

SPECIATION OF SELECTED METAL CONTAMINATION OF THE SURROUNDING AREA OF THE ABANDONED Hg-DEPOSIT MALACHOV (CENTRAL SLOVAKIA)

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ABSTRACT:

Mercury contamination of soil, dump sediments, groundwater, surface water and stream-sediments in the surroundings of the area of the abandoned Hg-deposit Malachov (Central Slovakia) was investigated. Soil was classified as cambis-soil (rendzina) and its rH_2 factor indicates moderately aerated soil type. The soil reaction (pH) varies from very acid (near the mine) to moderately alkaline in the Malachovský brook drainage. Maximum concentration of Hg ($411.3 \text{ mg}\cdot\text{kg}^{-1}$) was found in the dump sediment from the locality where the old Medieval Hg-fulminate production plant is situated. The correlation between the couples Hg/As, Hg/Sb, Hg/Fe and As/Sb is discussed.

The pH of the surface water is close to neutral whereas pH of the groundwater is moderately alkaline. In both cases, moderately reductive conditions were

determined. Hg contents are $0 - 403.32 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ (in surface water) and $0 - 0.989 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ (in groundwater). As and Sb content in surface water is below detection limit whereas, in groundwater, the As content ranges between <1 and $1.99 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ and the Sb content ranges between 0.92 and $1.99 \text{ }\mu\text{g}\cdot\text{L}^{-1}$. The stream sediments contain Hg mainly in the form of cinnabarite.

The Hg speciation both in soil and in water confirmed presence of Hg^{2+} (in the form of HgS) and, rarely, also in the form of Hg^0 . As and Sb are mainly present both in the soil/dump sediments and in the water in the very toxic form of three-valent inorganic As^{3+} and Sb^{3+} .

Keywords:

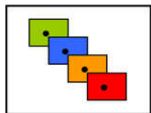
mercury, soil, dump sediment, water, stream-sediment, speciation

1. INTRODUCTION

The Eastern slopes of Kremnica Mts. are built by effusive and extrusive rocks of Neogene volcanism. In consequence of denudation, in the surroundings of Malachov both the older Mesozoic carbonates (limestones and dolomites) and the sand-silt series of Paleogene age are uncovered. Hg-mineralization is connected with young structures showing N-S to NE-SW direction and it is genetically related to postvolcanic stage of Neogene stratovolcano. Cinnabar and metacinnabar accumulations, accompanied by pyrite, marcasite and arsenopyrite, were formed in tectonically crushed carbonates of Mesozoic age and in Paleogene sandstones, below impermeable layers of argillite tuffs (Ivančík & Mitáček, 1986; Bancík & Jeleň, 1999), and show typical features of sinking structures described by Marschalko et al. (2012, 2012a).

The Hg-As mineralization at Malachov deposit is situated in the Eastern rim of Kremnica Mts., westwards of Banská Bystrica. Within an area of $80 - 100 \text{ km}^2$, numerous occurrences and anomalies are concentrated: Veľká Studňa, Nemecký Hill, Dolná Cliff, Trávný Ždiar, Mútne, Ortuťový Hill, Cipkove Jamy, Pri Jazere etc. (Koděra et al., 1990; Jeleň et al., 2010). The main mineral assemblage of Hg-ores belonging to Malachov area are cinnabarite - HgS and metacinnabar. Less frequent minerals are arsenopyrite - FeAsS , pyrite - FeS_2 , marcasite - FeS_2 , opigment - As_2S_3 , realgar - As_4S_4 and arsenolite - As_2O_3 . In the gangue mineral assemblage, various modifications of SiO_2 prevail (quartz, chalcedony, opal) as well as various modifications of carbonates: calcite - CaCO_3 , dolomite - $\text{CaMg}(\text{CO}_3)_2$ and gypsum - $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ (Koděra et al., 1990).

Cinnabar veins were in the past exploited in galleries and big amounts of ore were exploited close to the surface by shallow shafts (Bergfest, 1955; Jeleň et al., 2010). The Hg content in ore was about 0.5-1.0%. Mineralization is situated in Paleogene conglomerates, sandstones and Mesozoic carbonates, rarely also in Miocene volcanites. The Hg-As mineralization is connected to faults of N-S direction (Ivančík & Mitáček, 1986).



Mountainous forms of the country relief were formed by long-term mining activities, mainly from 14. to 17. centuries, and they are well visible until present times at localities Pri Jazere, Ortúty and Veľká Studňa. The last exploitation was realized from 1980 to 1990 at Veľká Studňa locality (Ivančík & Mitáček, 1986). The deposit has been closed since 1990 (Bancík & Jeleň, 1999).

2. MATERIALS AND METHODS

For research, the following set of samples was used (localisation of samples is shown on fig. 1):

- surface water (SW) and groundwater (GW) – 14 and 9 samples
- soil (SO) – 10 samples (within 4 samples, we distinguished A soil horizon and B soil horizon)
- dump sediments (TS) from the dump-field Veľká Studňa – 4 samples
- stream sediments (SS) – 9 samples.

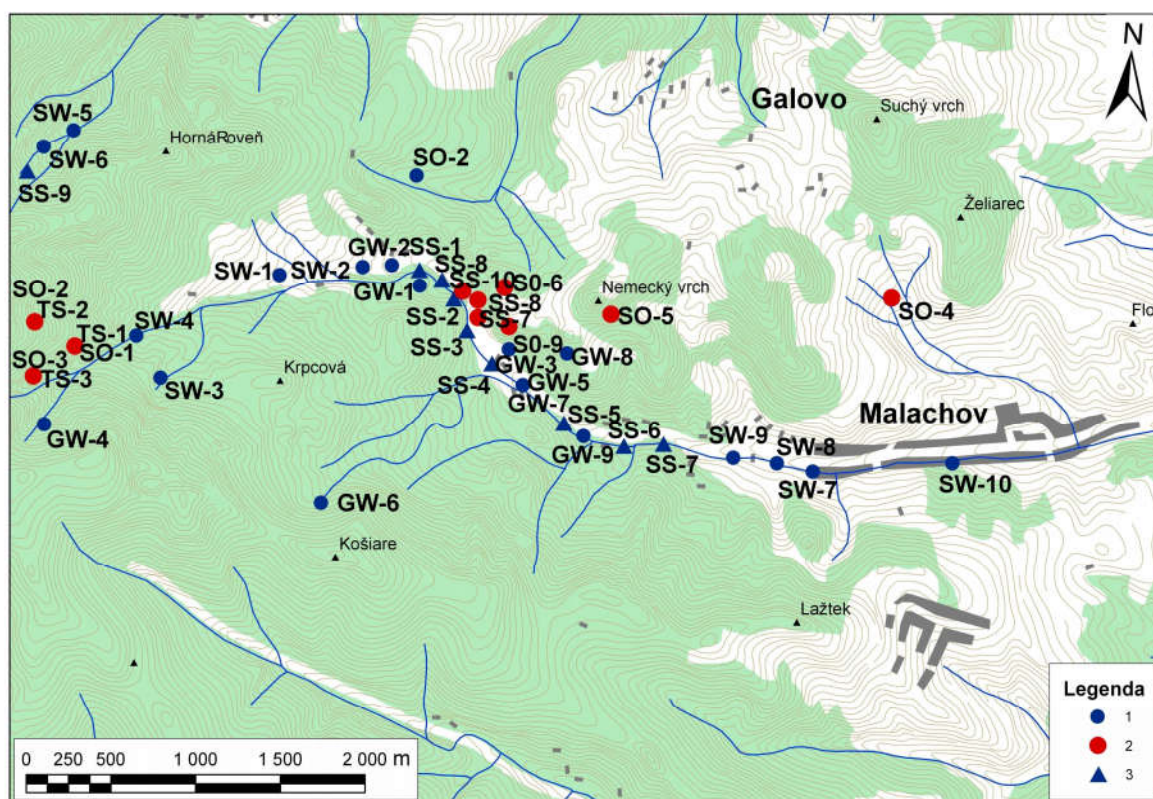
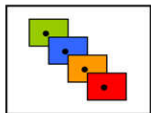


Figure 1. Locality map of samples in Malachovský brook Valley;
1 – water, 2 – soil, 3 – stream sediment

Surface water and groundwater samples of 500 mL in volume were obtained both in dry (June 2013) and in rainy periods (November 2013). Samples were conserved by adding 10 mL HCl. Both pH and Eh of water samples were measured on the field by pH-metre EUTECH Instruments and calculated to hydrogen electrode.

Hg and As contents, both in groundwater and in surface water, were determined using hydride generation atomic absorption analyse (tab. 1). Flame atomic absorption spectroscopy was used for quantitative determination of Cu, Fe, Cd, Co, Mn, Ni, Pb, Sb and Zn in the laboratory of Water Research Institute in Bratislava (tab. 2).

Samples of soil and of dump sediments from the dump-field were collected in September 2013, and stream sediments in November 2013. The samples were dried at laboratory temperature. Rinse and paste pH were measured according to Sobek et al. (1978). Rinse pH was determined in water suspension and paste pH in 1M KCl (64 g KCl/1000 mL H₂O) lixivium. To 5 g of sample in glass bake, 15 ml of distilled water or 1M solution of KCl were added and, after mixing this suspension for two hours by electromagnetic stirrers, both pH and Eh were measured in the laboratories of the Geological Institute of Slovak Academy of Science in Banská Bystrica by pH-metre EUTECH Instruments. The determined Eh values were calculated for standard hydrogen electrode according to Pitter (2009).



pH measured in water suspension is named rinse pH whereas pH in KCl-soil (NaCl-soil) suspension is known as paste pH. Paste pH represents not only the balance between the concentration of hydrogen (H^+) and hydroxyl (OH^-) ions in solution but it also reflects the function of adsorbed Al^{3+} ions in colloidal complexes of soil. Al^{3+} ions could be released into soil solution by activity of hydrolytically neutral salts ($NaCl$, KCl , $CaCl_2$). As the Eh is also dependant on pH of soil solution, the rH_2 factor could be used for better comparable Eh values at different pH:

$$rH_2 = Eh/30 + 2pH$$

In well aerated soils, rH_2 ranges between 28 and 34 whereas, in not aerated soils, rH_2 factor value is <20 (Richter & Hlúšek, 2003).

In the laboratory of Technical University in Zvolen, the Hg content in soils and in stream-sediments was determined by method of thermo-mechanical analysis by using automatic spectrometer AMA 254 (sample drying: 60 s; decomposition 180 s; measuring 45 s.). Each measure was repeated five times. The average value of these five measures was considered.

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

2 g of soil powder was wetted with a few drops of water and then digested to dry vapour in H_2O - HF - $HClO_4$ - HNO_3 mixture in rate: 2 : 2 : 1 : 1. After adding 10 ml of 50 % HCl , the samples were slowly heated on water bath under continual mixing. Cooled solution was refilled by HCl to exact volume and ICP-MS analysed.

In order to identify chemical forms of Hg in the studied samples, pH/Eh diagrams according to Davis et al. (1997) and Arbestain et al. (2009) were used whereas As and Sb speciation was studied by using pH/Eh diagrams according to Filella et al. (2002), Pokrovski et al. (2002) and Ryu et al. (2002). Correlations between two selected elements (metals) were calculated according to Spearman (1904):

$$r = 1 - \frac{6 \sum d_i^2}{n(n^2 - 1)}$$

where $d_i = X_i - Y_i$

$r = 1$ –(-1).

The resulting r value represents:

< 3 low correlation degree

0,3 – 0,5 moderate correlation degree

0,5 – 0,7 important correlation degree

0,7 – 0,9 high correlation degree

$> 0,9$ very high correlation degree

If there is utmost dependence (correlation) between two parameters (in our case between content of two elements), then the r coefficient is equal to value 1. If there is no correlation between two parameters, then the r coefficient is 0. Extreme negative correlation is expressed by $r = -1$.

3. RESULTS

3.1 Characteristics of surface water

The extent of surface water contamination caused by mining activities is relatively well-documented. pH in water of Malachovský brook and of its inflows shows moderately alkaline reaction (pH 6,53 – 7,93; tab. 1). both in dry and in rainy periods. Eh values are a little bit lower during dry season (Eh -20 to -94 mV) in comparison with values measured during rainy period (Eh -16 to -22 mV), so the water in rainy period is moderately more oxidic than during dry weather conditions.

Hg concentrations range between 0 and 403 $\mu g \cdot L^{-1}$. As and Sb concentrations are below detection limit. Hg contents are higher during dry period. In the surroundings of Ortútske Lake, the Hg contents were zero. It is interesting that the highest Hg contents were determined in the samples SW-8S (approximately 200 m above Malachov village) and SW-10S (inside Malachov village: 403 and 278 $\mu g \cdot L^{-1}$) and not in the surroundings of the abandoned mine. Hg concentrations exceeded the recommended value for surface water (1 $\mu g \cdot L^{-1}$) according to the Decree of the Government of the Slovak Republic No. 269/2010 Coll. in the samples SW-1S – SW-4S and SW-8S, SW-10S and SW-9D (the last in rainy period). The Hg content in the sample SW-10 D was at the border of the detection limit).

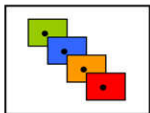


Table 1. pH, Eh values and Hg concentrations in surface water using AA hydride generation

Sample	pH	Eh _(mV)	°C	Hg
				µg·L ⁻¹
	Dry period (S)			
SW-1S	7.91	-92	13.9	111
SW-2S	7.54	-79	11.8	50
SW-3S	7.01	-45	8.9	104
SW-4S	7.10	-52	21.0	210
SW-5S	6.53	-24	11.7	0
SW-6S	7.92	-94	17.9	0
SW-7S	7.75	-20	7.89	0
SW-8S	7.80	-34	8.22	278
SW-9S	7.84	-17	7.09	0.50
SW-10S	7.60	-21	7.93	403
Rainy period (D)				
SW-7D	7.86	-18	6.00	0
SW-8D	7.56	-22	5.11	0.80
SW-9D	7.93	-18	6.52	42
SW-10D	7.11	-16	6.99	1

Note: As and Sb contents were below detection limit

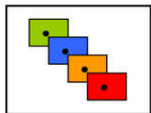
3.2 Groundwater features

pH in samples of groundwater vary from acidic (4.05 – 6.80) to alkaline values (7.52 – 8.21). Alkaline character of water (mainly in the surroundings of Cipkové Jamy locality, samples GW-1 to GW-3) is probably caused by abundant occurrence of dolomites. The most acidic reaction was found in the sample GW-8 (pH 4.05) from Hnedý spring, situated in the woods on the left bank of Malachovský brook (tab. 2). Oxidic Eh values (22 and 147) are only in the samples GW-8 and GW-9 from Hnedý and Žltý springs.

The highest Hg concentrations were ascertained in mine water from Maria gallery at Veľká Studňa – sample GW-4 (0.989 µg·L⁻¹) and in water from Žltý spring – sample GW-9 (0.804 µg·L⁻¹). Zero Hg content in water from spring Grófov Obed (sample GW-6) was expectable because this spring does not drain the ore-field, but the very low Hg contents in outflows from old galleries at territory Ortúty (so-called Cipkové Jamy) with important mining activity in 17. century (samples GW-1 and GW-2) was a surprise.

Table. 2 pH, Eh values and Hg concentrations in groundwater using AA hydride generation

Sample	pH	Eh _(mV)	°C	Hg
				µg·L ⁻¹
GW-1	8.21	-109	11.5	0.001
GW-2	8.42	-120	14.0	0.001
GW-3	7.52	-85	11.5	0.552
GW-4	6.56	-20	28.0	0.989
GW-5	6.51	-24	11.3	0.270
GW-6	6.60	-17	11.1	0
GW-7	6.80	-65	8.2	0.031
GW-8	4.05	147	11.0	0.342
GW-9	6.10	22	17.0	0.804



The Hg contents are, with the exception of single value in sample GW-4 ($0.989 \mu\text{g}\cdot\text{L}^{-1}$), relatively low. They correspond with the recommended values for „*rough water*“ according to Decree of the Ministry of Environmental Protection of the Slovak Republic No. 636/2004 Coll. and respect the law standards for drinking water according to the Government Decree No. 496/2010 Coll. ($1 \mu\text{g}\cdot\text{L}^{-1}$).

The information about As and Sb contents, supplemented with data about content of selected heavy metals, is presented in tab. 3.

Table. 3 Concentrations of selected metals in groundwater

Sample	As	Sb	Fe	Pb	Zn	Cu	Co	Ni	Cd	Mn
	$\mu\text{g}\cdot\text{L}^{-1}$		$\text{mg}\cdot\text{L}^{-1}$							
GW-7	<1	0.92	7.4	3.48	15	2.23	2.1	0.9	0.21	153
GW-8	<1	1.99	8.5	8.38	34	2.70	4.4	0.8	0.15	204
GW-9	1.22	1.11	10.0	0.01	16	3.58	1.2	1.5	0.18	307

Analyses of groundwater (tab. 3) were compared with valid limits of advertisement of Slovak Ministry of Environment No. 636/2004 (tab. 3) and with the ones of Regulation of Government No. 496/2010. The analytical results correspond with the law criterions only in case of As (limit $10 \mu\text{g}\cdot\text{L}^{-1}$) and Sb (limit $5 \mu\text{g}\cdot\text{L}^{-1}$). The metal contents in the rest of the samples exceed the limits for all analysed elements.

The highest exceed of the permitted limits was determined in cases of Mn (limit $0.05 \text{ mg}\cdot\text{L}^{-1}$), Pb (limit $0.02 \text{ mg}\cdot\text{L}^{-1}$), Fe ($0.2 \text{ mg}\cdot\text{L}^{-1}$), Ni ($0.02 \text{ mg}\cdot\text{L}^{-1}$), Zn ($3 \text{ mg}\cdot\text{L}^{-1}$) and Cu ($1 \text{ mg}\cdot\text{L}^{-1}$), and Cd ($0.005 \text{ mg}\cdot\text{L}^{-1}$).

3.3 Contamination of soils

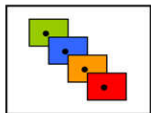
The soil in Malachovský brook valley was classified as cambi-soil (rendzina). The characteristics of rinse and paste pH, of $\text{Eh}_{(\text{H}_2\text{O})}$ and $\text{Eh}_{(\text{KCl})}$ as well as of $r\text{H}_2$ factor in soil samples is presented in tab. 4.

Tab. 4 pH, Eh and $r\text{H}_2$ values in soil samples

Sample	pH	Eh _(mV)	pH	Eh _(mV)	rH ₂
	H ₂ O		1M KCl		
SO-1	6.81	5	7.02	21	14.74
SO-2	3.74	-10	6.98	-4	12.83
SO-3A	7.05	-47	6.90	-30	12.80
SO-3B	7.44	-64	7.42	-63	12.74
SO-4	7.01	-42	6.91	-32	12.75
SO-5	7.39	-72	6.58	-23	12.39
SO-6A	6.22	4	5.37	51	12.44
SO-6B	6.99	-54	6.55	-20	12.40
SO-7	7.30	-66	6.43	-11	12.49
SO-8	7.44	-71	6.54	-22	12.31
SO-9A	6.20	4	5.62	51	12.94
SO-9B	7.11	-52	6.62	-25	12.49
SO-10A	7.50	-73	6.99	-45	12.48

Rinse $\text{pH}_{(\text{H}_2\text{O})}$ widely ranges from 3.74 to 7.50 (tab. 4). Both extreme values were determined in samples from Cipkové Jamy mining locality. If these extreme values are excluded, the $\text{pH}_{(\text{H}_2\text{O})}$ qualifies the soil sensu Čurlík & Šefčík (1999) as extremely acid to moderately alkaline soil.

As the pH of soil solution is higher during the rainy periods, it is more appropriate to measure paste pH in soil solutions (e.g. 0.01M CaCO_3 or 0.1M KCl), which also reflects, with the exception of free H^+ and OH^- ions, contents of H^+



and Al^{3+} ions adsorbed by soil colloidal complex (Čurlík & Šefčík, 1999). The paste pH in samples from Malachov varies from 5.37 to 7.42.

The rH_2 factor (sensu Richter and Hlůšek, 2003) was calculated as it follows: $rH_2 = Eh/30 + 2pH$, and it ranges from 12.31 to 14.74 (tab. 4). It means that the soils are medium aerated.

Tab. 5 ICP-MS analyses of soil samples

Sample	Fe	Mg	Hg	Pb	Zn	Cu	Ni	Co	Cr	Mn	As	Sb
	%		$mg \cdot kg^{-1}$								$\mu g \cdot kg^{-1}$	
SO-1	0.78	5.14	0.90								2.72	0.42
SO-2	1.33	4.18	2.10								1.10	0.43
SO-3A	2.12	5.21	2.11								0.60	0.42
SO-3B	0.98	5.14	3.05								0.56	0.49
SO-4	2.73	6.77	0.79								2.64	0.39
SO-5	1.18	4.32	1.88	48	50	10	14	15	40	941	1.02	0.42
SO-6A	0.90	6.92	20.02	121	64	12	7	6	16	325	35.28	17.02
SO-6B	0.55	11.02	5.96	32	33	7	4	4	11	231	24.11	11.00
SO-7	3.10	4.23	6.40	22	51	14	17	15	39	955	38.57	5.23
SO-8	3.79	4.50	2.52	15	71	10	10	13	21	903	9.67	3.12
SO-9A	2.43	2.44	16.03	50	65	12	16	12	33	690	42.33	7.40
SO-9B	2.33	3.10	15.52	34	53	12	12	9	25	589	38.72	7.35
SO-10A	3.13	3.89	33.14	46	105	20	15	16	45	749	16.23	8.12

Fe, Mg, Pb, Zn, Cu, Ni, Co, Cr and Mn contents do not show any extreme value. Hg contents are also relatively low. They vary from 0.79 to 33.14 $mg \cdot kg^{-1}$. The highest Hg, As and Sb contents were found in soil samples from the territory of abandoned mines at Cipkové Jamy (SO-6 and SO-10A). In comparison with Hg, the As contents are lower (0.56 – 42.33 $\mu g \cdot kg^{-1}$). The Sb contents are correlated with Hg and As ones (0.42 – 11.00 $\mu g \cdot kg^{-1}$; tab. 5).

Soil samples show overstep in the Hg content limits given by the Slovak law No. 220/2004 Z. z. about protection of agricultural soil for sandy-clay and clay soil (0.5 $mg \cdot kg^{-1}$ Hg) in all analysed samples. Also Pb contents exceed the limit (25 $mg \cdot kg^{-1}$) in several samples. The Co limit (15 $mg \cdot kg^{-1}$) is exceeded in three samples and the As limit (10 $mg \cdot kg^{-1}$) in half of samples. The law No. 220/2004 Z. z. does not contain any limit for Sb.

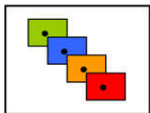
3.4 Contamination of dump sediments

Rinse $pH_{(H_2O)}$ of dump sediments locally shows (samples TS-1 and TS-3) relatively high degree of acidity, and it is possible if we consider the sulphide minerals degradation as anticipated in spite of the fact that the Eh values (-33 až -87; tab. 6) indicate only moderately oxidic conditions. Rinse pH varies in range 3.69 – 7.69 and the paste pH in the interval 3.55 – 7.68.

Tab. 6 pH and Eh values in soil samples

Sample	pH	Eh _(mV)	pH	Eh _(mV)
	H ₂ O		1M KCl	
TS-1	3.69	-43	3.55	-33
TS-2	6.19	-52	6.00	-47
TS-3	5.51	-33	5.43	-28
TS-4	7.69	-87	7.68	-86

Relatively high Hg contents (2.3 – 411.3 $mg \cdot kg^{-1}$) were determined in samples from the dump-field of Hg-mine Veľká Studňa. The As (0.55 – 10.03 $mg \cdot kg^{-1}$) and Sb (0.34 – 3 $mg \cdot kg^{-1}$; tab. 7) contents also reflect this situation.



Tab. 7 ICP-MS analyses of dump sediments

Sample	Fe	Mg	Hg	As	Sb
	%		mg·kg ⁻¹		
TS-1	0.90	10.20	411.3	2.85	0.47
TS-2	0.87	9.89	9.1	0.65	0.34
TS-3	0.65	9.99	2.3	0.55	0.41
TS-4	0.72	12.01	44.25	10.03	3.00

On the other hand, the contents of the other metals (tab. 7, continuation) show no anomalous values.

Tab. 7 (continuation) ICP-MS analyses
of dump sediments

Sample	Cu	Pb	Zn	Ni	Co	Cr	Mn
	mg·kg ⁻¹						
TS-1	33	12	17	6	3	13	120
TS-2	17	7	15	5	2	11	110
TS-3	21	6	20	7	4	10	100
TS-4	15	8	18	7	3	12	160

If we compare the data from the dump sediments with soil data, all samples exceed the limit for Hg (0.15 mg·kg⁻¹) and one sample (TS-4) also exceeds the limit for As (10 mg·kg⁻¹).

3.5 Characteristics of stream sediments

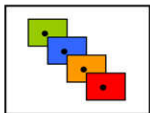
ICP-MS analytical data about the chemical character of stream sediments are presented in tab. 8.

The Hg contents in stream sediments are relatively high. They vary from 1.59 to 11.73. There is no gradual decrease in contents with respect to the distance from the deposit (fig. 1 and tab. 8).

Tab. 8 ICP-MS analyses of stream sediments

Sample	Fe	Ca	Mg	P	Hg	As	Sb	Cu	Pb	Zn	Mn
	%				mg·kg ⁻¹						
SS-1	4.10	3.88	2.47	0.057	1.71	14	1.9	12.3	17.9	92	990
SS-2	4.72	4.26	3.44	0.039	1.59	14	3.4	12.5	13.4	97	1197
SS-3	3.67	5.38	3.51	0.052	11.73	13	14.2	13.3	17.0	82	937
SS-4	2.10	13.34	6.75	0.029	4.34	49	4.0	11.3	12.5	33	407
SS-5	4.33	6.28	3.67	0.045	10.10	9	1.7	11.0	13.9	67	953
SS-6	4.11	6.25	4.22	0.044	2.63	10	4.3	17.3	15.4	79	975
SS-7	3.55	3.86	2.36	0.064	11.14	8	4.0	20.9	24.6	91	987
SS-8	4.12	5.12	3.76	0.057	2.36	7	2.0	10.4	13.0	76	921
SS-9	5.73	7.44	1.32	0.039	0.54	5	3.0	16.9	28.0	99	1335

The As contents are usually higher than Sb ones. Similarly, Cu, Pb and Zn contents exceed first tens of mg·kg⁻¹. Alike also the U and Th contents are low.



Tab. 8 (continuation) ICP-MS analyses of stream sediments

Sample	As	Sb	Cu	Pb	Zn	Mn	Cr	Cd	Ni	Co	U	Th
	mg·kg ⁻¹											
SS-1	14	1.9	12.3	17.9	92	990	26	<0.01	12.2	14.3	1.8	5.6
SS-2	14	3.4	12.5	13.4	97	1197	31	<0.01	17.3	19.1	1.2	4.3
SS-3	13	14.2	13.3	17.0	82	937	25	0.5	10.2	14.0	1.6	4.5
SS-4	49	4.0	11.3	12.5	33	407	18	0.2	9.4	7.3	1.1	3.3
SS-5	9	1.7	11.0	13.9	67	953	23	0.2	11.8	18.2	1.5	4.8
SS-6	10	4.3	17.3	15.4	79	975	21	0.2	7.3	15.4	1.6	4.6
SS-7	8	4.0	20.9	24.6	91	987	28	0.6	11.8	14.3	2.2	5.4
SS-8	7	2.0	10.4	13.0	76	921	21	<0.01	8.1	15.7	1.0	3.2
SS-9	5	3.0	16.9	28.0	99	1335	19	<0.01	8.0	22.9	2.4	4.0

3.6 Correlation of selected elements in soil and dump sediment

Correlation coefficients r of Hg vs. As and Sb, As vs. Sb respectively as well as of Hg vs. Fe in soil and in dump sediments are presented in tab 9.

Tab. 9 Correlation coefficients of element couples

Soil		Dump sediment	
Correlated elements	r	Correlated elements	r
Hg/As	0.565	Hg/As	-0.008
Hg/Sb	0.692	Hg/Sb	-0.212
As/Sb	0.762	As/Sb	0.979
Hg/Fe	0.236	Hg/Fe	0.634

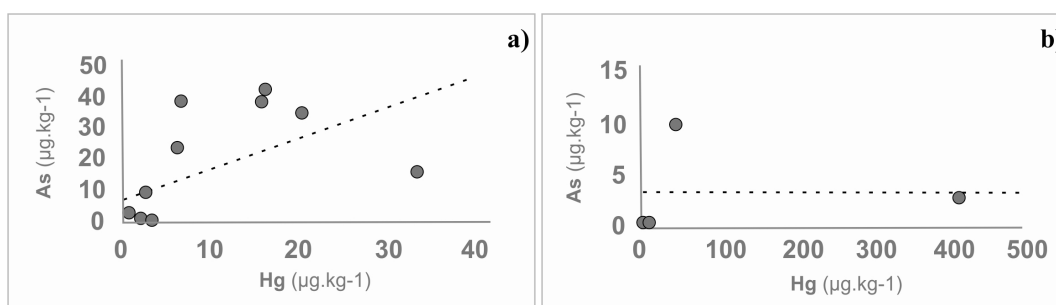


Figure 2. Hg/As correlation a) in soil samples; b) in dump sediments

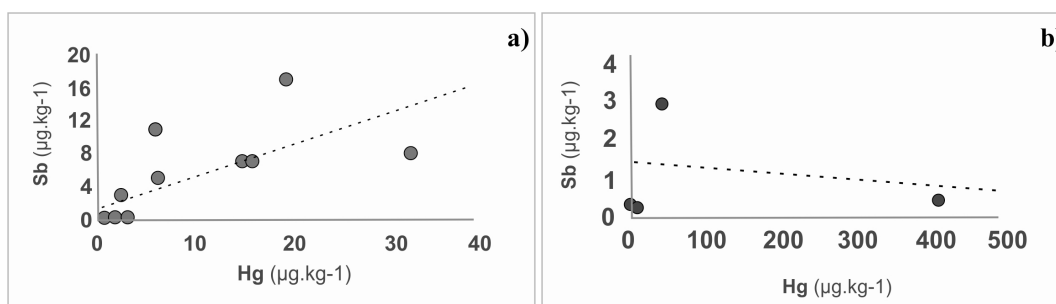
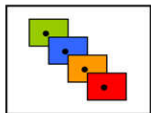


Figure 3. Hg/Sb correlation a) in soil samples; b) in dump sediments



As it is shown on correlation graphs (fig. 2), the correlation degree Hg vs. As substantially differs in soils with respect to dump sediments. The correlation coefficient r in soils is relatively high (0.565). The correlation degree in dump sediments is low ($r = -0.008$) and indicates low, indirect (negative) correlation. The difference in Hg-As couple relationship is caused by their geochemical behaviour. In soils, the content of the studied metal couple is a consequence of their distribution depending on the cations sorption on various sorbents (mainly on mould and clay minerals). This behaviour causes that the metals which are in dump sediments, bounded in different minerals (and thus at separate places), migrate after primary minerals degradation into ionic form until they are together sorbed on the same sorbents.

Actually the same, but more expressive dependence is possible to see also in case of Hg vs. Sb couple (fig. 3, tab. 9).

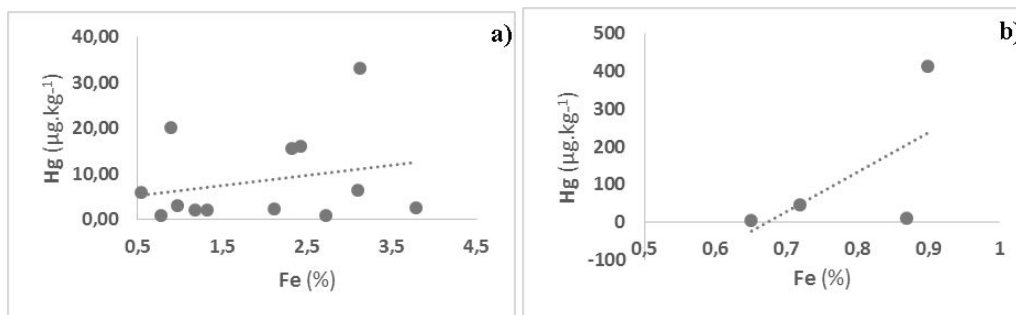


Figure 4. Hg/Fe correlation a) in soil samples;
b) in dump sediments

The Hg/Fe and As/Sb correlations in soil and in dump sediments are shown by the graphs on fig. 4 and 5. These correlations differ from Hg/As ones. In both cases (fig. 5a,b), the correlation is positive. Correlation coefficients Hg/Fe $r = 0.236$ and $r = 0.634$ reflect low degree and important degree of correlation. However, Hg does not enter to the Fe minerals and, at the same time, it forms mineral assemblages with Fe-containing minerals. This situation enables certain, although not very strong, degree of Hg/Fe correlation in dump sediments of the dump-field at Veľká Studňa locality. This (not very important) correlation degree is emphasized after common sorption of Hg and Fe into the soil sorption complex.

As vs. Sb correlation shows high ($r = 0.762$) and very high correlation degree ($r = 0.979$), even higher as in case of correlation between Hg vs. Fe couple. This high correlation reflects that As and Sb are predominantly bonded in the same minerals: arsenopyrite (FeAsS), orpiment (As_2S_3), arsenolite (As_2O_3) and realgar (As_4S_4), which very often contain, according to Andráš et al. (1995), Andráš & Chovan (2005) and Douglass et al. (1992), high Sb concentrations. Common As and Sb sorption on clay minerals and their incorporation into soil complex even accentuate the feature of their high natural correlation.

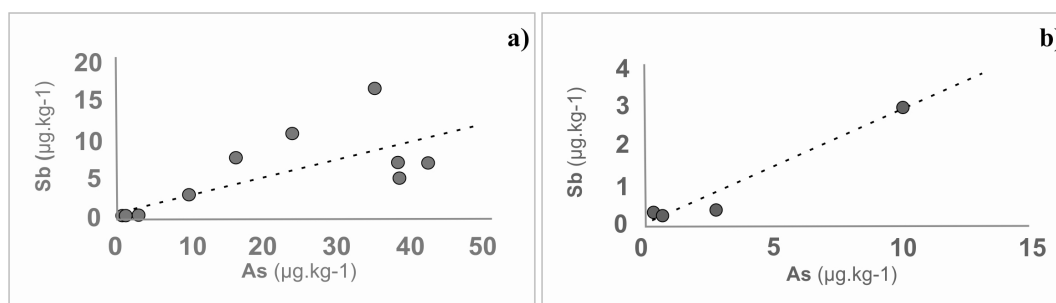


Figure 5. As/Sb correlation a) in soil samples; b) in dump sediments

3.7 Mercury speciation

Mercury forms many species. Some of them are stable complex ions. The different oxidation states of Hg-ions cause its variable solubility and toxicity. Tables 1, 2, 4 and 6 were used to construct the stability-field plots (figs. 6 - 10), which show the forms of Hg in solid as well as in liquid media according to conditions of pH and Eh.

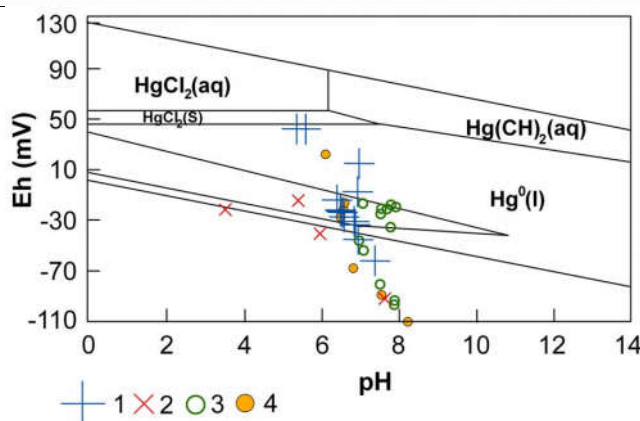
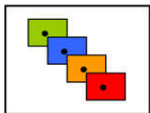


Figure 6. Stability fields for solid and liquid species of Hg using pH/Eh plot according to Davis et al. (1997)
Explanations to figs. 6 – 10: 1 – soil, 2 – dump sediment, 3 – surface water, 4 – groundwater

Surface water samples with high Hg content ($>100 \mu\text{g}\cdot\text{kg}^{-1}$ Hg) as well as the substantial part of the groundwater samples are situated in the stability field of cinnabarite (HgS) on the pH/Eh graph published by Davis et al. (1997; fig. 6). Also the main part of solid samples (soil and dump sediments) is concentrated in the same stability field or in the field of Hg^0 . No indication of methyl-forms was proved. Comparable results were obtained by application of pH/Eh plot according to Arbertain et al. (2009; fig. 7).

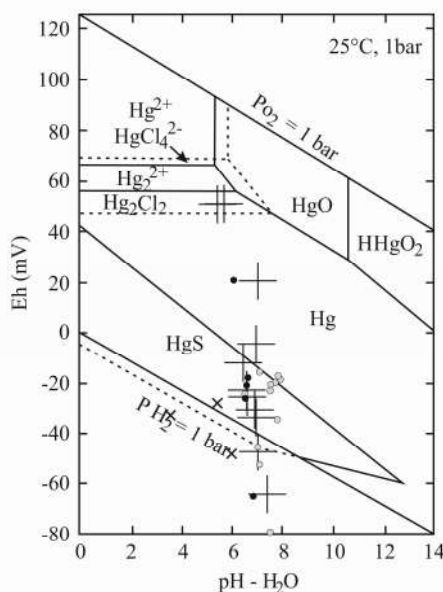
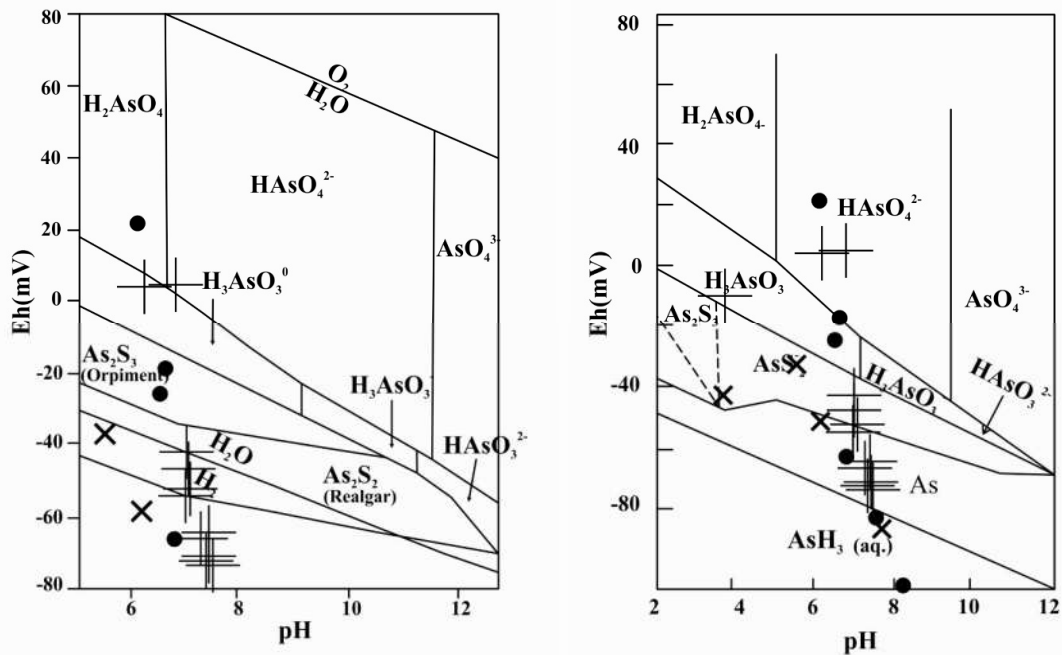
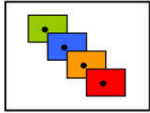


Figure 7 Stability fields for solid and liquid species of Hg using pH/Eh plot according to Arbertain et al. (2009)

3.8 Arsenic and antimony speciation

Eh-pH stability diagrams according to Ryu et al. (2002) and Ferguson & Gavis (1972) show in dump sediments and in soil samples presence of very toxic As^{3+} in the form of H_3AsO_3 , AsS_2^- , AsH_3 ions (figs. 8 and 9) and, only in one single case in speciation, of less toxic As^{5+} in the form of HAsO_4^{2-} (fig. 9). Unfortunately, great part of the samples fall out of the pH/Eh graph, as it was published by Ryu et al. (2002).

As and Sb concentrations in surface water are below the detection limit.



Figures 8 and 9. Eh/pH stability diagrams for As-H₂O-S system according to Ryu et al. (2002) and Ferguson & Gavis (1972)

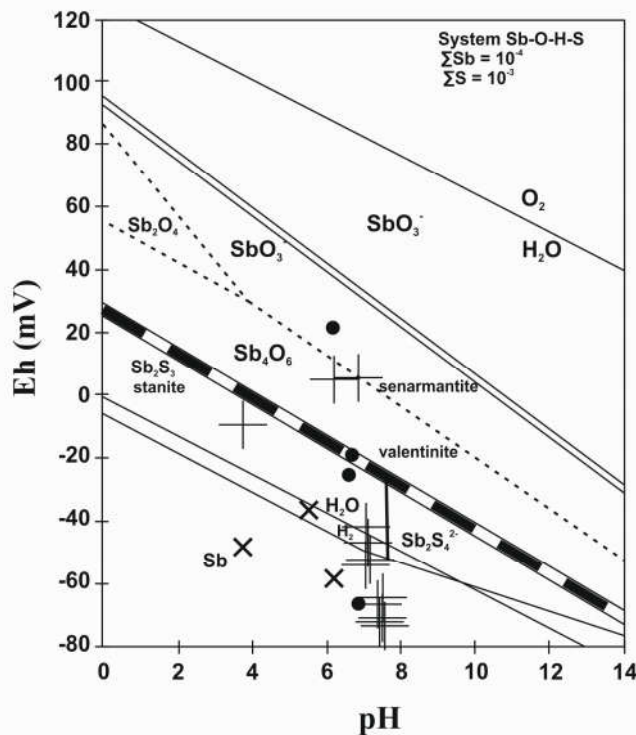
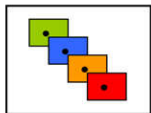


Figure 10. Stability diagram for Sb-O-H-S system using pH/Eh plot according to Vink (1996)

At the same way both As, and Sb are mobile elements in supergenic oxidic conditions according to Vink (1996). Application of pH/Eh diagram (Vink, 1996) allows to state that Sb is predominantly present, both in the soil and in dump sediments in Malachov, in the form of elementary Sb⁰, eventually in oxidation stage Sb³⁺ in the forms Sb₂O₃, Sb₂S₃ and Sb₂S₄²⁻ (fig. 10). The Sb speciation in groundwater confirmed occurrence of both forms: less toxic Sb⁵⁺ (SbO₃⁻) and also more toxic anion Sb³⁺ (Sb₂S₄²⁻, fig. 10).



4. DISCUSSION

In the Malachov ore field area, mercury is predominantly present in the form of sulphidic mineral cinnabarite (HgS). This mineral shows respectable stability in supergenic conditions, so the velocity of its weathering process is relatively low (Hickel & Pecora, 1970). This feature causes that cinnabarite at Malachov ore field area preferentially accumulated in dump sediments and in stream sediments. Similar situation is also at Merník cinnabarite and metacinnabarite deposit (Hančulák et al., 2006). Cinnabarite degradation and the next Hg mobilization to the surrounding area is limited (Navarro, 2008). Consequently, both surface water and groundwater usually contain low Hg contents (Davis et al., 1997). Hickel & Pecora (1970) published that the Hg content in surface water is generally less than 0.1 ppb. At Malachov deposit, the As and Sb contents are also low in water. The risk because of Hg toxicity only increases in areas where Hg is incorporated to metallo-organic complexes (methyl-mercury), which have received recent attention as potential water pollutants and biologic toxins (Langford & Ferner, 1999). The presence of this very toxic Hg-form at Malachov was not described yet but it could be found e.g. in fish entrails (livers, kidneys, spleens) or in benthos (Kuwabara et al., 2007).

Toxicity of As and Sb at Slovak deposits was studied e.g. by Franková et al. (2012) and Buccheri et al. (2013). The problem is discussed also by Kempa et al. (2013) and Marschalko et al. (2012b). The As and Sb contents at Malachov district are not very high but both As and Sb are in many cases represented by very toxic inorganic three-valent forms of these elements. This finding differs from the ones described at near (only several km of distance) Cu-Ag deposits Staré Hory and Ľubietová (Buccheri et al., 2013; Nagyová et al., 2013).

5. CONCLUSIONS

In the substantial part of soil and stream sediment samples as well as in water samples, Hg seems to be present in cinnabarite (HgS) form or as elementary Hg⁰. No indication of methyl-mercury formation was found. Both groundwater and surface water show moderately alkaline reaction. The Hg contents in water are only locally increased. The highest Hg contents were described in the surroundings of Veľká Studňa mine (actually in mine water from Mária gallery outflow 0.989 µg·L⁻¹). The Hg contents in water do not exceed the permitted law limits.

The soil reaction is close to neutral. The highest Hg, As, Sb and several heavy metal contents are in the area of abandoned old Hg mines Cipkové Jamy. High Hg contents are also proved at the dump-field of Veľká Studňa mine (411.3 mg·kg⁻¹). These metal contents in solid samples exceed the permitted limits of the Slovak Republic law.

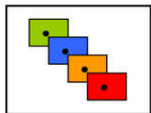
Stream sediments in the whole studied area contain lot of cinnabarite but the amount of the cinnabarite is not in correlation with the distance from the deposit.

There are differences in the Hg/As, Hg/Sb and As/Sb correlations between soil and technogenic samples. They reflect mineralogical conditions as well as the sorption mechanism of natural sorbents (e.g. clay minerals).

The speciation of Hg confirmed that, both in water and in solid samples, it is mainly present in the form of cinnabarite and, less, also of elementary Hg⁰. The As and Sb speciation mostly proved, both in water and in solid samples, presence of the very toxic three-valent forms of arsenic and antimony.

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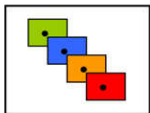


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