

**THE ROLE OF NATURAL SORBENTS AT THE ĽUBIETOVÁ  
REINER AND PODLIPA DUMP-FIELDS**

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**Abstract**

*This article presents the results of an environmental study at the Ľubietová Podlipa dump-field. The distribution of the selected elements and heavy metals is unequal and depends on the geochemical behaviour of the elements (mainly on their migration ability). The present natural sorbents are predominantly clay minerals (illite, muscovite, caolinite, smectite) and hydrogoethite. The clay minerals are good sorbents of K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta and Th, and for the hydrogoethite of Cu, Zn, Mo, Mn, Mg, P ( $\pm$  Fe, Cd, Co, Ca). In the case of the Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi, U proved also free sorption capacity.*

**Key words**

*dump-field, heavy metals, sediments, clay minerals, sorption*

**Introduction**

The Ľubietová – Podlipa deposit is among important deposits in the surroundings of Banská Bystrica. It is situated in the northeast part of the Slovenské Stredohorie Mountains which also include the north part of the Poľana neovolcanic massive and the north part of the Vepor Mountains. According to archeological findings, copper from the surface cementation zone in the surroundings of Ľubietová was exploited already in the time of the Bronze Age (Koděra et al., 1990).

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Ore bodies, formed mainly by ankerite –  $\text{Ca}(\text{Fe},\text{Mn},\text{Mg})(\text{CO}_3)_2$  and siderite –  $\text{FeCO}_3$ , are localised predominantly in acid crystalline rocks and in series of the Permian age. The main ore minerals are chalcopyrite –  $\text{CuFeS}_2$ , tetrahedrite –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  (often Ag-bearing) and pyrite –  $\text{FeS}_2$ . A substantial part of the territory is built by Permian rocks and, as is typical for Permian terraines, increased radioactivity of the rocks was described. In the locality it is possible to also find numerous rare secondary minerals [libethenite –  $\text{Cu}_2(\text{PO}_4)(\text{OH})$ , brochantite –  $\text{Cu}_4(\text{SO}_4)(\text{OH})_6$ , langite –  $\text{Cu}_4(\text{OH})_6(\text{SO}_4)\cdot 2\text{H}_2\text{O}$ , malachite –  $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ , azurite –  $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ , etc.].

Weathering of the reactive minerals first under acid conditions mobilises the heavy metals and numerous additional elements. This process causes contamination of the landscape components. A pH decrease in the technogenous sediments of the Cu-deposit at Lúbietová affects a heavy metals release (Cu, Fe, Cd, As, Sb, Pb, Zn, Mn, Ni, Co) from the solid phase, where are they present in the form of less soluble minerals or in a sorption complex to groundwater or to surface water. Resistance of the landscape components against heavy metal contamination is significantly conditioned by various natural sorbents (e.g. clay minerals and hydrogoethite). They form a natural geochemical barrier, on which the precipitation of the metals to stable bondings is realised. Utilisation of the present natural sorbents could be a very good method of remediation.

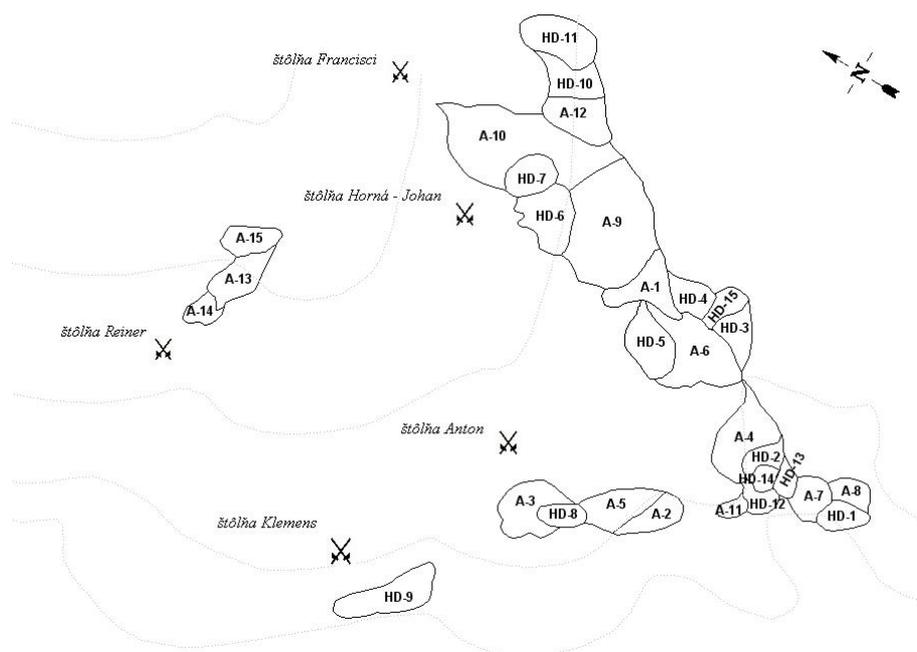
As very good sorbents for remediation, it is possible to utilise clay minerals (and zeolites). These predominantly crystalline aluminosilicates with foliated texture, usually have negative surface charges (Kozáč, 1969) and therefore they are able to fixate Ca(II), Mg(II), K(I), Na(I), Al(III), Mn(II) cations and heavy metal cations on their surface. These cations could be substituted by other cations (Čurlík, 2003).

Hydrogoethite -  $\text{FeOOH}\cdot\text{H}_2\text{O}$  („limonite“) can also be a very good sorbent. It is formed under weathering conditions by oxidation of Fe containing ores and of some mafic rock-forming minerals. Fe-hydroxide, which originates during the hydrolysis of  $\text{FeSO}_4$ , forms a well coagulating hydrosalt. The precipitated gel is partly dehydrated and results in Fe-monohydrate. As hydrogoethite has negative surface charge and enormous reaction surface, it is predetermined to be an excellent natural heavy metal sorbent.

## Experiment

### Sampling

The sampling was done during the summer months in 2007. Twenty-three samples of technogenous sediment (samples marked by indexes HD and A), and one sample of mud from the bottom of the terrain depression underneath the dump of the Andreas adit (sample JP-1) were collected. Each of them represent a 30 cm deep horizon and an area of 50 x 50 m (fig. 1). The grain size of the samples was below 1 cm and their weight about 30 – 35 kg. The set was supplemented by 2 samples of hydrogoethite rich rocks: A-17 and VZ-A. Sample A-17 represents several homogenised samples from sampling localities A-2, A-3 and A-5, and sample VZ-A was obtained at the sampling locality A-15.



**Fig. 1.** Location of samples

### Elaboration and analysis of the samples

The monomineral fractions of clay minerals were prepared according to Šucha et. al. (1991). This procedure consists of displacement of organic mater, of carbonates, of chlorides as well as of iron and manganese from the sample.

To remove carbonates from the sample pulverised to <0,16 mm grain size, 100 cm<sup>3</sup> of natrium acetate (SOTR) buffer is added to 10 g of the sample. The reacted solution is, after 2 days, segregated from the solid phase and the solid phase is dispersed by SOTR addition in an ultrasound device for 2 – 3 minutes. The sample is heated three times up to 90 °C, with 100 cm<sup>3</sup> SOTR addition, and then the suspension is decanted.

Organic matter was removed by reaction with 10 cm<sup>3</sup> of concentrated hydrogen peroxide and 100 cm<sup>3</sup> of SOTR. The mixture was heated at 70°C for 15 minutes. This procedure was repeated two times and the reacted solution was removed.

The free Fe and Mn oxides are removed by addition of 90 cm<sup>3</sup> citrate solution and by heating up to 75 – 85 °C. After 5 minutes, double additions of 2 g of natrium hydrosulphite was realised and the solution was decanted. The rest of the sample was irrigated by distilled water.

After completion of these procedures, it is possible to realize the true separation of individual clay minerals (<2 µm fraction). The colloidal rest of the sample in 2 dm<sup>3</sup> of distilled water is, after 41 hours and 8 minutes (the time is calculated according to Stokes rule for gravitation sedimentation), decanted to beakers and saturated solution of NaCl is added. After treating, the is solution fleeced. The remaining solid is transposed to calciferous form using 1 mol.dm<sup>-3</sup> CaCl<sub>2</sub> solution. This procedure regulates the replacable cations in clay minerals.

Dialysis is used for chloride removal and the presence of chlorides is verified by addition of  $\text{AgNO}_3$  solution. After removal of chlorides, the rest of the sample is drained at 30 °C.

To 0,14 g of the sample 3,5 cm<sup>3</sup> of distilled water was added and using ultrasound the sample was dispersed. Suspension was applied using a syringe on mount glass and the sample was drained at laboratory temperature to get an oriented mount. These oriented mounts were saturated by ethylenglycol gasses in an exicator for 8 hours on a ceramic skid at 60 °C to optimise the conditions of the rtg-diffraction analysis.

Rtg-diffraction analysis of clay fraction was done in laboratories of the Geological Institute of Slovak Academy of Sciences in Bratislava using a Philips rtg-difraktograph.

The pH of the sediments was measured in H<sub>2</sub>O and in 1M KCl lixivium, according to the method described by Lintnerová and Majerčík (2005). To 10 g of sample was added 25 ml of distilled water or 1M KCl and, after two hours mixing in the laboratory mixer, the pH and Eh were measured by pH-meter.

In samples of the technogenous sediments (HD-1 to HD-15), sediment from terraine depression beneath the Mária-Empfängnis adit (JP-1), fractions of the clay minerals (A-1c to A-8c) as well as in the samples of hydrogoethite (A-17, VZ-A), a set of 22 elements was analysed by ICP-MS analysis. The efficiency of the sorption was studied in the clay minerals and in the hydrogoethite. The samples for the sorption efficiency of clay mineral fraction (mixture of clay minerals) study were prepared by separation of the clay fraction based on dispersion of the sediment sample using distilled H<sub>2</sub>O in a volumetric cylinder (of 2 dm<sup>3</sup> volume). After 41 hours and 8 minutes sedimentation (calculated according to Stokes rule), the clay minerals containing suspension (< 2 µm fraction) were decanted. The clay fraction was drained at laboratory temperature.

The existence of clay mineral free sorption capacity was studied using heavy metals containing drainage water from a terraine depression beneath the dump of the Maria-Empfängnis adit. To 20 g of clay sample (A-1c to A7c and A-17), 50 cm<sup>3</sup> of 5-times concentrated drainage water was added. Analyses were completed from 1 g of sample (A-1c\* to A7c\* and A-17\*) after 14 days maceration in drainage water.

The samples for Ca, Na, K, Mg, Ti, Al, P, S, Cd, Bi, Co, Ni, As, Sb, Mn, Mo, Rb, Sr, Hf, V, Ba, Li, La, Cr, W, Zr, Ce, Sn, Y, Nb, Ta, Be, Sc, U and Th determination were melted using addition of Li-metraborate and Li-tetraborate mixture and solved in diluted nitric acid. The Au, Ag, Fe, Pb, Zn and Cu was determined from 0,5 g weight of sample after leaching by hot aqua regia. The samples were analysed using ICP – MS in ACME Analytical Laboratories Vancouver Ltd. Canada.

## Results

### Heavy metal distribution in technogenous sediment components

Heavy metal distribution in technogenous sediments and ores of the Ľubietová – Podlipa dump-field is variable (tab. 1 – 3). The distribution of individual elements reflects the primary concentration in separate parts of the dump-field as well as their geochemical relations (fig. 2 – 4), and their migration ability.

The pH of the sediments determined in water-lixivium range from 4.21 to 7.93. The pH interval of the sediments measured in 1M KCl lixivium range from 4.0 to 7.34.

ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS

Table 1

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Element	Unit	Sample																	
		HD-1	HD-2	HD-3	HD-4	HD-5	HD-6	HD-7	HD-8	HD-9	HD-10	HD-11	HD-12	HD-13	HD-14	HD-15	JP-1	VZ-A	
Ca	%	0.08	0.19	0.04	0.19	0.47	0.13	0.04	0.14	0.25	0.14	0.27	0.11	0.17	0.12	0.07	1.35	8.93	
Na		0.305	0.039	0.082	0.311	0.081	0.067	0.066	0.036	0.062	0.195	0.765	0.189	0.299	0.184	0.067	0.363	0.269	
K		2.49	4.27	3.96	4.29	4.29	4.14	3.48	3.47	4.23	2.44	2.43	3.24	2.91	2.79	2.66	0.62	0.28	
Fe		1.33	1.64	3.59	2.67	2.26	2.14	2.58	2.37	1.84	1.12	1.38	2.25	1.61	1.66	1.01	1.19	33.22	
Mg		0.49	0.64	0.63	0.61	1.07	1.41	0.52	0.61	0.85	0.34	0.53	0.61	0.52	0.46	0.48	1.98	0.32	
Ti		0.092	0.124	0.096	0.134	0.116	0.099	0.112	0.097	0.111	0.108	0.176	0.115	0.122	0.111	0.116	0.075	1.166	
Al		4.44	6.45	7.12	7.97	7.11	8.03	6.65	5.68	6.89	4.27	4.99	5.63	5.15	4.91	4.45	9.31	4.18	
P		0.041	0.049	0.098	0.081	0.076	0.081	0.112	0.055	0.079	0.039	0.032	0.075	0.058	0.066	0.034	0.009	0.419	
S		0.1	0.2	0.3	0.1	0.5	0.1	0.1	0.2	0.3	<1	<1	0.2	0.1	0.1	0.1	0.1	0.1	
Cu	ppm	4044	2956	2243	331	7486	1977	541	>10 000	5466	390	25	6766	1388	2402	29	5	>10 000	
Pb		10.4	15.8	27.9	30.3	15.6	7.9	24.1	13.5	17.8	53.6	16.1	17.7	16.2	20.1	29.8	9.1	114.6	
Zn		14	211	13	19	21	23	20	15	24	36	39	19	29	21	25	44	188	
Cd		<1.0	0.9	0.1	0.1	<1.0	0.1	0.1	0.1	0.1	0.3	0.2	<1.0	0.3	0.1	0.2	0.1	1.3	
Bi		3.5	3.1	102.7	0.4	3.8	2.2	9.2	2.6	8.1	1.7	0.2	7.1	3.8	5.1	0.5	0.5	38.8	
Co		59.3	69.9	43.2	15.5	82.5	36.2	53.6	84.5	96.3	7.1	5.1	34.9	15.1	15.5	2.1	0.5	50.1	
Ni		14.2	35.6	35.5	11.5	48.7	17.1	31.6	62.1	51.9	7.8	8.5	25.8	16.6	23.2	5.5	1.5	188.6	
As		60	77	397	58	138	34	294	206	130	32	7	153	85	105	11	12	1144	
Sb		15.5	25.6	98.2	12.1	5.2	15.6	39.2	36.3	27.7	17.5	10.4	26.4	17.7	18.3	13.4	14.2	62.6	
Mn		657	500	598	2755	486	377	517	1258	391	486	559	372	416	231	47	392	821	
Mo		0.2	0.1	0.4	0.4	0.2	0.1	0.6	0.7	0.2	0.3	0.3	0.3	0.2	0.2	0.3	0.2	4.8	
Au		<1	<1	<1	<1	0.1	<1	0.1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	0.2
Ag		0.4	0.3	3.4	0.1	0.9	0.3	1.6	0.3	0.6	0.3	0.1	0.7	0.6	0.8	0.1	<1	4.3	

ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS

Table 1 (continuation)

Element	Unit	Sample																
		HD-1	HD-2	HD-3	HD-4	HD-5	HD-6	HD-7	HD-8	HD-9	HD-10	HD-11	HD-12	HD-13	HD-14	HD-15	JP-1	VZ-A
Rb	ppm	93.9	149.3	148.6	166.2	147.3	134.2	131.8	119.2	151.4	103.3	88.4	123.9	108.5	103.2	119.4	12.5	12.5
Sr		23	44	57	32	33	18	35	16	23	37	40	25	33	27	21	137	218
Hf		0.5	0.8	0.8	0.7	0.7	0.9	0.9	0.6	0.7	0.6	1.4	0.9	0.9	0.7	0.7	3.2	11
V		22	33	46	26	32	43	51	29	32	22	31	36	31	30	19	5	400
Ba		349	390	350	531	315	216	410	343	269	346	391	375	370	314	377	608	74
Li		24.1	30.9	37.6	47.8	43.8	53.2	29.5	28.8	38.7	19.7	26.9	31.3	26.6	24.3	27.7	227.3	52.1
La		19.8	21.4	31.2	28.3	20.6	15.1	33.9	23.8	27.5	19.8	24.7	25.8	23.9	26.1	17.2	5.7	105.8
Cr		8.6	8.8	17.9	9.1	8.8	11.7	19.3	9.4	11.8	12.5	18.9	14.3	13.2	11.6	13.6	0.6	348.6
W		0.9	1.3	1.4	0.6	1.2	1.4	1.6	1.1	1.1	0.9	1.2	1.3	1.1	1.1	0.9	0.1	3.4
Zr		13.3	23.2	21.9	16	18.2	23.3	22.5	14.2	19.2	18.7	36.7	22.2	20.9	22.5	19.1	72.1	363.5
Ce		38	43	62	5	41	31	67	47	51	38	48	51	47	51	34	69	201
Sn		4.4	4.5	17.6	2.2	11.4	7.1	19.6	9.1	12.1	4.1	1.7	8.8	7.4	8.7	1.9	3.7	70.8
Y		4.4	5.6	6.2	9.1	4.8	4.4	7.1	5.1	5.6	3.4	6.6	6.5	5.2	5.1	3.1	16.2	74.2
Nb		2.5	2.5	2.1	2.6	2.4	1.9	2.6	1.9	2.2	2.9	4.1	2.9	2.9	2.5	3.1	45.5	38.7
Ta		0.3	0.3	0.2	0.2	0.3	0.2	0.2	2	0.2	0.3	0.4	0.3	0.3	0.3	0.3	5.2	2.9
Be		2	3	3	3	4	3	3	3	2	1	3	2	2	1	5	4	3
Sc		3	4	7	4	4	4	7	4	4	3	4	5	4	4	3	2	39
U		1.4	2.6	2.5	2.5	1.7	1.3	3.1	1.5	2.1	1.1	2.2	1.7	1.5	1.6	0.9	3.4	10.7
Th	7.2	6.9	10.9	8.4	7.3	5.7	10.1	7.1	8.8	6.4	7.7	8.3	7.5	7.4	5.9	35.9	30.9	

ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS AND OF CLAY FRACTION AND CLAY FRACTIONS  
AFTER 14 DAYS MACERATION IN DRAINAGE WATER CONTAINING HEAVY METALS

Table 2

Element	Unit	Sample															
		A-1	A-1c	A-1c*	A-2	A-2c	A-2c*	A-3	A-3c	A-3c*	A-4	A-4c	A-4c*	A-5	A-5c	A-5c*	
Ca	%	0,05	0,09	0,18	0,20	0,26	0,20	0,09	0,13	0,17	0,15	0,11	0,14	0,25	0,19	0,20	
Na		0.053	0.042	0.403	0.217	0.171	0.462	0.147	0.171	0.654	0.054	0.070	0.365	0.150	0.087	0.373	
K		2.86	3.42	4.80	2.40	3.59	4.36	2.22	3.66	4.33	2.06	3.60	4.74	2.25	3.58	4.82	
Fe		1.31	1.45	2.98	1.42	1.46	2.17	1.94	2.14	2.90	2.64	2.47	3.65	1.71	1.66	1.83	
Mg		0.51	0.47	0.99	1.01	0.93	1.50	0.81	0.77	1.16	0.70	0.67	1.26	0.71	0.73	1.35	
Ti		0.090	0.075	0.148	0.127	0.107	0.174	0.127	0.138	0.200	0.117	0.092	0.159	0.102	0.089	0.169	
Al		5.99	4.98	9.26	6.76	6.05	8.75	7.33	6.64	8.77	6.88	6.35	10.22	5.87	5.42	9.49	
P		0.048	0.074	0.144	0.047	0.048	0.030	0.065	0.065	0.056	0.080	0.080	0.079	0.053	0.047	0.020	
S		0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.02	<0.1	0.2	<0.1	<0.1	
Cu		ppm	2829	1693	2345	199	574	472	828	624	857	4471	3324	3112	3150	3001	2078
Pb			28.1	63.8	229.1	130	22.4	27.9	16.0	23.1	37.4	9.6	14.9	37.8	16.9	14.8	21.9
Zn			14	18	95	21	36	62	20	25	47	23	16	27	19	18	45
Cd			<0.1	<0.1	0.2	0.1	0.2	0.1	<0.1	<0.1	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	<0.1
Bi			2.8	4.5	14.6	0.2	1.4	1.5	8.5	7.2	12.1	23.7	39.2	90.9	1.7	2.1	3.2
Co			10.4	11.3	18.3	5.9	10.3	6.4	14.0	17.0	11.0	50.0	58.3	32.1	24.4	30.4	29.6
Ni	36.8		36.0	71.8	9.8	12.2	17.0	32.1	28.3	30.4	55.0	42.4	64.4	34.0	34.1	55.4	
As	162		258	628	10	19	15	71	110	105	169	237	300	60	64	105	
Sb	61.6		60.1	153.2	7.1	9.2	12.6	22.4	24.0	28.0	59.5	79.3	129.8	17.2	16.3	30.3	
Mn	34		64	87	212	348	133	252	334	207	420	446	216	570	631	512	
Mo	0.5		1.2	2.1	<0.1	0.2	0.2	<0.1	0.4	0.4	0.1	0.3	0.4	0.1	0.2	0.2	
Au	<0.1		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
Ag	0.7		0.8	1.7	<0.1	0.1	0.2	0.4	0.6	0.9	1.4	2.1	4.1	0.1	0.1	0.2	

Explanations to the tabs. 2 and 3: A-1 to A-8 technogenous sediments; A-1c to A-8c clay fractions\* clay fractions after 14 days maceration in drainage water; A-17 hydrogoethite

ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS AND OF CLAY FRACTION AND CLAY FRACTIONS  
AFTER 14 DAYS MACERATION IN DRAINAGE WATER CONTAINING HEAVY METALS

Table 2 (continuation)

Element	Unit	Sample														
		A-1	A-1c	A-1c*	A-2	A-2c	A-2c*	A-3	A-3c	A-3c*	A-4	A-4c	A-4c*	A-5	A-5c	A-5c*
Rb	ppm	116.2	129.7	173.2	93.9	143.5	144.8	91.7	156.7	172.7	85.6	142.1	160.8	90.0	132.4	156.9
Sr		27	24	49	26	25	27	16	22	41	24	28	63	16	13	21
Hf		0.5	0.5	0.9	0.6	0.7	0.9	0.7	0.9	1.2	0.6	0.6	1.0	0.4	0.5	0.8
V		29	22	49	39	33	46	57	50	77	52	39	70	38	30	50
Ba		397	381	548	343	351	481	246	267	385	349	320	498	251	261	432
Li		29.4	25.0	54.3	50.0	34.4	67.5	43.4	36.0	68.8	35.6	25.3	64.1	34.1	28.7	60.9
La		20.6	18.2	15.4	22.9	18.6	2.9	30.2	28.2	9.8	27.5	26.0	5.9	20.8	19.8	5.3
Cr		38	9	24	36	17	26	34	21	37	38	15	30	30	10	22
W		0.9	1.0	1.9	1.5	1.0	1.5	1.2	1.3	1.8	1.2	1.1	1.8	0.9	0.9	2.0
Zr		14.7	15.1	30.9	21.8	23.5	30.4	19.9	32.8	41.8	19.2	19.9	31.8	12.6	15.6	28.4
Ce		38	39	35	43	38	7	56	61	22	52	54	14	38	42	12
Sn		10.9	11.1	29.4	3.5	2.7	4.4	9.8	7.2	9.5	17.3	12.8	22.7	4.9	3.3	8.1
Y		3.5	3.7	5.3	5.4	4.7	2.6	5.5	6.1	4.6	5.1	5.1	3.6	4.6	4.8	2.8
Nb		1.9	2.3	3.8	3.2	3.3	4.4	2.9	4.0	5.7	2.2	2.6	3.6	2.0	2.4	3.8
Ta		0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2	0.3	0.1	0.1	0.2	0.2	0.2	0.2
Be		3	3	6	2	2	3	2	3	4	3	3	5	2	2	4
Sc		2	3	5	3	4	5	5	6	8	5	5	7	3	3	5
U		1.3	1.4	3.3	1.4	1.1	1.1	1.7	1.8	1.9	1.6	1.7	2.2	1.0	1.2	1.4
Th		5.8	6.0	9.5	7.6	5.9	2.2	9.1	9.2	5.2	8.3	7.8	5.0	5.9	5.8	4.0

ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS AND OF CLAY FRACTION AND CLAY FRACTIONS AFTER 14 DAYS MACERATION IN DRAINAGE WATER CONTAINING HEAVY METALS

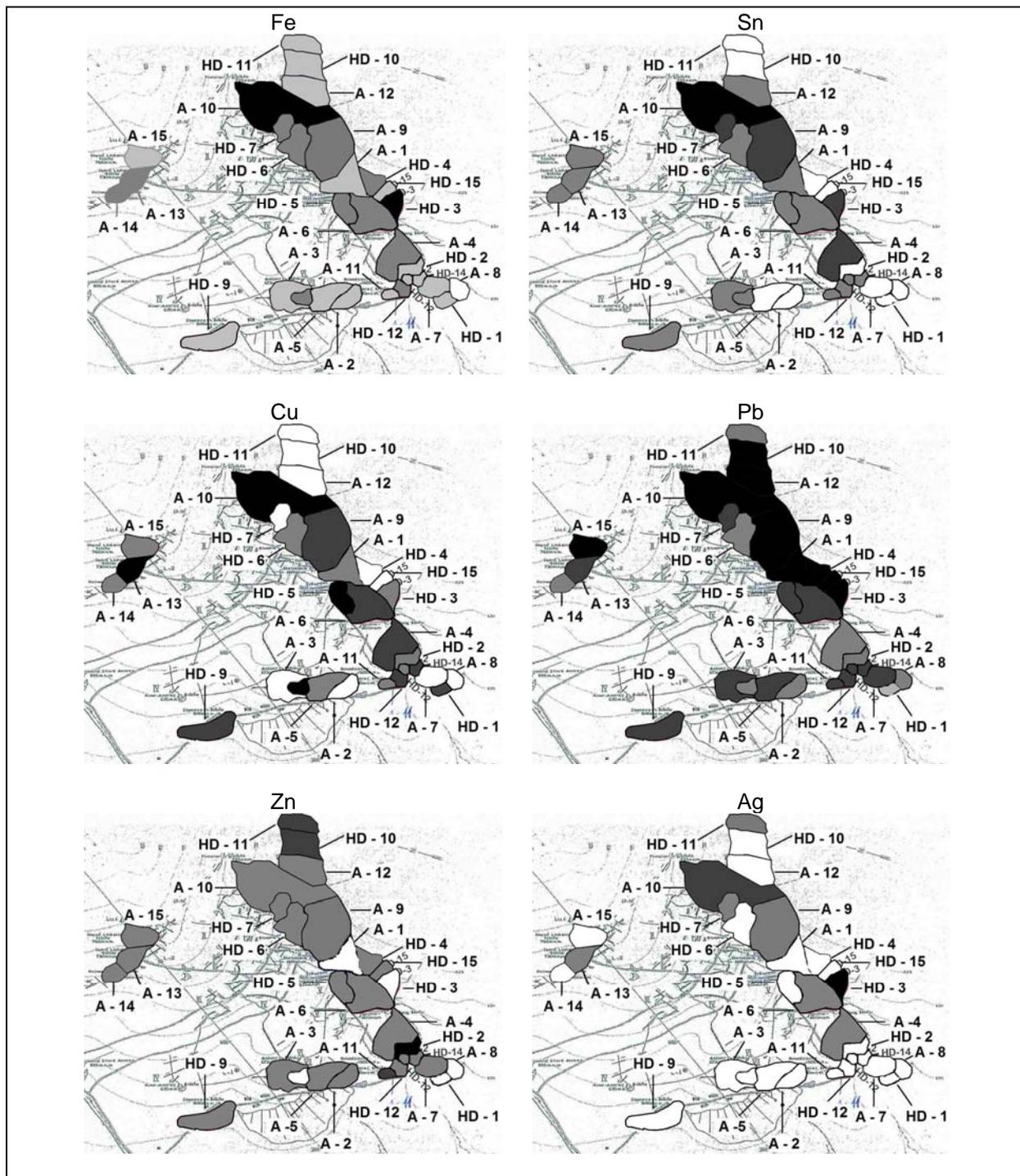
Table 3

Element	Unit	Sample											
		A-6	A-6c	A-6c*	A-7	A-7c	A-7c*	A-8	A-8c	A-8c*	A-17	A-17c	A-17c*
Ca	%	0.17	0.09	0.12	4.74	1.99	1.35	0.08	0.71	0.11	0.02	>100	<0.10
Na		0.076	0.061	0.302	0.819	0.606	0.911	0.034	0.111	0.109	0.110	<0.10	>100
K		2.16	3.92	4.69	2.01	1.99	4.49	2.22	4.70	3.18	0.022	0.040	1.020
Fe		2.06	2.09	3.36	1.32	1.43	2.81	0.91	1.29	0.79	1.72	1.50	13.10
Mg		0.80	0.71	1.25	3.15	1.61	1.75	0.47	0.91	0.46	12.92	11.80	0.20
Ti		0.128	0.102	0.171	0.111	0.114	0.198	0.112	0.190	0.086	0.01	<0.10	0.02
Al		7.60	6.70	10.02	4.91	4.51	8.79	6.37	10.43	5.66	0.36	0.37	1.90
P		0.067	0.070	0.081	0.041	0.041	0.069	0.054	0.056	0.051	0.90	1.00	0.40
S		0.2	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu		ppm	4797	2503	2918	756	855	2026	716	836	837	>10 000	20 360
Pb	15.6		24.6	72.3	16.8	20.2	73.7	6.5	6.3	4.2	8.4	49.0	60.0
Zn	13		14	65	26	33	176	7	14	4	59	80	50
Cd	0.2		<0.1	0.3	<0.1	0.2	0.7	<0.1	<0.1	<0.1	0.2	0.2	0.2
Bi	25.4		24.4	51.7	0.9	1.2	3.6	0.5	0.7	0.8	7.2	6.0	5.0
Co	41.8		40.9	32.0	10.2	12.0	15.5	89.9	69.7	104.5	73.4	70.0	83.0
Ni	51.6		45.1	61.7	10.4	10.1	26.0	58.0	66.5	62.5	51.7	43.0	58.0
As	134		224	305	16	17	33	61	52	46	289	260	280
Sb	49.8		56.2	92.3	11.5	7.1	17.4	17.9	20.2	18.9	43.2	40.0	34.0
Mn	198		254	147	372	547	931	1190	905	1458	1074	960	1010
Mo	<0.1		0.3	0.4	0.2	0.3	0.6	<0.1	0.3	0.3	2.2	2.0	30.0
Au	<0.1		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ag	1.0		1.6	3.0	0.2	0.2	0.4	<0.1	<0.1	0.1	0.8	1.0	1.0

ICP-MS ANALYSES OF TECHNOGENOUS SEDIMENTS AND OF CLAY FRACTION  
AND CLAY FRACTIONS AFTER 14 DAYS MACERATION IN DRAINAGE WATER  
CONTAINING HEAVY METALS

Table 3 (continuation)

Element	Unit	Sample											
		A-6	A-6c	A-6c*	A-7	A-7c	A-7c*	A-8	A-8c	A-8c*	A-17	A-17c	A-17c*
Rb	ppm	87.5	155.1	167.6	77.3	80.1	168.9	91.9	138.3	132.9	47.4	45.0	46.0
Sr		23	24	51	67	49	90	19	48	31	6	6	6
Hf		0.7	0.8	1.2	0.6	0.7	1.5	0.5	1.3	0.6	0.2	0.2	2.0
V		44	34	57	40	39	67	35	69	22	15	16	15
Ba		303	307	405	342	340	680	248	470	229	286	250	270
Li		40.5	32.0	73.4	20.7	14.4	67.0	35.8	65.3	31.9	5.6	6.0	11.0
La		24.9	20.9	4.4	17.3	17.6	21.3	40.6	15.0	34.2	24.8	21.0	23.0
Cr		31	11	23	28	11	35	23	21	7	7	8	8
W		1.2	1.4	2.0	1.5	0.7	1.5	1.4	2.2	1.5	0.4	0.4	0.5
Zr		20.2	23.5	37.1	18.3	22.1	48.9	14.7	43.9	23.1	7.7	9.0	9.0
Ce		46	47	10	31	35	43	77	41	68	49	40	50
Sn		14.9	12.9	19.6	4.0	2.6	6.8	3.9	7.1	3.0	8.8	4.0	9.0
Y		4.6	5.0	2.9	4.9	6.2	10.4	6.7	6.7	8.0	9.8	9.0	9.0
Nb		2.5	2.8	4.1	2.6	3.5	6.3	2.2	5.0	2.6	0.5	0.5	0.5
Ta		0.2	0.2	0.2	0.2	0.2	0.4	0.1	0.4	0.2	<0.1	<0.1	0.1
Be		3	4	5	1	1	4	3	5	2	2	2	3
Sc		4	4	6	3	4	7	4	6	3	4	5	5
U		1.4	1.6	2.2	1.1	1.1	2.3	2.6	2.5	2.1	2.3	2.0	1.0
Th	6.9	6.1	4.1	4.8	5.3	11.8	6.8	5.7	6.7	2.5	2.0	2.0	

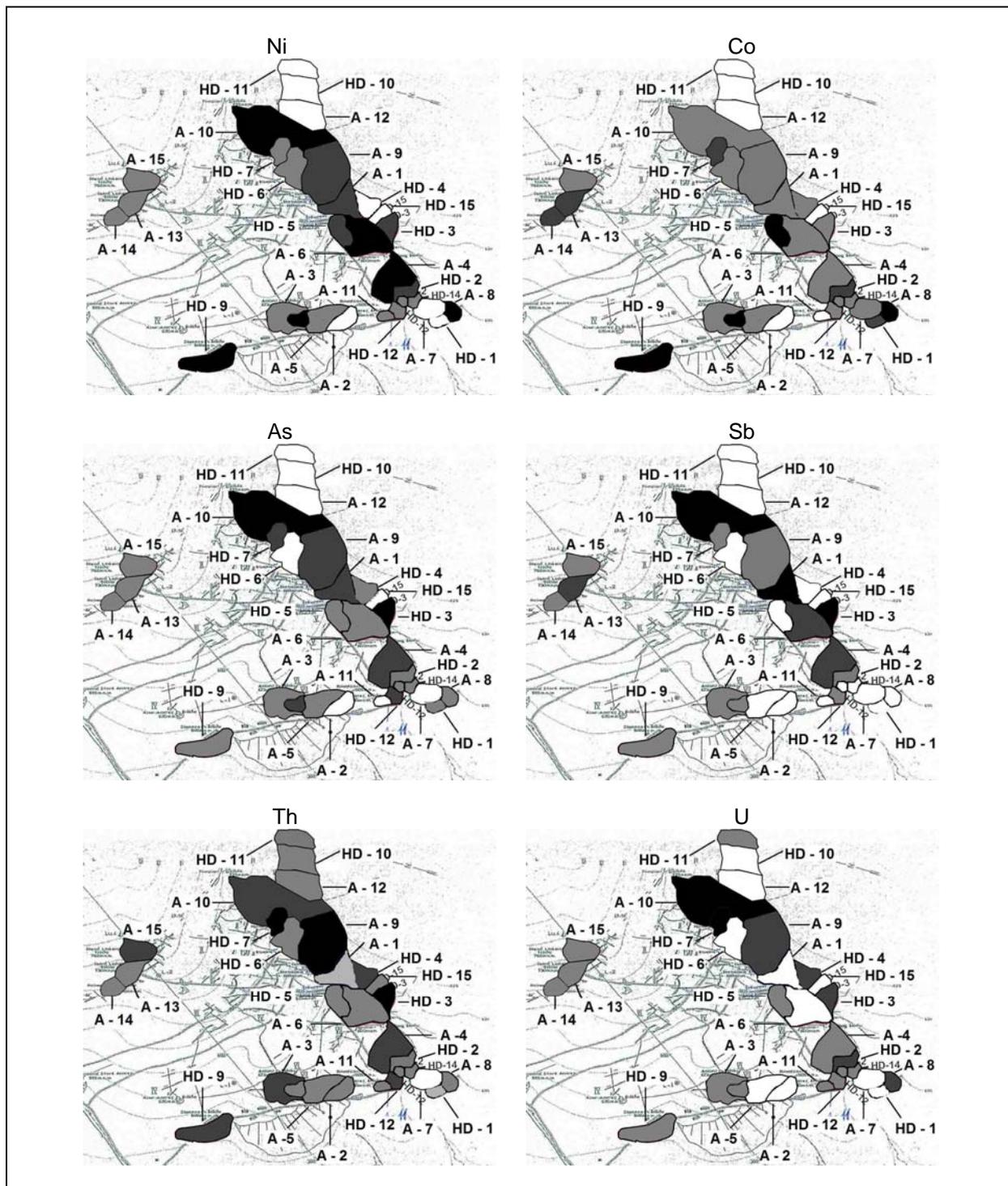


**Fig. 2** Distribution of Fe, Sn, Cu, Pb, Zn and Ag at dump-field Ľubietová - Podlipa

EXPLANATIONS TO Fig. 2 (Fe, Sn, Cu, Pb, Zn and Ag content)

Table 4

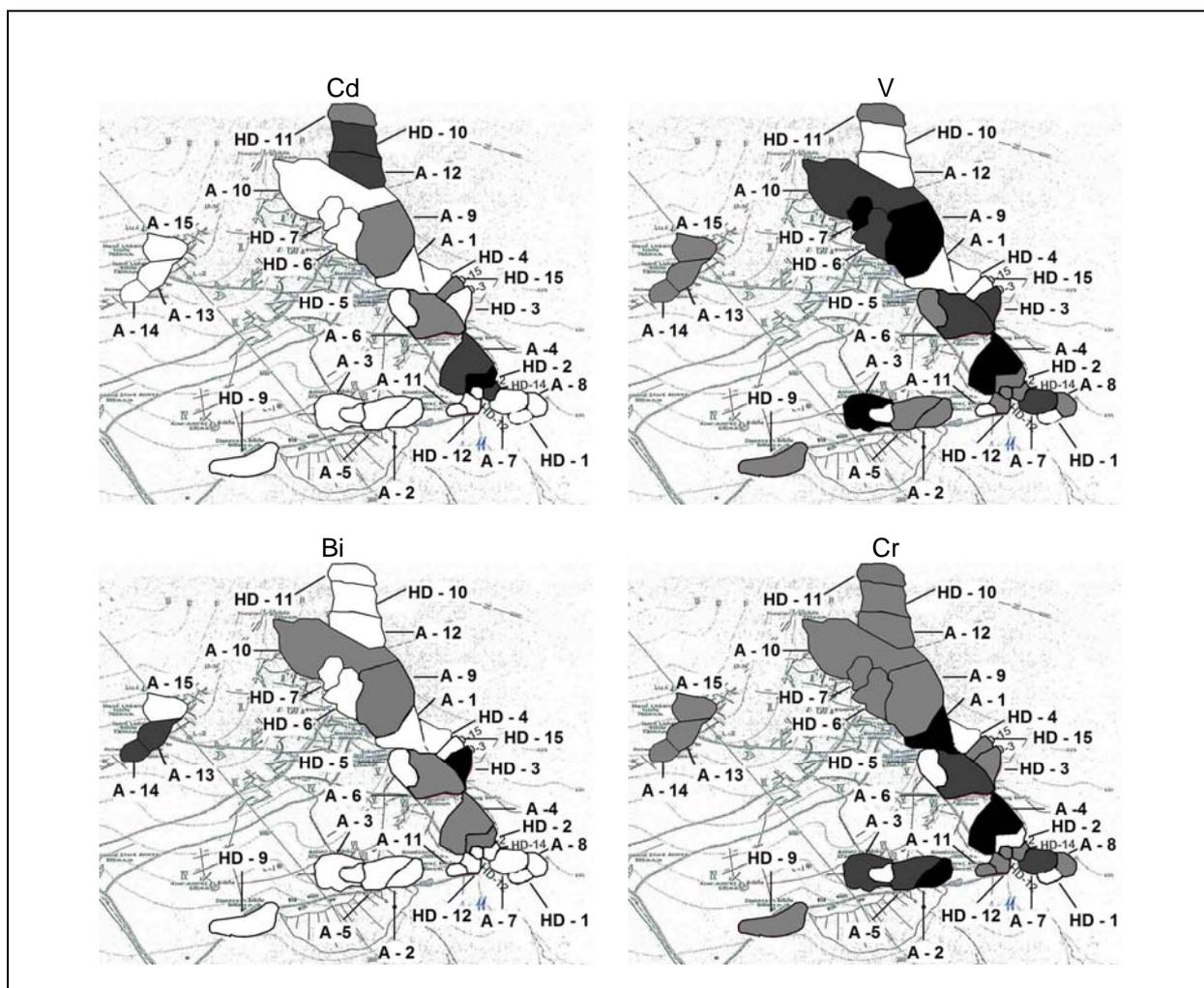
	Fe	Sn	Cu	Pb	Zn	Ag
	%	ppm				
	< 1	< 5	< 1000	< 5	< 15	< 1
	1 – 2	5-15	1000 -4000	5-15	15-35	1-2
	2 – 3	15-25	4000-7000	15-25	35-50	2-3
	> 3	> 25	> 7000	> 25	> 50	> 3



**Fig. 3.** Distribution of Ni, Co, As, Sb, Th and U at dump-field Lubietová - Podlipa

EXPLANATIONS TO Fig. 3 (Ni, Co, As, Sb, Th and U content) Table 5

	Ni	Co	As	Sb	Th	U
	ppm					
	< 15	< 10	< 50	< 20	< 5	< 1,5
	15 – 35	10-50	50-150	20-40	5-8	1,5-2,5
	35 – 50	50-80	150-350	40-60	8-10	2,5-3
	> 50	> 80	> 350	> 60	> 10	> 3



**Fig. 4.** Distribution of Cd, V, Bi and Cr at dump-field Lubietová - Podlipa

EXPLANATIONS TO Fig. 2 (Cd, V, Bi and Cr content)

Table 6

	Cd	V	Bi	Cr
	ppm			
	< 0,1	< 30	< 10	< 10
	0,2	30-40	10-30	10-25
	0,3	40-50	30-100	25-35
	0,9	> 50	> 100	> 35

The presented results show that the distribution of selected elements at the dump-field is non-uniform. The maximal concentration of theoretically extractable elements in the dump-field material ranges from 30 000 ppm (Fe) to 0,9 ppm (Cd). Also, important concentrations of Cu (7000 ppm) and As (350 ppm) were described. Noticeable are also high concentrations of Pb and Zn (Cd) at the reference area. We have no explanation for this evidence. (Both within the territory of the reference area and of the whole deposit, there are no occurrences of sphalerite or other minerals which could explain the high Zn and Cd contents.) The source of the increased U and Th contents at the reference area is in the Permian rocks (rauwackes). In

the dump range oriented in E – NE vs. W – NW direction (samples HD-6, A-2, A-3, A-5 and A-11) only low contents of Ag, Bi and Cd were described.

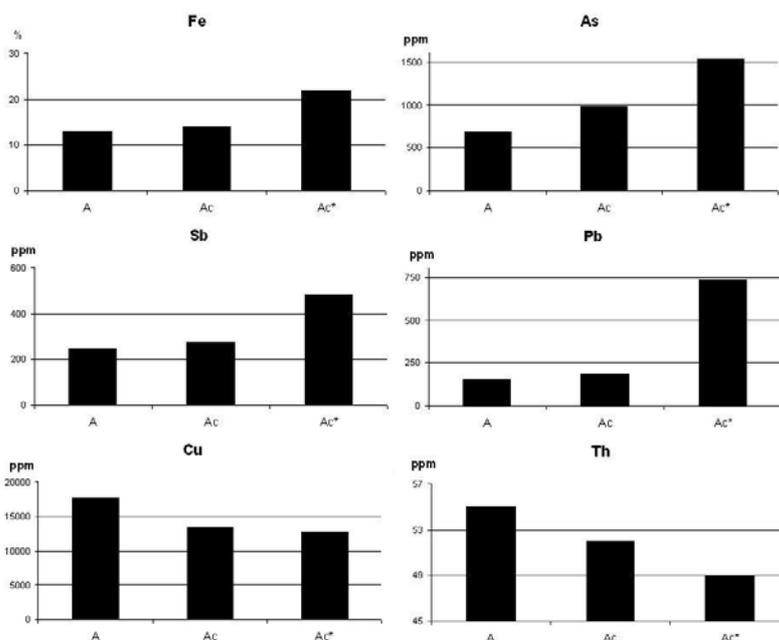
### Natural sorbents

Rtg.-diffraction analysis proved that the most important potential natural sorbents in the studied area are the clay minerals and hydrogoethite –  $\text{FeO(OH)} \cdot n\text{H}_2\text{O}$ , which are formed during the weathering process of rock-material. The research confirmed that the clay minerals are represented by illite –  $(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$  and muscovite –  $\text{KA}l_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$ , caolinite –  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , as well as smectite and chlorite mixture. Illite and muscovite are dominant in all samples. The next important mineral is smectite.

### Heavy metals sorption in clay minerals and hydrogoethite

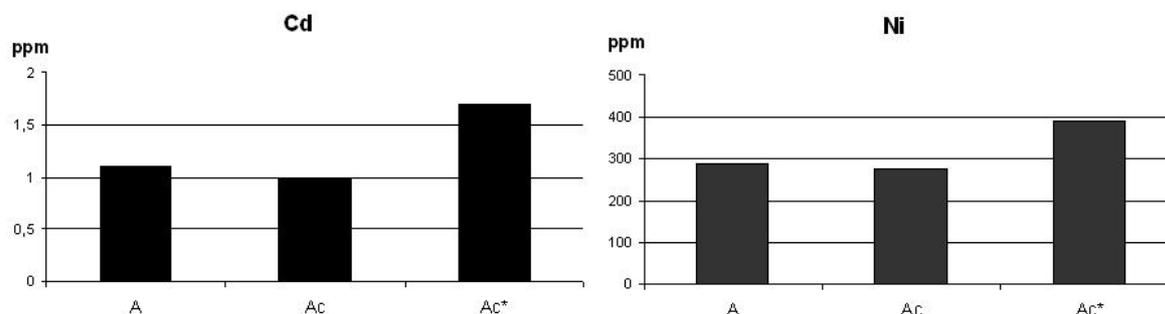
The heavy metal sorption study of clay minerals and hydrogoethite from technogenous dump sediments, and the study of the free sorption capacity of these natural sorbents in individual samples, is a relatively complex problem and the interpretation of these data is very confusing. Better reproducibility enables the complex interpretation of the results if the concentrations of the individual elements in technogenous sediment, in clay mineral mixture, and in clay fraction after maceration in drainage water, are presented in the form of total values for each element (tab. 2 and 3). Such total data enable better understanding of the studied processes and trends.

Preferential sorption of K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta and Th on surface of clay minerals in comparison with hydrogoethite was found. On the hydrogoethite surface, Cu, Zn, Mo, Mn, Mg, P ( $\pm$  Fe, Cd, Co, Ca) are preferentially fixed. The following elements: Sb, Bi, Ba, La, Ce, Sn, Y, Be, Sc, S, Pb, Ag, Ni, As and U show no legible trends of preferred sorption both on clay minerals and on hydrogoethite rich rock (tab. 2 and 3).



**Fig. 5.** Total content of Fe, As, Sb, Pb, Cu and Th in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (Ac\*)

The following heavy metals: Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi and U show not only good sorption efficiency on clay minerals but also free sorption capacity of the clay fraction. The opposite trend – lower heavy metal content in the clay component in comparison with the sediment and metal elements washing during maceration – was proved in the case of Th and Cu (fig. 5). Co shows a moderate increase of content in clay minerals but no free sorption capacity was proved. The Cd, Ni, Co, V and Cr behaviour is very complex (fig. 6).



**Fig. 6.** Total content of Cd and Ni in technogenous sediments (A), in clay fraction (Ac), in clay fraction after 14 days maceration in heavy metals containing drainage water (Ac\*)

Cd, Ni and V are preferentially fixed in the sediments; lower Cd, Ni and V contents are in the clay fraction but the clay mineral mixture proved to have a good ability to fix the mentioned heavy metals (Cd, Ni and V) on their surface (Fig. 6). The probable reason of this behaviour is the fact that the Cd, Ni and V majority is bound in the solid phase and only with difficulty create soluble forms, so in consequence of this behaviour in the weathering process the autochthonous clay minerals are insufficiently saturated by V. The same trend was described for Cd, Ni, V and Co in the case of hydrogoethite. The Cr behaviour is very similar, only with the difference that while V concentrations in macerated clay are higher than in the original sediment, the Cr concentrations are the highest in the original sediment. The most complex relations were recognized in the case of Co.

The highest Th content was described in sediments and in soil. The Th contents in clay minerals are lower than in the sediment, and after maceration Th washed out from the clays. This trend is noticeable because in general U considered to be more mobile than Th. The better mobility of U was described also at the Lubietová deposit (Andráš et al. 2008), where the content of Th in soil is several times higher than the content of U, while in plants the contents both of U and Th are in consequence of better U mobility approximately identical. The Th/U rate is about 1 : 1.

## Discussion

The mobility of most heavy metals in nature is determined mostly by their solubility and sorption ability on natural sorbents, among which the most important are clay minerals (Missanaet et al., 2008). According to sorption mechanics, it is possible to distinguish several of the following types: a) mechanic sorption, b) physical adsorption conditioned by surface tension at the phase interface, c) physical-chemical replaceable sorption, which is realised by ion replacement, d) chemical adsorption, which makes possible the anion fixation in form of coagulums, e) bioaccumulation – e.g. intake of biogenic elements by root systems of plants and by bacteria (Chmielewska and Lesný, 1995; Lischke and Frank, 1988). In the case of clay minerals, the dominant process is represented by ionic replacement between solution and solid phase but partially also the physical process of adsorption (Kozáč, 1969).

Caolinite is in general a very good sorbent of the majority of heavy metals (Wahba and Zaghloul, 2007). Cu, Pb, Zn and Cd are fixed preferentially on smectite, but Pb also on illite (Rybicka et al., 1995). Illite and smectite are very good sorbents of Pb and Cu. The sorption of Zn, Ni and Cd on illite and smectite is not so efficient. The sorption of Mg, Fe and Al on clay minerals is substantially more efficient at higher pH. It is caused by the lack of free H<sup>+</sup> ions and by the increase of negative charge on the surface of clay minerals (Kishk and Hassan, 1973). The pH<sub>(H<sub>2</sub>O)</sub> of technogenous sediments from the dump-field Podlipa (tab.7) range from 4.21 to 7.93 (pH<sub>(KCl)</sub> 4.00 – 7.34), so it is possible to observe that the sorption conditions of Cu, Pb, Zn and Cd on clay minerals are not the best but, on the other hand, they are not wholly ineffective.

From the viewpoint of environmental risk, according to Andráš et al. (2008), at the studied locality the most important metals are Cu, As and Sb.

The main sources of Cu at the dump-field are tetrahedrite, chalcopyrite and Cu-secondary minerals (libethenite, brochantite, langite, malachite, azurite and pseudomalachite). Cu released to the solutions during the weathering process contaminate the whole local water-table. Andráš et al. (2007) described at the locality a cementation process which enables Cu precipitation on Fe oxides (hydrogoethite) and on the iron surface. In natural water are present the following forms of Cu: hydrated Cu(II) ion, complexes [CuCO<sub>3</sub>(aq)]<sup>0</sup>, [Cu(CO<sub>3</sub>)<sub>2</sub>]<sup>2-</sup> and hydrocomplexes [CuOH], [Cu(OH)<sub>2</sub>(aq)]<sup>0</sup>, [Cu(OH)]<sup>3-</sup> and [Cu(OH)<sub>4</sub>]<sup>2-</sup> (Pitter 1990).

Cu sorption on clay mineral surfaces depends on pH. In the case of a lack of carbonate (as it is at Ľubietová-Podlipa), during the sorption process are formed complex compounds ≡SOCu<sup>+</sup>, ≡SOCuOH and ≡SOCu<sub>2</sub>(OH)<sub>2</sub><sup>+</sup>, less often also ≡Cu(OH)<sub>2</sub> and ≡SOCu<sub>2</sub>(OH)<sub>3</sub> precipitates (Quinga et al. 1996).

pH OF TECHNOGENOUS SEDIMENTS  
AND THEIR EH MEASURED IN H<sub>2</sub>O  
AND 1M KCl LIXIVIUM

Table 7

Sample	H <sub>2</sub> O		1M KCl	
	pH	Eh	pH	Eh
A-1	5.14	77	4.61	109
A-2	5.89	34	5.40	63
A-3	4.87	94	4.21	131
A-4	5.46	59	5.33	66
A-5	5.77	42	5.37	64
A-6	5.17	74	5.06	83
A-7	7.93	-84	7.34	-58
A-8	5.42	36	5.22	42
A-9	5.03	83	5.01	85
A-10	5.25	71	5.14	78
A-11	6.11	22	5.95	30
A-12	4.21	133	3.47	173
A-13	5.20	75	5.11	85
A-14	4.91	97	4.32	125
A-15	4.47	111	4.00	165

Note: Eh (mV)

The most important As source at the Ľubietová is tetrahedrite. The weathering of the As-minerals (their oxidation) causes modification of native As and As(III) to As(V) containing compounds of arsenic acid (Lin and Puls 2000). The arsenic acid is water soluble, but only

rarely migrates greater distances, because it quickly reacts with heavy metals and As is fixed in the form of various arsenates. As is in the water solutions, it is most often present in the following forms:  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$  and  $\text{HAsO}_2^0$  (Greenwood and Earnshaw 1990). As(III) is in the weathering zone much more mobile than As(V) (Manning and Goldberg, 1997).

In oxidation (weathering) conditions of the Lúbietová-Podlipa dump-field As(V) markedly prevails (Andráš et al. 2008). The sorption capacity of clay minerals, of hydrogoethite, and Fe-oxyhydroxides related to As is very high (up to  $76 \text{ mg As.g}^{-1}$  in Fe oxyhydroxides at pH 5). As sorption depend on pH, time, As concentration in solution, and on temperature (Mohapatra et al., 2007). The most efficient sorption was described at pH 4 (García-Sánchez et al. 2002; Lombi et al., 2000). According to Mohapatra et al. (2007), kaolinite is the best As(V) sorbent from the natural sorbents described at Lúbietová dump-field. The sorption of the less toxic As(V) in comparison to As(III) on clay minerals is much more efficient and more quantitative. As(III) is during this process oxidized to As(V). The reductive process during the sorption of As was not confirmed (Lin and Puls, 2000).

The most important part of Sb descends from tetrahedrite. Both Sb(III) and Sb(V) exist in environmental conditions in the following soluble compounds: Sb(V) in the form of  $\text{Sb(OH)}_6^-$  and Sb(III) in the form of  $\text{Sb(OH)}_3$  (Filella et al., 2002). Hydrogoethite and Fe-hydroxides are the most important Sb sorbents. Sb(III) as well as Sb(V) form complex compounds on the hydrogoethite and Fe-hydroxides surfaces. The best Sb(III) sorption conditions are at pH 3 – 12, and the maximal Sb(V) sorption was described at pH <7. The Sb(III) on the hydrogoethite and Fe-hydroxides surface can be, within a pH range from 3 to 5.9, oxidised during several days. At pH ~ 9 its mobilisation and dissolution start, while at pH <7 it is fixed on the Fe-oxides surface (Leuz et al., 2006).

The main soluble lead-compounds in nature are mainly Pb(II) and  $[\text{PbCO}_3(\text{aq})]^0$ . The latter one may be in a wide pH range the dominant form of occurrence. In alkaline conditions substantial concentrations of  $[\text{Pb}(\text{CO}_3)_2]^{2-}$ ,  $[\text{Pb}(\text{OH})_2(\text{aq})]^0$  and  $[\text{PbOH}]^+$  complexes are also formed (Pitter 1990). Lead is, in solid matter, present usually in the form of  $\text{PbCO}_3$  and  $\text{PbSO}_4$ , and the ulmous substances affect its immobilisation (Beneš and Pabianová 1987). Pb shows affinity to formation of complexes with insoluble ulmous matters and in consequence of the mentioned trend it is fixed in the upper part of the soil level (in the mould). Copper and Pb are usually, in comparison with Zn, fixed on clay mineral surface much more strongly (Sipos et al., 2008). The increasing pH causes increasing Cd sorption on clay minerals (Hayashi and Liu 2008).

Soluble Cd is present in water in the form of the simple hydrated ion Cd(II), in the form of inorganic complexes  $[\text{CdOH}]^+$ ,  $[\text{Cd}(\text{OH})_2(\text{aq})]^0$ ,  $[\text{Cd}(\text{OH})_3]$ ,  $[\text{CdCO}_3(\text{aq})]^0$ ,  $[\text{Cd}(\text{CO}_3)_2]^{2-}$ ,  $[\text{CdSO}_4]^0$ , as well as in the form of organic complexes with various organic ligands (Pitter 1990). The proportion of sorbed Cd(II) on clay minerals shows an important increase at pH 6.5 – 9.0, while on illite it is sorbed more intensively than on kaolinite (Reid and McDuffie, 2005).

## Conclusions

Heavy metal distribution in technogenous sediments and ores of the dump-field Lúbietová – Podlipa is variable and reflects the original concentration of metals in technogenous sediments as well as their migration abilities. Rtg-diffraction analysis proved that the main prevailing natural sorbents are illite, muscovite and smectite, and less so kaolinite and chlorites. Hydrogoethite is relatively rare. Results of the sorption properties of clay minerals and hydrogoethitised rocks show that the studied dumps are disposed to a certain level of

„self-cleaning ability.“ A substantial part of heavy metals and contaminants is caught in porous substances, in Fe-hydroxides (hydrogoethite) and in clay minerals (mainly K, Na, Li, Al, Rb, Sr, Hf, V, Cr, Ti, W, Zr, Nb, Ta and Th), which, in the case of Fe, As, Sb, Ag, Pb, Zn, Mn, Mo, Bi and U, show important free sorption capacity. The mentioned data enables expression of the following result: The arrangement (opening) of the dumps could cause massive release in this way of fixed heavy metals to the environment.

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