present natural sorbents are predominantly the clay minerals (illite, muscovite, caolinite, smectite) and hydrogoethite. The clay minerals are good sorbents of V, Cr, Ti, W, Zr, Nb, Ta a Th and at the hydrogoethite of Cu, Zn, Mo, Mn, Mg, (± Fe, Cd, Co, Ca). In the case of the Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi, U was proved also the free sorption capacity.

The paste or rinse pH of sediments measured in distilled H_2O is around 5.3 and only very few samples account acid values (< 5.0). Only several few samples show markedly acid reaction. The acidity production (AP) vary from 0.625 to 10.31 (in average 3.7) and the neutralisation potential (NP $CaCO_3$) from 0.66 to 12.71 $kg t^{-1}$ (in average ca 27.1 $kg t^{-1}$ $CaCO_3$). The value of the net neutralisation potential (NNP) and the NP : AP ratio show that the potential of the acid mine drainage water formation is very limited (NNP = 1.42; NP : AP = 1.72) and the environmental risk is negligible.

The concentrations of the heavy metals in plant tissues decrease seriately in rate: Fe, Zn, Pb and Cu. The highest concentrations of heavy metals are in roots, than in leaves and stems and the lowest concentrations are in flowers,

seeds and in fruits. The plant tissues from the dump-field are heavily damaged. The results of the research document the plant defence reactions under the influence of stress factors at the dump sites (absence of soil and water, the heavy metal contamination, mobility of the cohesionless slope material).

Botanic research indicated that the specific conditions at the dump-fields have evident influence on plants. Some damage spots are visible even by naked eye but some of them were proved also statistically, by histological study of *Pinus sylvestris* and by evaluation of morbid changes of *Acetosella vulgaris*.

The Ľubietová-Podlipa dump-field dispose by certain degree of "*self-cleaning ability*". Important part of the heavy metals and contaminants is fixed in porous dump-material, Fe-hydroxides and in clay minerals (mainly illite, caolinite, smectite and chlorite group), which show still an important free sorption capacity. The ability of the drainage water precipitate cementation copper (as well as Sb and probably also other heavy metals as As) on the iron surface give possibility to realize Fe^0-barrier for elimination of heavy metals from the groundwater and drainage water.

Acknowledgements

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