

ENVIRONMENTAL ASSESSMENT OF IMPACTS BY OLD COPPER MINING ACTIVITIES - A CASE STUDY AT ŠPANIA DOLINA STAROHORSKÉ MTS., SLOVAKIA

Iveta NAGYOVÁ¹, Zuzana MELICHOVÁ¹, Terézia KOMADELOVÁ¹, Peter BOHÁČ¹ & Peter ANDRÁŠ^{1,2}

¹Faculty of Natural Sciences, Matej Bel University, Tajovského 40, 974 01 Banská Bystrica, Slovakia;
e-mail: Iveta.Nagyova@umb.sk

²Geological Institute of Slovak Academy of Sciences, Ďumbierska 1, 974 11 Banská Bystrica, Slovakia;
e-mail: andras@savbb.sk

Abstract: This study is focused on environmental assessment of impacts by old copper mining activities at Špania Dolina in Central Slovakia. Špania Dolina was in 15th and 17th centuries world-famous for intense mining activity, especially for mining and processing of copper. The environmental assessment was done on the base of analysis of selected metal elements in the soil, surface and groundwater. The sampling sites were selected on the basis of their relative position to the Maximilian dump-field in order to assess its potential impact on environmental contamination. Soil samples and water samples were collected quarterly in course of the year 2011. The samples were analyzed for metals by the atomic absorption spectrometry method with electrothermal atomization (As, Sb, Ni, Pb, Cd, Co, Ag, Se, Cr) and flame atomization (Cu, Zn, Fe, Mn). The results of the soil samples analyses from the Maximilian dump-field showed excessive concentrations of Cu (516.4 – 3602.6 mg·kg⁻¹), Pb (30.0 – 454.9 mg·kg⁻¹), Cd (0.54 – 4.8 mg·kg⁻¹) and Fe (2168.3 – 3995.1 mg·kg⁻¹). The results of the water samples analyses showed excessive concentrations of Cu (385.2 – 429.1 µg·dm⁻³), As (33.2 – 77.0 µg·dm⁻³), and Sb (111.3 – 275.0 µg·dm⁻³) in surface waters and Cu (max. 753.1 µg·dm⁻³), As (2.5 – 75.0 µg·dm⁻³), and Sb (3.2 – 291.1 µg·dm⁻³) in groundwater. Speciation of As in water samples was performed by HPLC-ICP-MS system. The presence of less toxic form As(V) was found. Sorbent Bayoxide E33 was studied to eliminate As from drinking and natural waters. Sorption efficiency 95-100% was achieved. Maximum sorption capacity of 5.05 mg of As(V)/g dry sorbent was found experimental.

Keywords: Špania Dolina deposit, environmental assessment, metal contamination, water, soil, sorbent bayoxide E33

1. INTRODUCTION

Heavy metal contamination affects several areas in Slovakia due to long-term heavy metals exploitation and processing activities. Špania Dolina is located in Central Slovakia close to the town of Banská Bystrica, in Starohorské Mts. This region was worldwide-famous for its intense mining activity, which goes back to the 4th Millennium BC. The deposit was known mainly for the mining of copper with a rich admixture of silver in the 15th - 17th century, when Thurzo-Fugger company Ungarischer Handel operated. Špania Dolina belonged in the past to the most important copper deposits of the world. Later mining activities started decline and were

finally finished in the middle of the 20th century (Jeleň et al., 2009).

Dump-fields, as the results of mining activities, are associated with the releasing of toxic metal elements into the environment and with water sources pollution in mining communities within the catchment of mines. Many of the dumps are situated directly on the ground without any suitable facilities, these waste deposits being permanently subject of weathering processes due to natural environmental factors (wind, storm flows), all these promoting further expansion of affected areas. Monitoring of heavy metals in the environment is currently a major topic of research of many researchers around the world for their dangerous properties,

particularly toxicity and carcinogenicity (Sakan et al., 2007, Zobrist et al., 2009, Mohiuddin et al., 2010; Mohiuddin et al., 2011; Odukoya & Abimbola 2010; Zandsalimi et al., 2011).

The Maximilian dump-field represents a dominant element in the landscape of Špania Dolina and represents the potential source of environmental contamination because of its composition and exogenous factors (e.g. erosion, acidification). Toxic metal elements can migrate into the water and can accumulate in sediments, soils and biological materials. As a result of environmental contamination by toxic metals, the changes of the species composition of the vegetation are observed. The frequent accompanying phenomena is replacing less resistant plant species by more resistant one, the gradual withdrawal of vegetation to its complete disappearance in the most contaminated areas.

Region Špania Dolina was described by Mazurek (1989). His work was focused mainly on the mining system and the old mining equipment loads. It is devoted to a detailed description of the geological structure of the area, its geomorphology, hydrological characteristics, climatic conditions and description of forest ecosystem. Environmental risks resulting from the extraction are described by Rusková et al., (2003). Rusková (2003) also deals with the impact of mining activities on the health of the population in the village Špania Dolina. Aschenbrenner et al., (2011) describe the flora and vegetation dump-field Maximilián. Dubiel et al., (2011) deal with heavy metal sediment contamination and the possibilities of their sorption on

clay minerals present in the area Špania Dolina. The first aim of the article is to assess the risks arising out of release of toxic metals into the environment. The second aim was to find a suitable solution for arsenic removal from drinking and natural waters with high As concentration. The As and the other metals removal from water is nowadays very often discussed by many authors (Aker & Ali 2011; Bailey et al., 1999; Mohan & Pittman 2007, Stuckman et al., 2011, Cheng 2003). One of the extended methods is to use sorption on natural or synthetic sorbents. Sorbent Bayoxide E33 based on iron oxide was used in our study. According to available information from the literature selected sorbent has high sorption capacity and efficiency for As.

2. MATERIALS AND METHODS

2.1. Sampling and Sample Preparation

Water samples (surface water (V01-V06), groundwater (V07-V09)) and soil samples (P01-P24) were collected quarterly during 2011 period. The sampling sites for water and solid samples are shown in figure 1.

Water sampling containers were rinsed a few times with water from the sampling point before representative sampling from 15 cm below water surface. Samples were filtered in situ through a 1 µm pore-size paper filter and then in the laboratory through a 0.45 µm membrane filter.

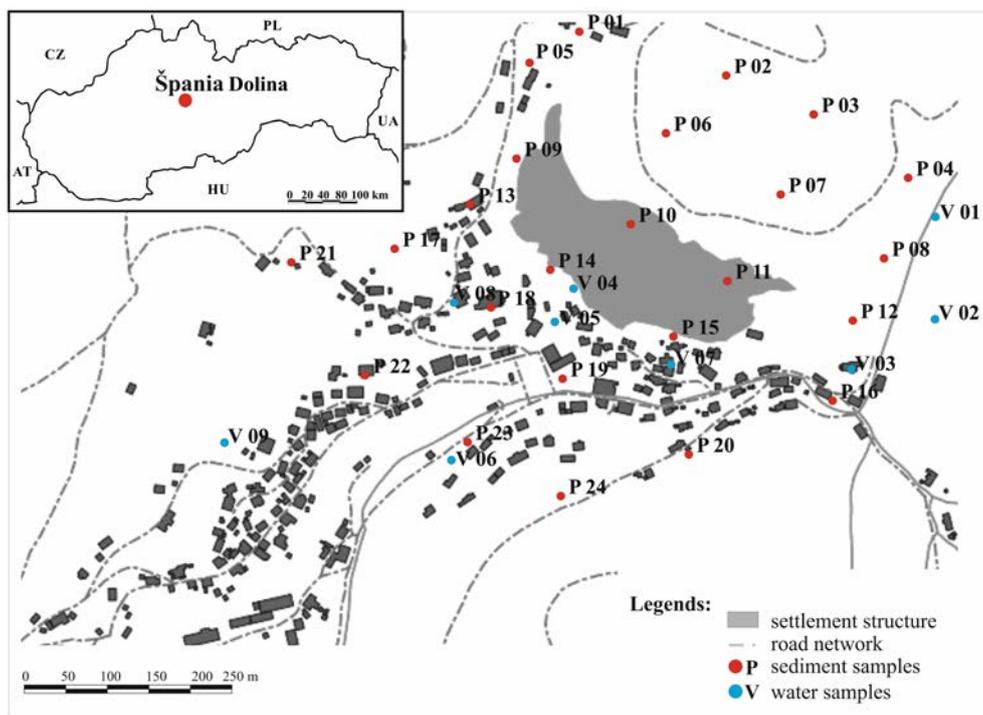


Figure 1. The sampling sites of water and sediment samples – Špania Dolina

Then the samples were acidified with HNO_3 , ($w = 65\%$; 0.5 cm^3 in 100 cm^3 sample) for metal analyses. Until the time of analysis, the samples were stored in a refrigerator at 5°C no longer than 1 month.

The pH values of water samples were measured in the field at the time of sampling using the Multi 340i instrument (WTW, Germany) equipped with SenTix_41 electrode.

The soil samples (1–2 kg) were collected from a depth of 0–15 cm in plastic bags. The collected soil samples were air dried and all the vegetation material (e.g. roots) and rocks were removed from the samples. Soil samples were sieved and the fraction smaller than 2 mm was used for the analysis. The soil samples (10 g) were introduced into the Erlenmeyer flasks together with 100 cm^3 2 mol dm^{-3} nitric acid and were extracted in a horizontal shaker for 2 hours. After extraction, the soil suspensions were filtrated under reduced pressure. Filtrates were stored in the refrigerator until the analysis of metals at temperature 5°C , no longer than 1 month.

To determine the soil reaction pH/ H_2O deionized water was added to the sample in a ratio 1 : 2.5 and the suspension was allowed to stand for 24 hours at room temperature. Before measuring pH the suspension was stirred (Hrivňáková & Makovníková, 2011).

2.2. Instrumentation and chemicals

The water samples were analyzed for metals by the atomic absorption spectrometry method with electrothermal atomization – ET AAS (As, Sb, Ni, Pb, Cd, Co, Ag, Se, Cr) and flame atomization – F AAS (Cu, Zn, Fe, Mn). Determinations were performed by the atomic absorption spectrometer AAS Spectra DUO 240 FS (Varian, Australia) with flame atomization and electrothermal atomization (type 240 Zeeman). Evaluation of the results as well as the operation of the device were performed by software SPECTRAA, AA version 5.1 PRO.

The soil samples were analyzed by the ET AAS (Cd, Co) and by the F AAS (Cu, Zn, Fe, Mn). Determinations were performed by the atomic absorption spectrometer Avanta Σ with deuterium background correction (GBC, Australia) equipped with GF 3000 graphite furnace. Evaluation of the results as well as the operation of the device were performed by software GBC Avanta version 2.0.

Analysis of the each sample was done in

triplicate and the results were expressed as mean \pm standard deviation (SD).

For speciation analysis of As(III) and As(V) was used HPLC-ICP-MS system (Perkin Elmer, Canada). HPLC system consists of the pump - Perkin Elmer Series 200 Pump (Perkin Elmer, Canada), the oven - Series 200 Peltier Oven (DBS Strumenti Scientifici. S.r.l., Italy) and the dispenser - Rheodyne LLC dispenser with $200\ \mu\text{l}$ injection loop (PEEK). Column - HAMILTON PRP-X100, $250 \times 2.1\text{ mm}$, 10 mm (PEEK) (Hamilton, USA) was used. Column output was directly connected to the input of PFA concentric nebulizer ICP-MS system via PEEK tubing of 150 mm length. Determination of As was performed by ICP-MS spectrometer Perkin Elmer Elan DRC-e (Perkin Elmer SCIEX Instrument, Canada). ^{75}As isotope was measured.

Speciation of As was performed according to techniques published in Handbook of Hyphenated ICP-MS Applications, Agilent Technologies (2012). Limits of detection for both forms As(III) and As(V) are $0.1\ \mu\text{g dm}^{-3}$. The uncertainties of measurement for As(III) and As(V) in calibration range $20 - 100\ \mu\text{g}\cdot\text{dm}^{-3}$ are $\pm 3.5\%$ and $\pm 5.4\%$, respectively.

The methodology described in the work of Bhattacharyya & Gupta (2006) was used for sorption experiments and evaluation of measured results. Kinetics of sorption process was studied by means of batch adsorption laboratory experiments. Langmuir sorption isotherm parameters were calculated and maximum sorption capacity of the sorbent was determined. Sorption efficiency of sorbent for real natural water samples from the studied area was studied.

Phosphates were determined by CZE method (Kaniansky et al., 1996) using electrophoretic analyser EA 102 (Villa Labeco, Spišská Nová Ves, Slovakia). Limit of quantification is 0.3 mg dm^{-3} . Analysis and evaluation were supported by Dušan Kaniansky Consulting ACES ver.1.53 software.

Silicates were determined by spectrometric method according the STN 757485 (2007) in Biotika, a.s. Slovenská Lupča. Limit of quantification is 0.6 mg dm^{-3} .

The pretreatment of samples and preparation of solutions have been done with chemicals and solutions with the highest purity. Water quality was grade 1, ($\leq 0.01\text{ mS}\cdot\text{m}^{-1}$).

Nitric acid ($w = 65\%$; Suprapur®, Merck, Germany);

Certified reference materials: ρ (Pb, Sb, Cd,

Ag, Se) = $1.000 \pm 0.002 \text{ g dm}^{-3}$, ρ (Ni) = $1.0003 \pm 0.0019 \text{ g}\cdot\text{dm}^{-3}$; ρ (Co) = $1.0029 \pm 0.0019 \text{ g}\cdot\text{dm}^{-3}$, ρ (As) = $1.0010 \pm 0.0025 \text{ g}\cdot\text{dm}^{-3}$; ρ (Cr) = $0.9997 \pm 0.0022 \text{ g}\cdot\text{dm}^{-3}$ (SMI, Slovakia).

Palladium matrix modifier for graphite furnace AAS, ρ (Pd) = $10.0 \pm 0.2 \text{ g}\cdot\text{dm}^{-3}$ ($\text{Pd}(\text{NO}_3)_2$ in HNO_3 , $w = 15 \%$), (Merck, Germany).

Magnesium matrix modifier for graphite furnace AAS ρ (Mg) = $10.0 \pm 0.2 \text{ g}\cdot\text{dm}^{-3}$ ($\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$ in HNO_3 , $w = 17 \%$) (Merck, Germany).

Mixed matrix modifier: Palladium matrix modifier/ Magnesium matrix modifier

For HPLC-ICP-MS speciation analysis of the As(III) and As(V) stock solutions of standards As(III) and As(V), of concentration 1.0000 g dm^{-3} were prepared from solid substances of maximum purity: As_2O_3 (Fluka, Switzerland) and $\text{As}_2\text{O}_5 \cdot \text{H}_2\text{O}$ (Sigma Aldrich, USA).

Sorbent Bayoxide E33 was used for sorption experiments. It is granular sorbent based on the iron oxide with a high specific surface ($120\text{--}200 \text{ m}^2\cdot\text{g}^{-1}$) and high specific sorption capacity. Sorbent grain size is 0.5 - 2 mm and sorbent porosity is 85%. Sorbent pH working area is from 6.0 to 8.0 (Ilavský, 2008).

3. RESULTS AND DISCUSSIONS

For both spectrometers have been optimized techniques using flame and electrothermal atomization in order to find suitable measuring conditions for both kind of samples. Based on the results of repeated measurements of certified reference materials were determined basic validation parameters and performed calculation of uncertainty. Limits of detection and quantification were calculated using method of the upper limit approach (ULA), recommended by IUPAC (Mocák et al., 1997). The calculation is based on the accuracy of the calibration curve and uses the residual standard deviation of the linear regression and the critical value of the t-distribution.

To determine the uncertainty, calculation of the reproducibility standard deviation s_R (RSDR) by the Horwitz function (Horwitz 1982) was used. Horwitz function expresses the empirical relationship between the precision of the method and the concentration of analyte, irrespective of the kind of analyte, matrix and used methods. For simple analytical methods without any sample pretreatment is sufficient to

use 1/3 or 1/4 calculated value, for simple methods, with a simple sample pretreatment is used 1/2 calculated value and for multistage sample pretreatment 2/3 calculated value.

Samples from 6 surface water sampling sites (V01 - V06) and from 3 groundwater sampling sites (V07 - V09) were collected for the analysis. 24 surface water samples and 12 groundwater samples were analyzed during one year. Groundwater is used as a source of drinking water by the village inhabitants. No regular inspection of this groundwater is performed because it is not a public water supply. To study seasonal effects (season, rainfall, temperature, etc.) on metals concentration in waters, sampling planning was suggested. The concentrations of toxic metals in groundwater and in surface water are shown in table 1. The mean, minimum and maximum measured metals concentrations are described. The quality assessment of the surface, ground, and drinking water from studied sampling sites was done under the current legislation which corresponds to the European legislation (Government Regulation of SR No.269 2010 and No. 496 2010).

Analysis of both surface and groundwater samples from the Špania Dolina show higher As, Cu and Sb concentrations. Cu concentrations in surface water exceed 40–400 times the annual average ($1.1\text{--}8.8 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$, general requirements), which is depending on water hardness expressed by the CaCO_3 content. Cu concentrations in groundwater do not exceed the limit ($2 \text{ mg}\cdot\text{dm}^{-3}$). As concentrations in surface water exceed the annual average ($7.5 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$, general requirements) 7 times and in rare cases up to 10 times. As concentrations in groundwater exceed the limit ($10 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$) 3 times and in rare cases up to 7 times. Sb concentrations in surface water are assessed only if the water is used for drinking purposes. The limits depend on the method of treatment for drinking water and are in the range $5\text{--}25 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$. Surface water from the studied area is not used for drinking and so it was not assessed in that sense. Sb concentrations in groundwater exceed the limit ($5 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$) 20 times, and in rare cases up to 60 times. Ni concentrations in rare cases reach limits ($20 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$) in groundwater ($19.9 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$) and surface water ($18.3 \text{ }\mu\text{g}\cdot\text{dm}^{-3}$). Zn concentrations in surface waters ($0.021\text{--}0.038 \text{ mg}\cdot\text{dm}^{-3}$) slightly exceed the limit values ($0.0078\text{--}0.052 \text{ mg}\cdot\text{dm}^{-3}$), depending on the water hardness. The other metals concentration values are under limit values and do not influence the water quality.

Based on the analysis results it can be concluded that the indicators of quality of monitored surface water from Špania Dolina are not in agreement with the general requirements for surface water quality. At the same time it can be concluded that the monitored groundwater from Špania Dolina does not conform to the quality of drinking water and is not recommended to be used for drinking purposes.

In order to determine the proportion of As(III) and As(V), speciation analysis in 2 samples from Špania Dolina was done. Speciation of As was performed by HPLC-ICP-MS system. The water samples from the Daily shaft (V07, Fig. 1) and Mining water supply - pond under dump-field (V04, Fig. 1) were used for analysis. Analysis was done for two parallel samples that were measured for 3 times. The water from the Daily shaft is groundwater, which is used for drinking. Water from Mining water supply is the surface water. Sampling was done in May 2012; the weather was sunny without any longer-term rainfall. Both water samples are flowing waters which are aerated, so that there is the natural oxygen oxidation. The results show the presence of As(V) only (V07: $31.3 \pm 1.7 \mu\text{g}\cdot\text{dm}^{-3}$ and V04: $31.5 \pm 1.7 \mu\text{g}\cdot\text{dm}^{-3}$, respectively), which is according to our expectations. As(V) is less toxic form of As compared to As(III).

Soil samples from 24 sampling sites (P01 - P24, Fig. 1) were collected for the analysis. Metal concentrations are shown in Table 2. Results are presented as the mean, minimum and maximum concentrations for group of the measured samples directly from the dump, over the dump (reference site) and under the dump. Assessment of soil quality from the monitored sampling sites was done under the Law No. 220 (Collection of Laws SR Law No. 220 2004) on the conservation and use of agricultural soil. Measured metal content values were compared with the limits for a sandy-loamy soil. Analysis of soil samples from the Špania Dolina shows higher Cu, Pb, Zn and Cd concentrations, which are significantly above the limits for sandy-loamy soil. Copper concentrations in the soil exceed 30–60 times the limit value on the dump, under the dump 6–15 times and rarely 4 times over the dump as well. Pb concentrations in the soil exceed 2–7 times the limit value on the dump, without influence to the lead content in the soil under the dump. The Zn concentrations in the soil reach the limit values on the dump and under the dump and rarely exceed the limit concentration 2 times over the dump as well. Cd concentrations in the soil exceed 3–7 times the limit value on the dump, 2–9 times under the dump. Based on the our results it can be concluded that monitored

soil from the Maximilian dump-field of from Špania Dolina does not conform to the soil quality and affects the soil quality under the dump. At the same time it can be stated that the reference site over the dump exhibits limit exceeding values of Cu and Zn concentrations.

To reduce over-limit As concentrations in waters the method of As sorption on the sorbent was used in our study. Sorbent Bayoxide E33 based on iron oxides with high sorption capacity and efficiency for As was used. Selected sorbent is used when initial As concentration in water does not exceed $100 \mu\text{g}\cdot\text{dm}^{-3}$. Sorption batch laboratory experiments at temperature $20 \pm 2^\circ\text{C}$ were performed, coefficients of Langmuir isotherm were calculated and maximal sorption capacity of Bayoxide E33 (5.05 mg of As(V) / g dry sorbent) was determined. Sorption efficiency of As was investigated on the samples of natural waters from the studied locality. The As sorption on the sorbent Bayoxide E33 depends on pH (6-8), on the content of silicates ($< 40 \text{ mg}\cdot\text{dm}^{-3}$) and phosphates ($< 0.5 \text{ mg}\cdot\text{dm}^{-3}$) in the natural water samples. According to results in the Table 3, we can see, that efficiency of As removal is from 95 to 100% even for the samples with pH higher than 8 (8.5, 8.7 and 9.0) and initial As concentration higher than $100 \mu\text{g}\cdot\text{dm}^{-3}$ ($988.0 \mu\text{g}\cdot\text{dm}^{-3}$).

4. CONCLUSIONS

The methods of atomic absorption spectrometry with thermal and flame atomization and on-line coupling HPLC-ICP-MS (Wahlen & Woods, 2012) are used to determine the concentrations of metals and ionic forms of As in natural waters and soils from the dump-field Špania Dolina.

Higher Cu, Zn, Pb and Cd concentrations are observed in soil in studied locality. The results indicate that natural waters are mostly Cu, As and Sb loaded and less (in the limit concentrations) by Ni and Zn. Copper concentrations in surface water exceed limit from 40 to 400 times, which correlates with increased copper content in soil from dump-field (30–60 times more than the limit), in the soil under dump-field (6–15 times more than the limit) and in soil from the reference site over dump-field (4 times exceed the limit). The As content in natural waters exceeding the limit up to 10-fold is considered as especially dangerous from a toxicologic point of view. The speciation analysis showed the presence of less toxic form As(V), which is according to our expectations.

Table 1. Metal concentrations and pH values in surface water and groundwater (used for drinking) – Špania Dolina

Water	Value	$\rho/(\mu\text{g}\cdot\text{dm}^{-3})$						
		Cu	Sb	As	Ni	Co	Pb	Cr
Surface	Mean	402.5±17.4	208.7±10.0	49.3±2.9	15.6±1.1	8.2±0.6	1.7±0.2	ND
	Min	385.2±16.8	111.3±5.8	33.2±2.1	9.6±0.7	6.5±0.5	1.3±0.1	ND
	Max	429.1±18.4	275.0±12.6	77.0±4.3	18.3±1.3	10.1±0.8	2.0±0.2	2.0±0.2
Ground	Mean	177.5±8.7	107.0±5.7	27.5±1.8	8.8±0.7	3.0±0.3	ND	1.4±0.1
	Min	ND	3.2±0.3	2.5±0.2	< 1.9	ND	ND	ND
	Max	753.1±29.6	291.1±13.2	75.0±4.2	19.9±1.4	9.4±0.7	2.8±0.3	12.8±0.9

Water	Value	$\rho/(\mu\text{g}\cdot\text{dm}^{-3})$			$\rho/(\text{mg}\cdot\text{dm}^{-3})$			pH
		Ag	Cd	Se	Mn	Fe	Zn	
Surface	Mean	0.71±0.08	0.15±0.02	ND	0.015±0.003	0.019±0.004	0.031±0.006	8.5±0.1
	Min	0.63±0.07	< 0.16	ND	0.012±0.003	0.014±0.003	0.021±0.004	8.4±0.1
	Max	0.75±0.08	0.61±0.07	2.0±0.2	0.017±0.003	0.024±0.005	0.038±0.007	8.7±0.1
Ground	Mean	ND	ND	ND	ND	0.026±0.005	0.09±0.01	7.7±0.1
	Min	ND	ND	ND	ND	< 0.01	ND	6.7±0.1
	Max	0.76±0.08	0.23±0.03	1.8±0.2	0.016±0.003	0.149±0.021	0.77±0.09	8.4±0.1

Table 2. Metal concentrations in soils – Maximilian dump-field, Špania Dolina

Sites	Value	pH (H ₂ O)	$\rho/(\text{mg}\cdot\text{kg}^{-1})$					
			Cu	Pb	Fe	Zn	Ni	Cd
Over dump	Mean	7.1±0.1	44.9±2.7	28.8±1.9	878.5±33.8	64.1±3.6	1.5±0.2	0.180±0.025
	Min	6.3±0.1	9.8±0.7	17.0±1.2	588.9±24.1	7.0±0.6	0.21±0.03	0.020±0.004
	Max	7.8±0.1	223.4±10.6	43.1±2.6	1342.6±48.4	374.3±16.4	2.7±0.3	0.51±0.06
Dump	Mean	5.8±0.1	1595.0±56.1	172.2±8.5	2856.2±92.0	75.8±4.2	7.3±0.6	2.0±0.2
	Min	4.9±0.1	516.4±21.5	30.0±1.9	2168.3±72.8	17.0±1.2	1.4±0.1	0.54±0.06
	Max	6.4±0.1	3602.6±112.0	454.9±19.3	3995.1±122.3	180.1±8.8	15.2±1.1	4.8±0.4
Under dump	Mean	5.8±0.1	389.5±16.9	35.4±2.2	1505.9±53.4	54.8±3.2	2.7±0.3	1.34±0.14
	Min	4.4±0.1	16.5±1.2	18.3±1.3	297.0±13.4	12.6±0.9	0.34±0.04	0.10±0.02
	Max	6.8±0.1	886.4±34.0	51.2±3.0	2883.6±92.7	128.0±6.6	8.6±0.7	6.33±0.51
Limit*		-	60.0	70.0	-	150.0	50.0	0.70

*Limit values of hazardous elements in agricultural soils for a sandy-loamy and loamy soils, according to Law No. 220/2004.

Table 3. The sorption of As on the sorbent Bayoxide E33 from the natural and drinking waters from Špania Dolina and Špania Dolina - Piesky

Sample	Concentration before sorption ($\mu\text{g}\cdot\text{dm}^{-3}$)	Concentration after sorption ($\mu\text{g}\cdot\text{dm}^{-3}$)	Sorption efficiency (%)	pH-water	pH-water with sorbent	SiO ₃ ²⁻ (mg dm ⁻³)	PO ₄ ³⁻ (mg dm ⁻³)
V04	38.4±2.3	ND	100.0	8.7±0.1	8.5±0.1	2.0±0.2	ND
V07	36.7±2.2	1.7±0.2	95.3	9.0±0.1	8.7±0.1	5.1±0.5	1.7±0.2
V10	35.2±2.2	ND	100.0	8.0±0.1	7.8±0.1	2.9±0.3	ND
V11	988.0±37.0	1.9±0.2	99.8	8.0±0.1	8.0±0.1	2.9±0.3	ND

ND – not detected, V10 – drinking water from tavern, V11- drainage water from Špania Dolina - Piesky

It deals about running waters, which are aerated. Limited Sb concentration, which is also dangerous from a toxicological point of view, is exceeded in drinking water 20–60 times. There are occurred higher Zn concentrations in the soil that are reaching threshold concentrations in waters as well. Limited concentrations of Pb and Cd in soils are exceeded more than 10 times, without affecting the contents of these metals in natural waters. Based on the measurement results it can be concluded that natural water at Špania Dolina does not conform the requirements for the quality of surface water and groundwater (used as drinking water) and so is not recommended to use the water by inhabitants. The pH values of soil (mean 5.76–7.11, the minimum under the dump-field occasionally 4.37) show no presence of acid mine water that could cause massive release of metals into the water as the locality have a sufficient neutralizing capacity. Similarly of pH values in groundwater and surface water (groundwater - mean value pH 7.73, minimum value 6.70; surface water - mean value pH 8.47, minimum value 8.40) is neutral or slightly alkaline. The precipitation of the metals can be presented and increasing metal content in the sediments can be observed. As elimination from the natural waters was performed by the sorption on Bayoxide E33 sorbent, with effective sorption 95–100% using batch sorption experiments. Maximum sorption capacity of Bayoxide E33 sorbent, 5.05 mg As(V)/gram of dry sorbent was determined.

In general it can be concluded that the massive leak of toxic metals into the environment will not occur due to the geological bedrock, which is largely similar to the studied area Lubietová (Andráš et al., 2012) and contains enough natural sorbents based on clay minerals, where the majority forms illite, and less kaolinite and smectite, having a free sorption capacity, and form natural geochemical barrier. Measuring the pH of natural waters and soils shows that the formation of acid mine drainage is minimal because the buffering capacity of the geological bedrock is sufficient.

ACKNOWLEDGEMENTS

Authors thanks to Grant Agency of Slovak Republic (project VEGA MŠ SR and SAV No. 2/0065/11 and APVV 0663-10) for financial support. Sorbent Bayoxide E33 for sorption experiments was provided by EUROWATER, spol. s.r.o., Bratislava (www.eurowater.sk), which deals with the technologies for treatment of drinking water.

REFERENCES

- Akter, A., Ali, M.H.**, 2011. *Arsenic contamination in groundwater and its proposed remedial measures*. International Journal of Environmental Science and Technology, 8, 433-443.
- Andráš, P., Nagyová, I., Samešová, D., Melichová, Z.**, 2012. *Study of Environmental Risks at an Old Spoil Dump-Field*. Polish Journal of Environmental Studies, 21, 1529-1538.
- Aschenbrenner, Š., Turisová, I. & Štrba, T.**, 2011. *Flora and vegetation of dump-field in Špania Dolina*. Acta Universitatis Matthiae Belii, ser. Environmentálne manažérstvo, 13(2), 48-57. (in Slovak)
- Bailey, S. E., Olin, T. J., Bricka, R. M., Adrian, O. A.**, 1999. *A review of potentially low-cost sorbents for heavy metals*. Water Research, 33, 2469-2479.
- Bhattacharyya, K.G. & Gupta, S.S.**, 2006. *Kaolinite, montmorillonite, and their modified derivatives as adsorbents for removal of Cu (II) from aqueous solution*. Separation and Purification Technology, 50, 388-397.
- Cheng, S.**, 2003. *Heavy metals in plants and phytoremediation*. Environmental Science and Pollution Research, 10, 335-340.
- Dubiel, J., Aschenbrenner, Š. & Štrba, T.**, 2011. *Heavy metals in the mining area Špania Dolina and their potential*. In: Interactive Conference of Young Scientists 2011. Preveda, Bratislava, p 87 (in Slovak)
- Government Regulation of Slovak Republic (2010) No. 269**, which setting requirements on good state of water (Collection of Laws), part 106, pp. 2186-2287. (in Slovak)
- Government Regulation of Slovak Republic (2010) No. 496**, which changes and completes Government Regulation of Slovak Republic No. 354/2006, which setting requirements on water for human consumption and control quality of water for human consumption. (Collection of Laws), part 188, pp. 4207-4225. (in Slovak)
- Horwitz, W.**, 1982. *Evaluation of Analytical Methods Used for Regulation of Foods and Drugs*. Analytical Chemistry, 54, 67A-76A.
- Hrivňáková, K., & Makovníková, J., (ed.)** (2011). *Uniform techniques of analysis of soils*. Soil Science and Conservation Research Institute, Bratislava, 136 p. (in Slovak)
- Ilavský, J.**, 2008. *Removal of antimony from water by sorption materials*. Slovak Journal of Civil Engineering, 2, 1-6.
- Jeleň, S., Galvánek, J., Andráš, P., Bendík, A., Beláček, B., Bozalková, I., Gaál, E., Gajdoš, A., Háber, M., Končný, V., Križani, I., Luptáková, L., Mazúrek, J., Michal, P., Soták, J., Staňová, S., Šimo, V., Šurka, J. & Wetter, R.**, 2009.

- Educational-cognitive guide to geological and geographical locations of Central Slovakia. Geological Institute of the Slovak Academy of Sciences, Bratislava. 320 p. (in Slovak)
- Kaniansky, D., Zelenská, V. & Baluchová, D.,** 1996. *CZE of inorganic anions with conductivity detection*. *Elektrophoresis*, 17, 1890-1897.
- Law of Slovak Republic (2004) No. 220** on the conservation and use of agricultural land and on the Law No. 245/2003 concerning integrated pollution prevention and control of the environment and amending certain laws. (Collection of Laws), part 96, pp. 2278-2315 Bratislava (in Slovak)
- Mazúrek, J.,** 1989. *Mining natural-technical system in mining Špania Dolina - Old Mountain*. *Prírodné vedy*, 8, 23-68. (in Slovak)
- Mocák, J., Bond, A.M., Mitchell, S. & Schollary, G.,** 1997. *A statistical overview of standard (IUPAC and ACS) and new procedures for determining the limits of detection and quantification: Application to voltammetric and stripping techniques (Technical Report)*. *Pure and Applied Chemistry*, 69, 297-328.
- Mohan, D. & Pittman, Ch.U. Jr.,** 2007. *Arsenic removal from water/wastewater using adsorbents - A critical review*. *Journal of Hazardous Materials*, 142, 1-53.
- Mohiuddin, K.M., Ogawa, Y., Zakir, H.M., Otomo, K. & Shikazono, N.,** 2011. *Heavy metals contamination in water and sediments of polluted urban river in developing country*. *International Journal of Environmental Science and Technology*, 8, 723-736.
- Mohiuddin, K.M., Zakir, H.M., Otomo, K., Sharmin, S. & Shikazono, N.,** 2010. *Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river*. *International Journal of Environmental Science and Technology*, 7, 17-28.
- Odukoya, A.M. & Abimbola, A.F.,** 2010. *Contamination assessment of surface and groundwater within and around two dumpsites*. *International Journal of Environmental Science and Technology*, 7, 367-376.
- Rusková, J.,** 2003. *The impact of mining activities on the health of inhabitants in the village Špania Dolina*. *Acta Universitatis Matthiae Belii, Séria Environmentálna Ekológia, IV/V*, 22-27. (in Slovak)
- Rusková, J., Rusko, I., Andráš, P., Jeleň, S. & Gajdoš, A.,** 2003. *The environmental load of the country after heavy metals extraction Cu-Ag ores around Špania Dolina*. In *Geochemistry 2003, UK, Bratislava* pp. 60-65. (in Slovak)
- Sakan, S., Gržetić, I. & Dordević, D.,** 2007. *Distribution and fractionation of heavy metals in the Tisa (Tisza) River sediments*. *Environmental Science and Pollution Research*, 14, 229-236.
- Slovak Technical Standard STN 75 7485. (2007)** Water quality, determination of silicates. Spectrophotometric determination of silicate with ammonium molybdate. Slovak Standards Institute, Bratislava. (in Slovak), 8 p.
- Stuckman, Y., Lenhart, J.J. & Walker, H.W.,** 2011. *Abiotic properties of landfill leachate controlling arsenic release from drinking water adsorbents*. *Water Research*, 45, 4782-4792.
- Wahlen, R. & Woods, G.,** 2012. Application of Compound Independent Calibration Software to Arsenic Speciation (by HPLC-ICP-MS). In: *Handbook of Hyphenated ICP-MS Applications*. 2nd edn. Agilent Technologies.
- Zandsalimi, S., Karimi, N. & Kohandel, A.,** 2011. *Arsenic in soil, vegetation and water of a contaminated region*. *International Journal of Environmental Science and Technology*, 8, 331-338.
- Zobrist, J., Sima, M., Dogaru, D., Senila, M., Yang, H., Popescu, C., Roman, C., Bela, A., Frei, L., Dold, B. & Balteanu, D.,** 2009. *Environmental and socioeconomic assessment of impacts by mining activities - a case study in the Certej River catchment, Western Carpathians, Romania*. *Environmental Science and Pollution Research*, 16, 14-20.

Received at: 19. 07. 2013

Revised at: 24. 09. 2013

Accepted for publication at: 26. 09. 2013

Published online at: 28. 09. 2013