HEAVY METAL CONTAMINATION OF LANDSCAPE COMPONETS IN SURROUNDINGS OF CLOSED MERCURY DEPOSIT IN MALACHOV (SLOVAKIA)

KONTAMINCE KRAJINNÝCH SLOŽEK TĚŽKÝMI KOVY V OKOLÍ UZAVŘENÉHO DOLU NA RTUŤ V MALACHOVĚ (SLOVENSKO)

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Abstract

The present study investigates mercury contamination of soil, groundwater, surface water, vegetation and food commodities (fruit, vegetable, mushroom, and fish) close to the abandoned Hg deposit in Malachov, Central Slovakia. The soil was classified as cambi-soil (rendzina). Maximum concentrations of Hg (44.24 ppm) were found in the soil from the area nearby old mining activities in the Veľká Studňa locality. In the groundwater, 0.84 µg.L^{-1}, and in the surface water, even 394 µg.L^{-1} of Hg content was found. Also plant tissues and mushrooms are Hg-contaminated (in the root of *Salix fragilis*, the Hg content was 22 mg.kg^{-1}). The Hg concentration decreases in general in the following order: root, branch/stem, and leaf/needle. In the food commodities, the Hg content does not exceed the Slovak law limits. The Hg content in trout muscle (from the local Malachovský brook) is 252 µg.kg^{-1} and in liver 402 µg.kg^{-1}.

The calculation of an AMD formation potential (neutralisation potential, total acidity production, net neutralisation potential) is discussed as well. The value of the total acidity production potential (sensu Sobek et al., 1978) is low (1.562 – 3.125; with exception of a single sample, in which it increased to 9.375). On the other hand, the abundant presence of dolomite rocks causes a high neutralization potential value (up to 812.84). This result suggests that the assumption of the AMD production is excluded and the environmental risk from this viewpoint might be neglected.

Abstrakt

Kontaminace půdy, podzemních a povrchových vod, vegetace a potravin (ovoce, zelenina, houby, ryby) rtutí v okolí uzavřeného dolu Malachov na středním Slovensku byla zkoumána v této studii. Půdní typ byl klasifikován jako kambizem (rendzina). Maximální koncentrace rtuti (44,24 mg.kg^{-1}) byly zjištěny v půdě poblíž starých hornických aktivit na lokalitě Veľká Studňa. Koncentrace rtuti v podzemních vodách je 0,84 µg.L^{-1} a v povrchových vodách byla popsána koncentrace až 394 µg.L^{-1}. Rovněž tkáně rostlin a houby jsou rtutí kontaminovány (v kořenech *Salix fragilis* byl stanoven obsah Hg 22 mg.kg^{-1}). Koncentrace Hg obecně klesá

v pořadí: kořen - větve/stonek - listy/jehlice. Obsah rtuti v potravinách nepřekročil limity dané slovenskou legislativou. Obsah rtuti ve svalovině pstruhů (z místního Malachovského potoka) činil 252 µg.kg^{-1} a v játrech 402 µg.kg^{-1}.

Také výpočet potenciálu tvorby AMD (neutralizační potenciál, celková tvorba acidity, čistý neutralizační potenciál) je diskutován. Hodnota celkového potenciálu tvorby acidity (sensu Sobek et al., 1978) je nízká (1,562 - 3,125; s výjimkou jednoho vzorku, kde byl zaznamenán nárůst na 9,375). Na druhé straně bohaté zastoupení dolomitických hornin vykazuje vysoký neutralizační potenciál (až do 812,84). Tento výsledek naznačuje, že předpoklad produkce AMD je vyloučen a tudíž riziko pro životní prostředí je z tohoto hlediska zanedbatelné.

Key words: mercury, soil, groundwater, surface water, plant, food, speciation

1 INTRODUCTION

The eastern slopes of the Kremnica Mts. are built by effusive and extrusive rocks of Neogene volcanism. In consequence of denudation, in surroundings of Malachov, older Mesozoic carbonates (limestones and dolomites) and sand-silt series of Paleogene period are uncovered. Hg mineralization is connected with young structures in the N-S to NE-SW directions and is genetically related to the post-volcanic stage of a 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).

The Hg-As mineralization at the Malachov deposit is situated in the Eastern rim of the Kremnica Mts., west from Banská Bystrica. Numerous occurrences and anomalies are concentrated on an area of 80 – 100 km^2: Veľká Studňa, Nemecký Hill, Dolná Cliff, Trávny Ždiar, Mútne, Ortuťový Hill, Cipkove Jamy, Pri Jazere etc. (Koděra et al., 1990; Jeleň et al., 2010). The main mineral assemblages of Hg ores in the Malachov ore field are cinnabar – HgS and metacinnabar. Arsenopyrite – FeAsS, pyrite – FeS$_2$, marcasite – FeS$_2$, auripigment – As$_2$S$_3$, realgar – As$_4$S$_4$ and arsenolite – As$_2$O$_3$ are less frequent minerals. In the gangue mineral assemblage, various modifications of SiO$_2$: quartz, chalcedony, opal and carbonates: calcite – CaCO$_3$ and dolomite – CaMg(CO$_3$)$_2$ and gypsum – CaSO$_4$.2H$_2$O prevail(Koděra et al., 1990).

In the past, cinnabar veins were exploited in galleries and voluminous accumulations of ore 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 found in Paleogene conglomerates, sandstones and Mesozoic carbonates, rarely also in Miocene volcanites. The Hg-As mineralization is connected to faults in the N-S direction (Ivančík & Mitáček, 1986).

Montaneous forms of the country relief were created by long-term mining activities, mainly from the 14th to the 17th centuries and have been being noticeably visible until present times in the localities of Pri Jazere, Ortúty and Veľká Studňa. The last exploitation was realised from 1980 to 1990 in the locality of Veľká Studňa (Ivančík & Mitáček, 1986). The deposit has been closed since 1990 (Bancík & Jeleň, 1999).

2 EXPERIMENTAL PART

In the surroundings of Malachov, 11 soil and sediment samples (OP-1 to OP-8B) were collected during 2012 (Fig. 1). In several cases, the sampling was realised both from A and B horizons to have a possibility to compare the heavy metal contents in separate horizons and receive the data about the preferential bonding of metals to selective soil components.

The soil samples for the Mg, Ti, Co, Ni, As, Sb, Mn, Rb, Sr, V, Ba, Cr, Zr, S determination were melted with a Li-metaborate and Li-tetraborate mixture, and consecutively dissolved in diluted nitric acid. In order to determine Fe, Pb, Zn and Cu contents, 0.5 g of a sample was lixiviated by aqua regia. The determination of individual elements was realised by an ICP–MS analysis at the ACME Analytical Laboratories Vancouver Ltd. in Canada. The presented data represent an average value calculated from four parallel determinations.
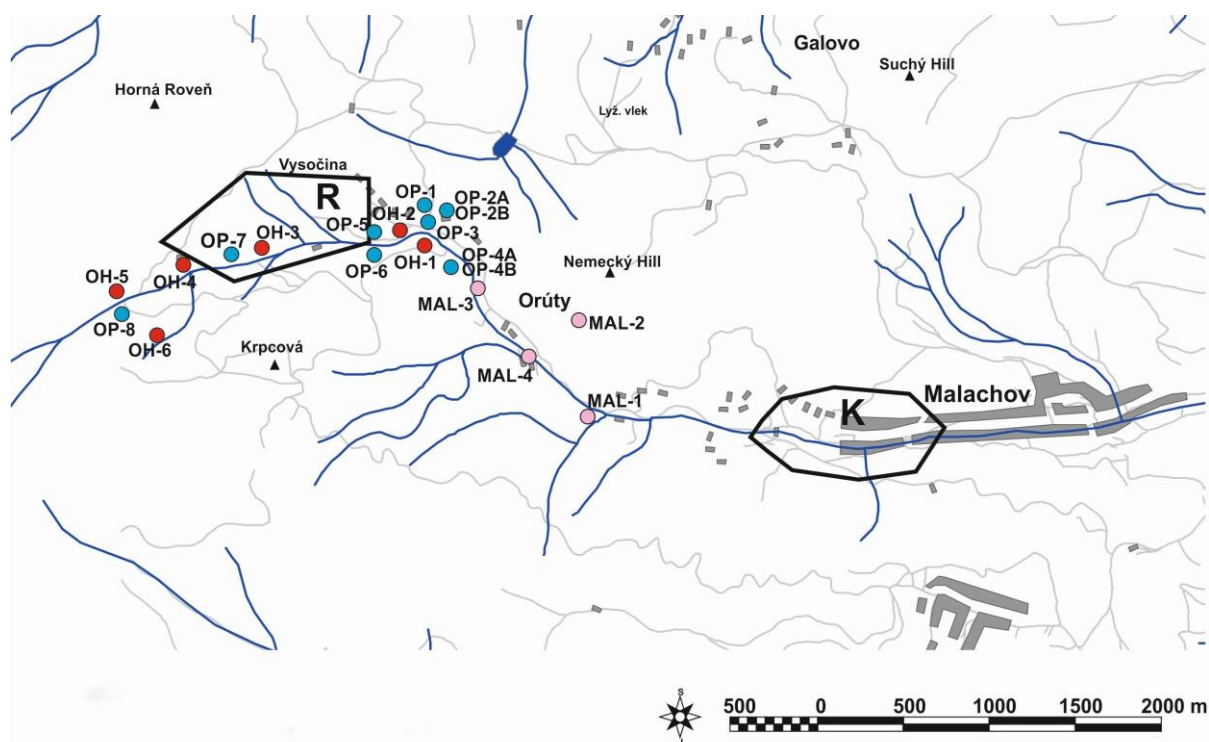
Fig. 1 Map of soil, water and plant samples localization
Explanations: OP – soil and sediment samples, MAL – groundwater, 0H – surface water;
R – area of plant sampling, K – area of food commodities sampling

The groundwater sample set was taken from the Žltý spring on the Malachov brook bank (MAL-1), from the Hnedý spring on the Nemecký Hill slope (MAL-2), from mining water at Cipkové Jamy (Krvavá spring, sample MAL-3) and from the Turistický spring (MAL-4). In addition, a set of 8 surface water samples from the Malachov brook were collected. Both the groundwater and surface water samples of a 1000mL volume were stabilized by 10 mL of concentrated HCl. The water samples were analysed using a flame atom absorption analysis with a hydride system in the National Water Reference Laboratory in Slovakia at the Water Research Institute in Bratislava.

The plant samples were divided into roots, branches/stems, and leaves/needles and dried at a laboratory temperature. 0.5 g of a vegetation sample was after split digestion in concentrated HNO_3 and then in aqua regia analysed by ICP-MS for ultralow detection limits in the same laboratory as soils.

Also two fishes from the Malachov brook, vegetable and fruit samples were subject the flame atom absorption analysis in a laboratory of the Regional Institute of Public Health in Banská Bystrica. The localization of sampling sites is presented on the attached map (Fig. 1).

The Hg content in soil, plant and fish samples were determined by a thermomechanical analysis using the device AMA 254, KEI, at the Faculty of Environmental Engineering of the Technical University in Zvolen (Ing. Emília Hroncová, PhD).

Paste and rinse pH (as well as Eh) was determined in soils in a suspension of a 20g sample and 50 mL of distilled water or 1 M KCl, respectively, according to the method described by VanReeuwijka (1995) using the pH meter WTW Multi 3420 with the combined redox-electrode SenTix ORP and with a reference system Ag/AgCl containing 3 M KCl electrolyte. Also the pH and Eh values in groundwater and surface water were measured by the same pH meter.

To calculate the acidity production potential (AP) and the neutralization potential (NP), the Eh and pH values of soil and sediments, as well as the sulphur and carbon contents, must be determined. For the acidification risk calculation, the method was used which was published in the Acid Mine Drainage Prediction EPA530-R-94-036 (1994) and adapted by Lintnerová and Majerčík (2005).

The total carbon ($C_{tot.}$), organic carbon ($C_{org.}$) and inorganic carbon ($C_{inorg.}$) contents in the sediments were IR analysed using the furnace Ströhlein C-MAT 4000 in laboratories of the Geological Institute of the Slovak

Academy of Sciences (Alžbeta Svitáčová). A static test of the total acid potential was realized according to Sobek et al. (1978).

The acidification risk was calculated according to the method published by Sobek et al. (1978).

The neutralisation potential in soil samples was determined by titration to pH 3.5 using hydrochloric acid, and the obtained value was recalculated to $CaCO_3$ kg.t^{-1} in laboratories of the Geological Institute of the Slovak Academy of Sciences in Banská Bystrica.

2 RESULTS

2.1 Heavy metals distribution in soil

Tab. 1 Paste and rinse pH/Eh and soil analyses

Sample	pH	Eh (mV)	pH	Eh (mV)	Fe	Mg	Zn	Hg	Cu	Pb
	H$_2$O		1M KCl		%		mg.kg^{-1}			
OP-1	6.93	-43	6.80	-36	3.05	4.17	50	6.31	12	21
OP-2A	7.04	-52	6.81	-35	0.89	6.85	64	19.32	11	117
OP-2B	7.34	-60	7.31	-65	0.53	10.09	30	6.00	6	29
OP-3	7.42	-69	6.60	-21	3.80	4.38	73	2.49	8	12
OP-4A	6.18	2	5.54	46	2.37	2.36	67	15.95	11	48
OP-4B	7.02	-49	6.57	-22	2.27	3.06	54	15.51	11	35
OP-5	7.26	-62	6.35	-7	4.10	3.73	75	2.36	10	12
OP-6A	7.43	-70	6.95	-45	3.03	3.76	102	32.13	22	44
OP-7	7.75	-85	7.70	-84	0.70	11.37	17	44.24	15	7
OP-8A	6.11	9	5.71	36	5.73	2.48	108	0.56	17	27
OP-8B	6.93	-43	6.80	-36	3.92	1.30	92	0.43	10	33

Tab. 1 (Continuation) paste and rinse pH/Eh and soil analyses

Sample	Zn	Ni	Co	Cr	As	Sb	Mn	V	Sr	Zr	Ba	Ti
	mg.kg^{-1}											
OP-1	50	15	14	38	37	4	937	89	111	53.6	170	2770
OP-2A	64	6	5	17	33	16	300	23	80	18.8	82	810
OP-2B	30	3	3	12	23	13	222	11	82	10.4	48	480
OP-3	73	8	15	20	8	2	894	87	161	75.7	312	3150
OP-4A	67	15	11	32	42	6	686	60	86	45.8	173	2370
OP-4B	54	13	10	27	38	6	601	61	98	43.7	171	2380
OP-5	75	8	15	21	7	2	921	88	167	78.4	316	3360
OP-6A	102	14	14	47	16	7	756	70	100	57.1	226	3070
OP-7	17	7	2	11	10	3	156	14	78	9.7	51	530
OP-8A	108	6	23	19	4	3	1332	142	220	125.4	412	5720
OP-8B	92	8	15	20	6	2	2741	73	227	104.6	426	3800

The Hg contents in soil (Tab. 1) vary from 0.56 to 44.24 ppm. The highest content was found from a dump material (sample OP-7), and the lowest in the stream sediment sample OP-8. The Hg contents in stream sediments are lower as those from soils. An amazingly low Hg (6.314 mg.kg^{-1}) content is in stream sediments, mainly in the sample OP-5 from the Malachov brook. The A soil horizon seems to be Hg enriched.

In the soil and stream sediment samples from Malachov surroundings, high Fe contents (0.53 – 5.73 %; Tab. 1) were determined; in average – 2.81 %. Next abundant metals are: Mg (1.30 – 11.37 %), Mn (156 – 2741 mg.kg^{-1}) and Pb (6.9 – 117.0 mg.kg^{-1}). Also Sr (78 – 227 mg.kg^{-1}), Ba (51 – 426 mg.kg^{-1}), and Zr (9.7 – 125.4 mg.kg^{-1}) contents are relatively high. Cu, Zn, Co, Cr, V, As, Sb and Ti are present only in several tens of mg.kg^{-1} (Tab. 1).

2.2 Heavy metal contamination of water

The groundwater analyses (Tab. 2) showed that the samples MAL-1 and MAL-2, of so called „*rough water*", respect the law standards for drinking water (sensu SR Government Decree No. 354/2006 Coll. on drinking water) from a viewpoint of selected analysed elements with exception of Fe. The Eh value 140 in the sample MAL-2 indicates toxic conditions. The Fe and Mn contents are higher than the recommended values for „*raugh water*" (according to Decree of the Ministry of Environmental Protection of the Slovak Republic No. 496/2010 Coll.). On the other hand, the Hg contents in the water samples MAL-3 and MAL-4 respect the regulations.

Tab. 2 Heavy metal concentrations in groundwater

Sample	pH_{H2O}	Eh_{H2O}	°C	Fe	Hg	As	Sb	Mn	Pb	Cd	Cu	Co	Ni	Zn
				$mg.L^{-1}$	$\mu g.L^{-1}$									
MAL-1	6,15	19	16.6	9.95	0.84	1.16	1.07	282	7	0.2	3.6	1.0	1.5	15
MAL-2	3.90	140	10.8	8.45	0.32	<1	2.04	185	5	0.1	2.6	4.2	<1	32
MAL-3	6.80	24	9.4	8.12	0.53	1.02	2.03	150	6	0.1	2.5	3.1	<1	15
MAL-4	5.12	40	12.0	7.33	0.24	0.98	0.99	144	3	0.2	2.2	2.0	<1	16

The heavy metal contents in surface water are presented in Tab. 3. The water pH is close to a value of 7 and is slightly alkaline (pH up to 7.87). The As concentrations were below the detection limit ($0.01 \mu g.L^{-1}$).

Tab. 3 Heavy metal concentrations in surface water (Malachov brook)

Sample	pH_{H2O}	Eh(mV) H2O	pH_{KCl}	Eh(mV) KCl	°C	Hg	As
						$\mu g.L^{-1}$	
OH – 1	7.82	-86	7.26	-76	14.5	n.d	n.d.
OH – 2	7.68	-80	7.15	-70	11.0	<2	n.d.
OH – 3	6.99	-46	6.45	-32	7.9	394	<0.01
OH – 4	7.02	-50	6.89	-41	19.5	265	<0.01
OH – 5	6.71	-29	6.60	-16	11.2	<2	n.d
OH – 6	7.87	-88	7.54	-80	18,3	40	n.d

The Hg concentrations in water of the Malachov brook exceed the standard for Hg contents in surface water ($1 \mu g.L^{-1}$) recommended by Decree of the Government of the Slovak Republic No. 269/2010 Coll. in the samples from surroundings of old mining activities in the Veľká Studňa locality.

2.3 Heavy metal contamination of plants and selected food commodities

In plant tissues from the area of the Veľká Studňa locality, high Hg contents (in roots of *Salix fragilis* up to 22 $mg.kg^{-1}$) were determined. The results of thermomechanical Hg analyses of individual plant tissues for *Pinus sylvestris*, *Salix fragilis* and *Juncus articulatus* are presented in Tab. 4. The contamination generally decreases in the following order: root – branch/stem – leaf/needle.

Tab. 4 Mercury contents in plant samples from Veľká Studňa area

Plant	Part of plant	Hg
		$mg.kg^{-1}$
Pinus sylvestris	root	9.85
	branch	6.02
	needles	2.30
Salix fragilis	root	22.00
	branch	0.21
	leafs	1.04
Juncus articulatus	root	5.94
	steem	0.64
	leafs	0.51

The Hg contents in analysed samples of selected food commodities from Malachov (Tab.5) did not exceed the standards (limits) given by Decree of the Ministry of Health of the Slovak Republic 608/3/2004-100 Coll. and Decree No. 14300/2007-OL.

Tab. 5 Hg content in selected food commodities and animals

Food commodity/animal	Part of plant/animal	Hg	Limit* μg.kg^{-1}
apple	fruit	<1.6	30
bean	hull	1.7	50
onion	leafs	8.2	50
nut	fruit	5.1	50
carrot	root	3.0	50
parsley	root	4.7	50
		6.8	50
potato	tuber	2.9	20
salmon trout	muscles	252	50
(*Salmo trutta*)	vitals	402	-
bullhead Siberian	muscles	136	50
(*Cottus poecilopus*)	vitals	473	-

Note: * Decree of the Ministry of Health of the Slovak Republic No. 608/3/2004-100 Coll. and Decree No. 14300/2007-OL.

The analysis of salmon trout (*Salmo trutta*) captured in the brook in the Malachov village proved a relatively high Hg contents both in muscles (252 μg.kg^{-1}) and in vitals (in liver 402 μg.kg^{-1}, Tab. 5). We obtained similar results also from the analysis of the second fish - bullhead Siberian (*Cottus poecilopus*). Although these contents don′t exceed the standards given in Decree of the Ministry of Health of the Slovak Republic 608/3/2004-100 Coll. and Decree No. 14300/2007-OL for Hg (0.5 mg.kg^{-1} for overall product and 0.1 mg.kg^{-1} for vitals), they indicate that the excess of the limit is colourable and probably depends on the living-space of the fishes (animals).

2.4 Acidification of landscape components

In order to assess a risk of acidity production, a set of 10 samples of soil, sediments and stream sediments representing the landscape were used. The pH$_{(H2O)}$ in the sediments and soil from these samples, determined in the distilled water leachate in the heap field, moves in a range of 6.11 – 7.75 (Tab. 1). The Eh$_{(H2O)}$ values are relatively low (up to -70). Only in the samples OP-2 and OP-4, we can see higher Eh values in the A horizon vs. B horizon (-52 vs. -60 and 2 vs. -49) which indicate more oxic conditions in surface soil layers (and sediment) in comparison with the B horizon. The Eh values in 1M KCl lixivium show similar results (Tab. 1).

The content of sulphur is another important piece of data for the acidification risk calculation. This ranges from 0.05 to 0.30 % (Tab. 6). The result indicates that the content of the primary sulphide minerals, the oxidation of which can form the acidity, is relatively low.

The acidity production potential (AP) is mainly influenced by the inorganic carbon content, which reflects the content of carbonates able to cause the neutralization of acidity. The total carbon (C$_{tot.}$) content is fortunately high (0.69 to 13.62 %); the average C$_{tot.}$ content is 7.31 % (Tab. 6). The unfavourable assignment is caused by that most of the carbon is represented by organic carbon (C$_{org.}$). In spite of this negative effect, it is possible to state that the inorganic carbon content is satisfactory (in average 4.15 %).

The average pH$_{(H2O)}$ value in surface water is 6.99 (Tab. 3) and the average pH$_{(KCl)}$ value is nearly the same 6.82. Such pH rates close to the neutral value indicate that the formation of acid mine drainage water is not probable. The negative Eh values (up to -96) are characteristic for anoxic and anaerobic conditions.

Indeed the Eh values are more unstable (they range in groundwater from -11 to -108 and in surface water from -29 to -88; Tabs. 2 and 3), they generally reflect reducing conditions.

The pH and Eh values in water indicate that the acidification risk is not acute.

Tab. 6 Values of acidity production (AP), neutralization potential (NP) and net neutralization potential (NNP)

Sample	$S_{tot.}$	$C_{tot,}$	$C_{org,}$	$C_{inorg,}$	CO_2	$CaCO_3$	AP	NP	NP:AP
				%					
OP-1	0.05	6.95	3.67	3.28	12.02	27.33	1.562	226.73	145.20
OP-2A	0.05	9.86	6.02	3.84	14.07	31.99	1.562	265.39	169.87
OP-2B	0.05	12.40	0.64	11.76	43.09	97.98	1.562	812.84	519.38
OP-3	0.05	3.48	0.73	2.75	10.08	22.91	1.562	190.06	121.68
OP-4A	0.10	13.62	11.95	1.67	6.12	13.91	3.125	115.40	36.93
OP-4B	0.05	5.24	4.46	0.78	2.86	6.50	1.562	53.92	34.52
OP-5	0.05	2.96	0.62	2.34	8.57	19.50	1.562	161.77	103.57
OP-6A	0.05	6.98	2.58	4.40	16.12	36.66	1.562	304.13	194.71
OP-7	0.30	10.96	0.26	10.70	39.20	89.15	9.375	739.59	78.89
OP-8	0.05	0.69	0.68	tr.	tr.	tr.	1.562	n.d.	n.d

In Malachov surroundings there are the main minerals which can potentially cause acidification –cinnabar – HgS and pyrite – FeS_2. The present condition of acidification seems to be not acute, but it is necessary to realize that in many mining regions, the acidification process has started only after several decades since the time when the mine had been closed.

The recalculation of S % to H_2SO_4 gives the maximum amount of the acid per ton of soil or sediment which can be produced. The total acidity production (AP) is calculated using the following formula: AP = 31.25 x % S and corresponds to the amount of the acid that can be produced potentially by the soil and sediment material. In Malachov, the AP varies in a range of 1.562 – 9.375, on average 2.5, respectively (Tab. 6).

The neutralization potential (NP) which gives the content of neutralizing substances in the soil and sediments that are able to neutralize the acidity produced by the material varies in surroundings of Malachov from 0 to 812.84; x = 286.98 (Tab. 6). The highest NP (35.80) is in the sample OP-2B (Tab. 6) with relatively high contents of $C_{tot.}$ (12.40 %) and C_{inor} (11.76 %), and after the recalculation it corresponds to 97.98 kg.t^{-1} of $CaCO_3$.

The value of NP:AP informs about the risk of production of acid in mine drainage water the best. In the Malachov region, the range of the NP:AP ratio is 0 – 519.38 (in average 140.48). If this ratio is close to the value of 1, the probability of the acidity formation is high; if the value is equal to or higher than 3, the risk of AMD production is negligible (Sobek et al., 1978). All the values of NP:AP in Malachov with exception of that in the sample OP-8 are so high (34.52 – 519.38) that according to this calculation, the risk of the acidity production is excluded.

4 DISCUSSION

The source of Fe in soils and sediments is predominantly from pyrite (FeS_2) and marcasite (FeS_2). As a result of their degradation, the formation of hydrogoethite („limonite" – $Fe_2O_3.nH_2O$) occurs. The Pb and Ba origin is less apparent. Probably both of them come from abundant dolomite rocks. The increased Zr contents is possibly derived from zirconium.

According to Beneš and Pabianová (1987), the Hg contents in soil is in a range from 0.02 to 0.2 mg.kg^{-1} and the average Hg content is 0.098 mg.kg^{-1} (Kabata-Pendias & Pendias, 2000). The soil in the Malachov brook drainage is cambi-soil (rendzina). The Hg content in soils and in sediments is not very high despite of the vicinity of the mercury deposit (0.558 – 44.238 mg.kg^{-1}), although exceeds the limits (Hg 0.5 mg.kg^{-1}) sensu Decree No. 220/2004 Coll. of the Slovak Republic, on agricultural soil utilization (for sandy-clay and clay soil). The results can be compared with those of Rusková (2009) which for a mining locality exploited in 17th century, described 0.411 ppm Hg content in soil mixed with technogenous sediments from the dump.

According to Greenwood and Earnshaw (1990), Kabata-Pendias and Pendias (2000), Hg is in soil present in several forms: a) elementary - Hg^0 (volatile and only slightly soluble in water), b) Hg^{2+}, which forms CH_3Hg^+ compounds in a form of cations. In soil, it is present mainly in a form of slightly mobile organocomplexes. Its mobility is influenced by the type of soil/sediment, mainly by the value of physical and chemical parameters as

pH and Eh values. The oxidation of the metallic Hg starts at Eh >390 mV (Greenwood & Earnshaw, 1990), while the highest Eh value in Malachov (sample OP-4A, Tab.1) was only 52 mV.

Sensu pedological classification (Čurlík & Šefčík, 1999; McNeill, 1992, VanReeuwijk, 1995), the soils in Malachov (classification based on pH_{H2O}) are slightly acid (samples OP-4A, OP- 8), neutral (samples OP-1, OP-2A, OP-4B, OP-5) to slightly alkaline (OP-3, OP-6A, OP-7; Tab. 1).

The increased Hg contents in the A horizon are probably caused by cinnabar grains or by Hg bonding on mould (eventually on carbon and sulphur) and the data are conformable with the information that Hg ions are not well sorbed on clay minerals (Kabata-Pendias & Pendias, 1992), but Hg^{2+} show a good sorption property on mould (Kolář, 1988). A higher sorption capacity was described at pH 4-5 (Babčan & Ševc, 1994). As the mould horizon is resistant against the degradation, only a negligible part of Hg is released and permeates to the B horizon rich in clay minerals.

The main Hg mineral – cinnabar (HgS) is not well soluble during the oxidation process. Mechanically disintegrated grains are usually accumulated in the stream sediments (Polański & Smulikowski, 1978). This assumption was confirmed by the analyses of stream sediments, published by Matúš (2004, in Rusková, 2009). A high As (±Sb) content was described as well.

Stream sediments with high sludge and organic components have usually higher Hg contents in comparison with sandy or gravel stream sediments. The brooks and creeks in the surrounding of Malachov have predominantly a gravel bed with boulders bottom so there is a great chance that the water takes away the released Hg to the Hron River where it is dispersed in a great volume of water and causes no environmental risk. In spite of this situation, the stream sediments in the Malachov brook contain a great portion of cinnabar grains because of its weight. The Hg content in the stream sediments varies from 0.37 to 45.4 ppm (Grofčík, 2009, Rusková, 2009). This Hg can migrate from the sediments to the fytobenthos and from them to the zoobenthos.

The sorption of Hg on organic matter is very good (Kabata-Pendias & Pendias, 1992; Melicherčík & Melicherčíková, 2010), so Hg is often transformed to one of the most soluble and most toxic compounds – methylmercury (CH_3Hg^+) which contaminates the water, poisons water organisms, and through them the whole surrounding ecosystem (Virčíková & Pálfy, 1997; Kafka & Punčochářová, 2002).

In fresh water there is the main methyl form of Hg the CH_3HgOH and in sea-water there are CH_3HgCl compounds (Moore & Ramamoorthy, 1984). Methylmercury (CH_3Hg^+) is very mobile and thus contaminates the plants. Bacteria can cause the reduction of Hg^{2+} to Hg^0 and the following Hg volatilization from soil (Kabata-Pendias & Pendias, 1992). The dominant inorganic Hg form in surface water is $Hg(OH)_2$ (Moore & Ramamoorthy, 1984). The Hg speciation in aqueous systems influences mainly chlorides and sulphides. Under acid and oxidic conditions, chlorides prevail, under alkaline oxidic conditions mainly oxides and hydroxides and under reductive conditions, sulphides are dominant. Under alkaline conditions, the solubility of HgS increases in consequence of complex anion $[HgS_2]^{2-}$ formation (Fergusson, 1990). Hg forms stable complexes with various organic ligands, mainly with those which contain ligands as cysteine, amino-acids and hydroxyl-carboxyl acids.

High concentrations of methylmercury were described in humid countries (Gray, 2001). Methylmercury degradation in water surrounding is realized due to a microbiological activity and oxidation operations. The degradation of methylmercury by germs produce Hg^{2+} and CH_4, while following the oxidation process CO_2, CH_4 and Hg^{2+}, final products are formed (Bailey et al., 2001).

The mercury content in groundwater from the surrounding of the mine galleries does not exceed in most cases the allowed limit sensu Decree of the Government of Slovak Republic No. 496/2010 Coll. on drinking water or sensu Decree of the Ministry of Environmental Protection of the Slovak Republic No. 636/2004 Coll. on „rough water" used in water-supplies. In some analyses (Rusková, 2009), an excess of limits for Fe, Mn and As concentrations was proved. Also in the surface water, the Hg contents are higher as the allowed limits imposed by Decree of the Government of the Slovak Republic No. 269/2010 Coll.

According to the previous investigations (Matúš 2004 in Rusková, 2009) in Malachov, Hg contamined mainly stream sediments, benthos, fishes, plants and mushrooms. It is interesting that the present study proved a relatively low Hg content in the stream sediment of the sample OP-5 (Tab. 1). The Hg, As and Sb contents in plant tissues decrease in the following order: root → branch/stem → leaf/needle.

Fishes as a top of the food chain under aqueous conditions contain the highest Hg contents. In animals, the highest Hg accumulations are in kidneys and in livers. The lowest Hg contents are in muscles (Kafka & Punčochářová, 2002; Kaneko & Ralston, 2007). This tendency was confirmed also in Malachov. The Hg content in muscles (255 and 136 $\mu g.kg^{-1}$) was two times lower than in livers (402 and 473 $\mu g.kg^{-1}$). Vitals of fishes from fresh waters are not used for consumption so it is necessary to follow only the Hg (and other heavy metal) contents in muscles. The Hg accumulations in fish-tissues depend on Hg concentrations in aqueous

medium and environs. The water temperature, concentration of water-dissolved oxygen and less also the pH values are important as well. The ability of Hg accumulation increases at lower temperatures (Kaneko & Ralston, 2007). In surroundings of Malachov, the situation is favourable for Hg accumulations because of relatively cold climate (average temperature is 7.04 – 8.30 °C, but even lower temperatures are also common: 1.9, 3.6 or 4.3 °C).

According to Bukový (1990 in Rusková, 2009), the average Hg concentration increases in benthos from 56 to 118 $\mu g.kg^{-1}$ (the Hg content in benthos above the Veľká Studňa locality is 699 $\mu g.kg^{-1}$ and beneath the village Malachov decreases to 362 $\mu g.kg^{-1}$). The Hg contents in muscles of *bullhead Siberian* and *salmon trout* vary in a range from 136 to 252 $\mu g.kg^{-1}$. In vitals, the Hg contents were higher (473 and 402 $\mu g.kg^{-1}$) and we can assume that the concentrations increase during the life of fish. Although Hg contents in muscles and livers don't exceed the standards given in Decree of the Ministry of Health of the Slovak Republic 608/3/2004-100, Hg (0.5 $mg.kg^{-1}$, i.e. 500 $\mu g.kg^{-1}$), they indicate that the Hg accumulations in fish bodies are near the limit values and probably such localities exist where they can exceed the limit. In the present time, the mentioned Decree is not valid any longer, and is gradually replaced by several more benevolent regulations. The excess of the allowed limit concentrations in vitals (liver) doesn't represent any health risk because the parts of fishes are not consumed.

The Hg contents (tab. 5) in food commodities (fruits and vegetables) respect the limits for Hg given in Decree of the Ministry of Health of the Slovak Republic 608/3/2004-100 Coll. and Decree No. 14300/2007-OL. Only the mushrooms exceed the allowed limits for Hg (0.25 $mg.kg^{-1}$), As (0.5 $mg.kg^{-1}$) and Sb (0.3 $mg.kg^{-1}$).

The acidification process in mining landscapes cause increasing acidity, which has range of direct undesirable consequences such as soil degradation (e.g. mould, Ca and Mg removal), an increase in heavy metal mobility and consequently increasing contamination of the landscape, depressing metabolic rates, depressing the immune responses of organisms etc. The acidification is a multi-stage process which starts with the acid-producing material decomposition (usually sulphide minerals, mainly pyrite). Its kinetics depends on numerous factors as a bacterial activity impact, abundance of O_2, presence of water etc. During the initial phase, the acidification is attenuated by neutralisation efficiency of surrounding rocks (carbonates, clay minerals, organic matter...). After exceeding the pufration efficiency of neutralisation agents (mainly carbonates), usually (if there is sufficient acid producing material) the massive acidification starts.

The pH of soil and water are the first values which are important for the acidification process study. The pH in surface water is close to the neutral value 7, and suggests very limited or no risk of acidification. A relatively low pH value in groundwater from the spring from Nemecký Hill (sample MAL-3, pH 3.90; Tab. 2) and from the Turistický spring (MAL-4, pH 5.12; Tab. 2) indicates only a local process of acidification, connected with the oxidation of Hg-mineralization. The limited volume of water from the springs cannot substantially influence the acidity of the supergene processes in a wider region.

Measuring pH in soil is realised by several methods. All of them have certain advantages, as well as disadvantages. The pH is measured usually in a soil solution (suspension). The pH value changes also seasonally. During the dry season, the acid components (SO_4^{2-}, NO_3^-, Cl^-) aren't′t removed by percolating waters. Such an increased concentration has no influence on the pH value measured in water. If the salts are removed during the wet period, the pH increases. This dilution effect causes an increase in pH in the soil suspension. It is the reason why some pedologists prefer measuring pH in solutions of 0.01M $CaCO_3$ or 0.1M KCl.

The pH_{KCl} and Eh_{KCl} is so-called pufration pH/Eh. This value indicates the cation exchange capacity and the cation sorption complex composition. In acid soils, the values are lower than the pH/Eh value in water. The D value, calculated using the formula pH: $DpH = pH_{H2O} - pH_{KCl}$, enables to estimate the presence of a prevailing charge on the colloids surface. The positive D value indicates the presence of negative charges, and vice versa, the negative D value indicates the presence of positively charged colloids. For soil in Malachov, the D is calculated from the average of the pH_{H2O} and pH_{KCl} values 0.38. It suggests that in soil colloids with a negative surface charge prevail. This determination suggests also a relatively limited ability of soil to bind anions which represent usually the neutralization agents under natural conditions.

The comparison of the $C_{tot.}$ content with the neutralization potential (NP) indicates that it depends mainly on the $C_{inorg.}$ content. The highest $C_{tot.}$ content is in the sample OP-4A (13.62 %), but the $C_{inorg.}$ content here is lower (10.70 %) than in the sample OP–2B (11.76 %) so the NP for the sample OP-4A is lower (739.59) than the NP for the sample OP-2B (812.84).

The acidity production potential (AP) is low, on average, 2.5. On the other hand, the neutralization potential (NP) values are high, on average, 286.98. The value of AP:NP, which is in the Malachov range 140.48 on average, informs about the acidification risk the best. According to Sobek et al. (1978), if the value is equal to or higher than 3, the risk might be neglected.

5 CONCLUSIONS

In soils/sediments, relatively high Hg contents (varying from 0.56 to 44.24 mg.kg^{-1}), as well as Fe (0.53 – 5.73 %), Mg (1.30 – 11.37 %), Mn (156 – 2741 mg.kg^{-1}) and Pb contents (6.9 – 117.0 mg.kg^{-1}) were described. Also increased Sr (78 – 227 mg.kg^{-1}), Ba (51 – 426 mg.kg^{-1}) and Zr (9.7 – 125.4 mg.kg^{-1}) contents were proved. Cu, Zn, Co, Cr, V, As, Sb and Ti contents are low. Mercury is bounded preferentially on mould in the A soil horizon.

The Hg content in groundwater, in most cases, does not exceed the limit sensu Decree of the Government of the Slovak Republic No. 496/2010 Coll. on drinking water, eventually of Decree of the Ministry of Environmental Protection of the Slovak Republic No. 636/2004 Coll. The Fe, Mn contents and in some older samples (Rusková et al., 2009) also As contents exceeds the limits.

In surface water, the recommended Hg contents are exceeded in several cases (sensu Decree of the Government of the Slovak Republic No. 269/2010 Coll.).

Mercury contaminates mainly stream sediments, benthos, fishes, plants and mushrooms. The Hg, As and Sb concentrations in plants decrease in the following order: root – branch/stem – leaf/needle.

Food commodities (fruits, vegetable and fishes) respect from the viewpoint the standards stated in Decree of the Ministry of Health of the Slovak Republic No. 608/3/2004–100 on food commodities and in Decree of the Ministry of Health of the Slovak Republic No.14300/2007-OL. On the other hand, the Hg contents in a great part of the mushrooms substantially exceed the allowed limits.

The low average value of the acidity production (AP) 2.5 and the extraordinary high values of neutralization potential (NP), on average, 286.98, indicate that the acidity production and the formation of acid mining waters and the subsequent acidification of landscape components (soil, water, plants...) seem to be out of the question. This assumption is confirmed also by the AP:NP ratio value (140.48).

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RESUMÉ

Východní svahy Kremnických vrchů jsou budovány výlevnými a explozívními produkty neogénního vulkanizmu. Hg-mineralizace je prostorově spjatá s mladými poklesovými strukturami S-J až SV-JZ směrů a geneticky s postvulkanickou etapou vývoje neogénního stratovulkánu. Ložiskové akumulace cinabaritu a metacinabaritu, doprovázené pyritem, markazitem a arzenopyritem se tvořily v tektonicky rozdrcených karbonátech mezozoika a v pískovcích paleogénu, pod nepropustnými vrstvami argilitizovaných sopečných tufů (Ivančík & Mitáček, 1986; Bancík & Jeleň, 1999). Žilky cinabaritu se dříve dobývaly pomocí štol a úpadnic, větší shluky blíže k povrchu pomocí plytkých šachtic (Bergfest, 1955; Jeleň et al., 2010). Výskyty Hg-As mineralizace jsou vázány na zlomy, většinou S-J směru, které sloužily jako kolektor rudonosných roztoků (Ivančík & Mitáček, 1986). Ložisko je v současnosti uzavřené (Bancík & Jeleň, 1999).

V půdách v okolí ložiska se zjistily vysoké obsahy Hg (0,56 po 44,24 mg.kg^{-1}), Fe (0,53 – 5,73 %), Mg (1,30 – 11,37 %), Mn (156 – 2741 mg.kg^{-1}) a Pb (6,9 – 117,0 mg.kg^{-1}). Poměrně vysoké jsou také obsahy Sr (78 – 227 mg.kg^{-1}), Ba (51 – 426 mg.kg^{-1}) a Zr (9,7 – 125,4 mg.kg^{-1}). Obsahy Cu, Zn, Co, Cr, V, As, Sb a Ti jsou nízké. Rtuť se váže především na humusový A horizont půdy.

Obsahy Hg v podzemních vodách nepřesáhly ve většině případů přípustný limit (ve smyslu Nařízení vlády SR č. 496/2010 Sb., kterým se ustanovují požadavky na vodu určenou na lidskou spotřebu a kontrolu kvality vody určené pro lidskou spotřebu, případně Vyhlášky MŽP SR č. 636/2004 Sb., kterou se ustanovují požadavky na kvalitu surové vody a na sledování vody vo veřejných vodovodech. Zjistilo se překročení limitů pro Fe, Mn a v některých starších analýzách lokálně také As.

V povrchových vodách jsou doporučené hodnoty pro Hg v některých případech překročené (ve smyslu Nařízení vlády SR č. 269/2010 Sb).

Rtutí jsou kontaminovány především říční sedimenty, bentos, ryby, rostlinstvo a houby. Koncentrace Hg, As a Sb v rostlinných pletivech klesají v pořadí: kořen - větev – jehlice resp. kořen – stonek - list.

Potravinové komodity (ovoce, zelenina a ryby) z hlediska obsahu Hg spĺňují požadavky na hladinu přípustných koncentrací ve smyslu Vyhlášky MP SR a MZ SR č. 608/3/2004–100, kterým se vydává hlava Potravinového kodexu SR upravující kontaminanty v potravinách a Vyhláška MP SR a MZ SR č. 14300/2007-OL. Naopak, velká část hub vykazuje překročení přípustných limitů koncentrace Hg, přičemž klobouky hub bývají často více kontaminované než jejich třeň.

Nízká průměrná hodnota potenciálu tvorby kyselosti (AP) 2,5 a mimořádně vysoké hodnoty neutralizačního potenciálu (NP), v průměru 286,98, indikují, že tvorba kyselých baňských vod a následná acidifikace krajinných složek jsou prakticky vyloučené. Tento předpoklad jednoznačně potvrdzuje rovněž poměr AP : NP 140,48.