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COMPARATIVE STUDY OF Cu, As AND Sb TOXICITY BETWEEN DUMP-FIELDS OF ABANDONED Cu-DEPOSITS ĽUBIETOVÁ AND ŠPANIA DOLINA (CENTRAL SLOVAKIA)

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Abstract: Ľubietová and Špania Dolina mining areas belong to the most important Central European historic Cu-deposits. The ore mineralization contain not only Cu but also toxic As and Sb which contaminate the country components. The Eh/pH diagrams enable informative indication of As speciation in sediments and soils in the surrounding of the abandoned deposits. The most important As form in technogenous sediments of both studied ore fields Ľubietová and Špania Dolina is the less toxic As^{5+} speciation. The Eh/pH stability diagrams indicates predominantly occurrence of $Fe(OH)_4As$, H_2AsO^{4-}, $HAsO_4^{2-}$ forms. Only in several few samples of technogenous sediments and soils As falls to the As^{3+} stability fields, e.g. to the $Fe^{2+} + As^{3+}_{(aq)}$ field. Arsenic content in water depend on arsenopyrite *FeAsS* and tetrahedrite $(Cu,Fe,Ag,Zn)_{12}(AsSb)_4S_{13}$ decomposition. Its redeposition is realized by adsorption on Fe-oxyhydroxides surface. Arsenic content is controlled also by next degradation of secondary As phases under changed thermodynamical conditions. Both main As speciations (As^{3+} and As^{5+}) occurs in groundwater approximately in a balanced portions. Arsenic in samples falls mainly to the $H_2As^{5+}O^{3-}$, $HAs^{5+}O_4^{2-}$ and $H_3As^{3+}O_3^0$ stability fields. Arsenic speciation in surface water from both localities is in comparison with those of groundwater more close to the less toxic form As^{5+} (H_2AsO^{3-}, $HAsO_4^{2-}$, $H_3AsO_3^0$). Technogenous sediments and waters at Ľubietová and Špania Dolina are also contaminated by Sb. In sediments and soil from Ľubietová Sb prevail in less toxic degree Sb^{5+} and is present in SbO^{3-} form, while in dump-field and in tailings at Špania Dolina one part of samples characterized by Eh<0,1 values is concentrated in Sb^{3+} stability fields of valentinite Sb_2O_3 and stibnite Sb_2S_3. Arsenic and antimony in surface waters and groundwater at both localities indicate application of Eh/pH stability diagrams presence of Sb predominantly in Sb_4O_6 and Sb_2O_3 forms, it means in form of more toxic Sb^{3+}. The samples from Špania Dolina are in comparison with those from Ľubietová mowed down to more negative Eh values.

Keywords: Cu, As, Sb, Eh/pH stability diagrams, speciation, toxicity

1. INTRODUCTION

The surroundings of Ľubietová and Špania Dolina were the areas of the Cu ore mining as early as in the pre-historical period. By the end of 15th century, most of the mines were bought by the Fugger family with support of Ján Thurzo. In this period the local mines were parts of the most important Cu mines in Austria-Hungary and Europe. The last mine was closed during the World War I. Nowadays only extensive dump fields can be found on the locality of old mines (Andráš et al., 2009).

Changes of pH and Eh in technogenous sediments result in release of heavy metals (especially Cu, Fe, Cd, As, Sb, Pb, Zn, Mn, Ni, Co) from the solid phase where they are present in the form of minerals with heavier solubility or in sorption complex, to the ground or surface water. Mobility of heavier metals in solutions and complex compounds is also evidence of origin of numerous secondary minerals: carbonates, orthophosphates, sulphates and oxides (Andráš et al., 2009). The above-mentioned secondary mineral phases came into existence primarily in the process of precipitation from solutions circulating in technogenous sediments and soils, but also a result of primary minerals oxidation. Their origin controls and slows down migration of heavy metals which is a result of their stability in surface conditions (Ashley et al., 2003).

According to Andráš et al., (2008) the most important toxic metals at the study localities are Cu, As and Sb, from the point of view of environmental risk. Most of Cu in the area of Ľubietová and Špania Dolina come from chalcopyrite *CuFeS*$_2$ and prevailing part of As and Sb come from tetrahedrite $(Cu,Fe,Ag,Zn)_{12}(AsSb)_4S_{13}$.

Findings on various extent of toxic effects and qualitatively different influences of the toxic metals individual compounds onto live organisms resulted in attempts to specify forms of toxic metals. From the point of view of the living environment Cu, As and Sb present a serious danger as a consequence of a highly-toxic nature of their compounds.

2. MATERIALS AND METHODS

90 samples of technogenous sediments were taken from the surface of dump fields Podlipa and Reiner in Ľubietová (Fig. 1) on the whole surface in regular network. The number of samples taken from the dump field Maximilián (Fig. 2) in Špania Dolina was 81. Each sample was is present mixture of 8 – 10 smaller samples of 2 kg weight. After subsequent quartation of the material the resulting sample was approx. 3 kg. The samples of the surface and draining waters in the area of Ľubietová were taken from mountain streams and marshes in the vicinity of mining dumps and from the stream running through the village (Fig. 1). The map of sampling points of water and sediment samples in the area of Špania Dolina is illustrated in the figure 2.

The values of pH and Eh were determined in the groundwater and surface waters of the dump fields wider surroundings and in draining waters percolating through dump sediments „in situ“ directly in the process of sampling. The above-mentioned values were measured in the suspension of 20 g of the sample and 50 ml of distilled water, or more precisely 1M KCl according to the VanReeuwijk ´s methodology (1995) applied for earths and soils with the help of pH meter WTW Multi 3420 with combined redox-electrode SenTix ORP with referential system Ag/AgCl containing electrolyte 3 M KCl. Monitoring places are shown in figures no. 1 and 2.

In field conditions the sediment samples were pre-homogenized and large particles were removed out of them. In the laboratory conditions we were homogenizing the samples or lyophilizing as the case may be. On technical scales we weighed 20 g of the sample dried on air and sieved through the shaker screen with 20-millimeter- holes. We poured the sample into the 200 ml flask and poured it with 50 ml of distilled water. The flask was closed with the rubber and we were shaking with it for 5 minutes. After we stopped shaking the flask content was poured into the 200 ml beaker and while the suspension was constantly mixed the value of Eh was measured.

The samples of technogenous sediments and soils were subject to analysis for heavy metals and numerous other elements. The analysis was taken from the weight of 1 g of samples. The samples specified for determination of As and Sb were melted down while using the addition of mixture of tetraborate and Li-tetraborate and subsequently they were dissolved in the diluted nitric acid.

For determination of Cu it was necessary to lye 0.5 g of the sample with a hot nitrohydrochloric acid. Analysis of individual elements was implemented with the help of the ICP–MS method in laboratories of ACME Analytical Laboratories Vancouver Ltd. Canada.

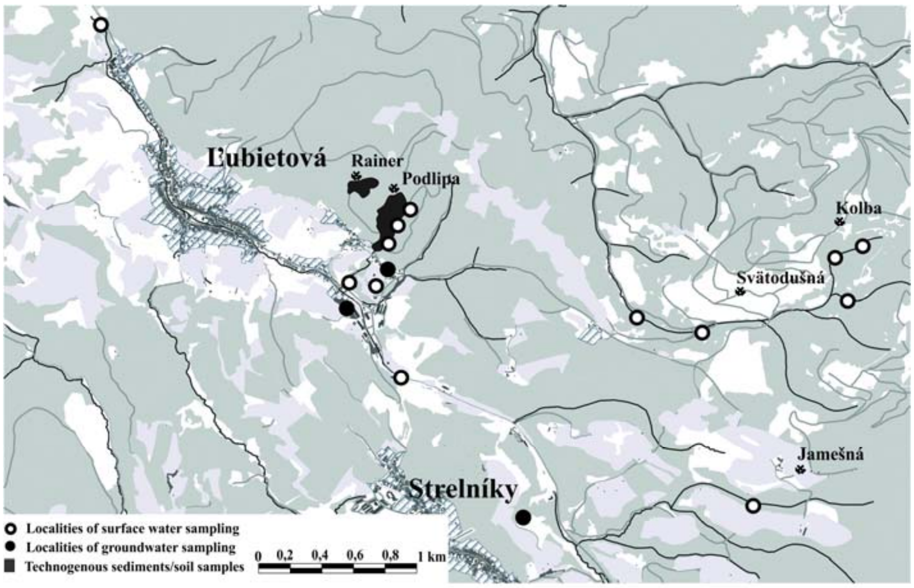

Figure 1. Ľubietová: Sampling location of technogenous sediments/soils and water.

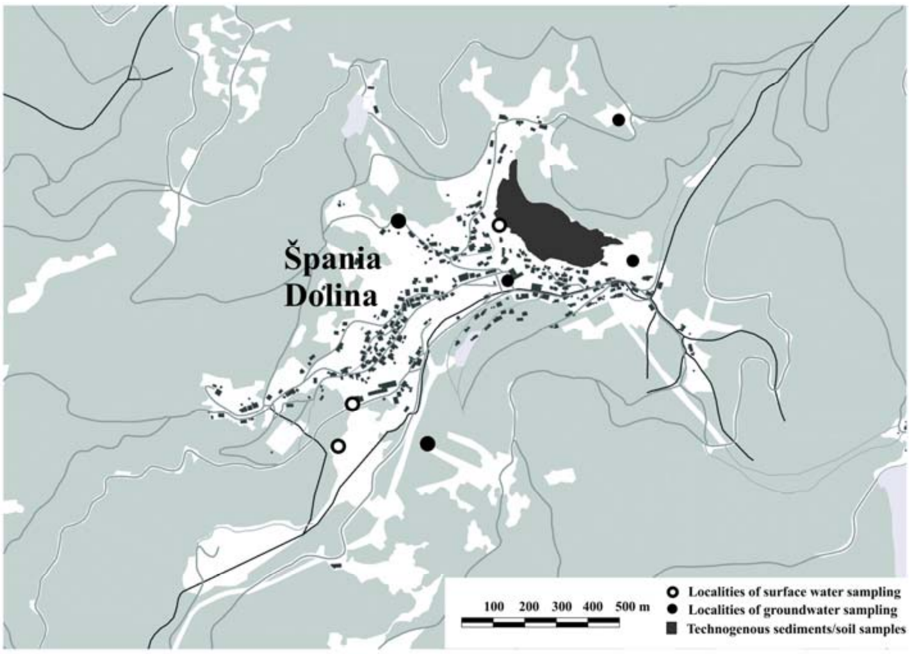

Figure 2. Map of sampling sites of sediment/soil and water in the Špania Dolina.

Resulting values of determination of individual metals represent mean values from two checking parallel determinations. The samples of surface and draining waters were stabilized with 10 $ml.l^{-1}$ HNO_3 and analyzed with the help of the atomic absorption spectrometric analysis with hydride system in the Research Institute of Water Economy in Bratislava.

3. RESULTS

Concentrations of Cu, As and Sb in technogenous sediments, soils, groundwater, surface and draining waters at the study localities are greatly variable (Table 1). Such irregularity of contents is a result of an uneven distribution of sulphide minerals and secondary minerals coming into existence from degraded primary minerals in the process of weathering.

Copper in technogenous sediments/soil from the locality of Ľubietová belongs in pH-Eh diagram according to Faithorne et al., (1997; (Fig. 3A) predominantly to the stability field Cu^{2+} (Fe_2O_3), and only the insignificant part of samples show tendency to Cu^{3+} speciation in the form of Cu_2O_3 and as elementary Cu^0. In Špania Dolina the part of samples are situated also in stability fields of $Cu_2SFe_2O_3$, CuS + FeS_2 (pyrite) and $CuFeS_2$ (i.e. in the field of chalcopyrite). In groundwater and surface water on the deposit of Ľubietová the Cu is prevailing in the form of $Cu_2SFe_2O_3$, and less also in the form of elementary Cu^0 with limonite Fe_2O_3 and Cu_2S with pyrite FeS_2. Data of pH vs. Eh of both the groundwater and surface waters from Špania Dolina move the samples beyond the pH-Eh diagram for Cu-Fe-S- H_2O system (Fig. 3B).

Graphs A and B (Figs. 4 and 5) provide documentary evidence of arsenopyrite weathering in surface conditions under presence of Fe^{2+} (aq) and soluble As^{3+}-compounds. These compounds can be found in broad range of pH from 4 to 10. Individual As^{3+} compounds are changed depending on pH, whereas the most stable speciation of arsenic (As^{3+}) occurrence in the form H_3AsO_3.

In case we apply results of Eh and pH specification in sediments/soil and water from localities of study onto the pH-Eh stability diagrams of the As-Fe-O-S system as elaborated by Vink (1996) and Pokrovski et al., (2002), we can see that As in samples of technogenous sediments and soil preferentially come under stability fields H_2AsO_4 in Ľubietová (Fig. 4) and in Špania Dolina (Fig. 5), thus this is As in oxidation degree As^{5+}. Špania Dolina is also a place where occurrence of samples with less importance was recorded. These samples belong to the stability field of auripigment – As_2S_3 *a* AsS_2^- (Fig. 5). Other forms of occurrence are rare.

According to Vink (1996) As can be found in the groundwater of Ľubietová in the form of $H_3AsO_3^0$, whereas most of samples belong to the stability fields of the graph on figure 4 A. In pH-Eh diagram, according to Pokrovský et al., (2002) As falls within the fields of $HAsO_4^{2-}$ and less to the As field in the oxidation grade As^{3+}: H_3AsO_3 (Fig. 4 B).

The majority of groundwater samples from Špania Dolina show tendency toward stability field of As and AsH_3(aq) (Fig. 5 B).

Table 1. The concentrations range of Cu, As and Sb in technogenous sediments/soils, groundwater and surface water at locations Ľubietová and Špania Dolina

Component	Ľubietová			Špania Dolina		
	Cu	As	Sb	Cu	As	Sb
Technogenous sediments/soil (mg.kg^{-1})	621 – 16 250	10 – 504	7 – 138	386 – 4630	37 - 983	46.3 – 1403
Groundwater (mg.L^{-1})	6 – 131	0 – 61	6 - 131	0 – 311	3 – 28	0 - 311
Surface and drainage water (mg.L^{-1})	5 – 14 000	<1.0 – 61.5	0 – 14 000	22 – 429	0 – 150	22 - 429

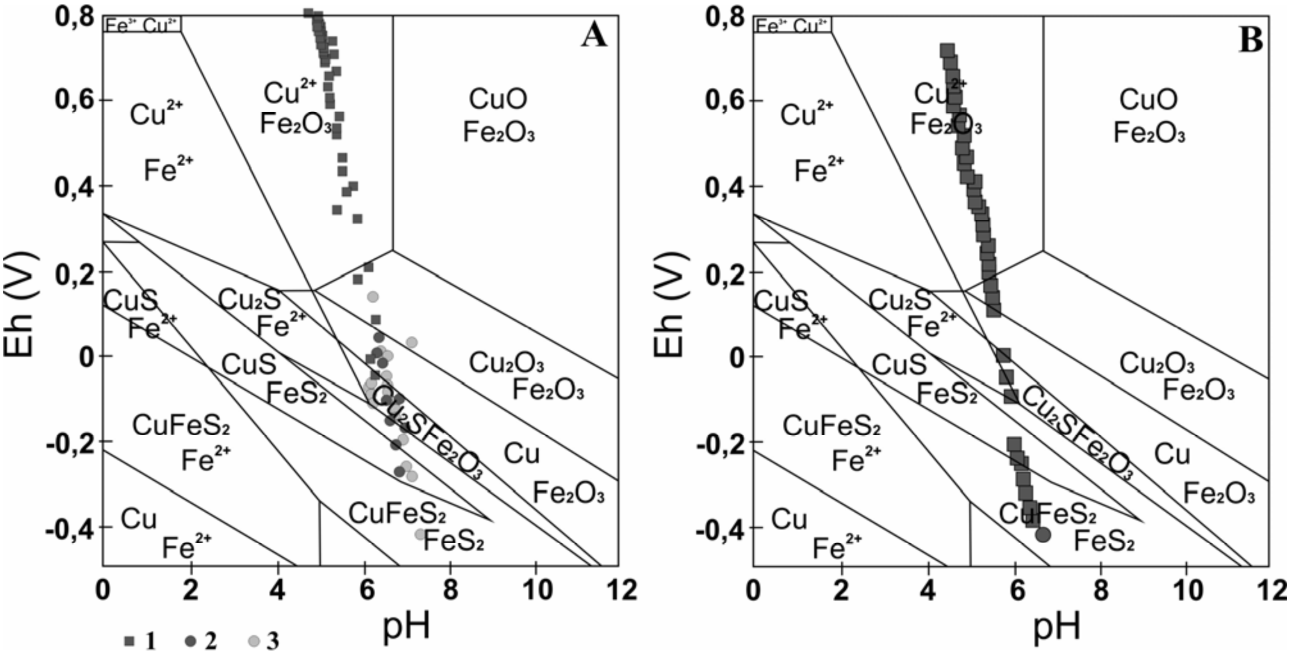

Figure 3. Eh/pH stability diagram for the system Cu-Fe-S- H_2O (edited by Faithorne et al., 1997). A- Ľubietová, B – Špania Dolina; Explanatory notes to figures 3 –7: 1 – technogenous sediments and soils, 2 – groundwater, 3 – surface waters.

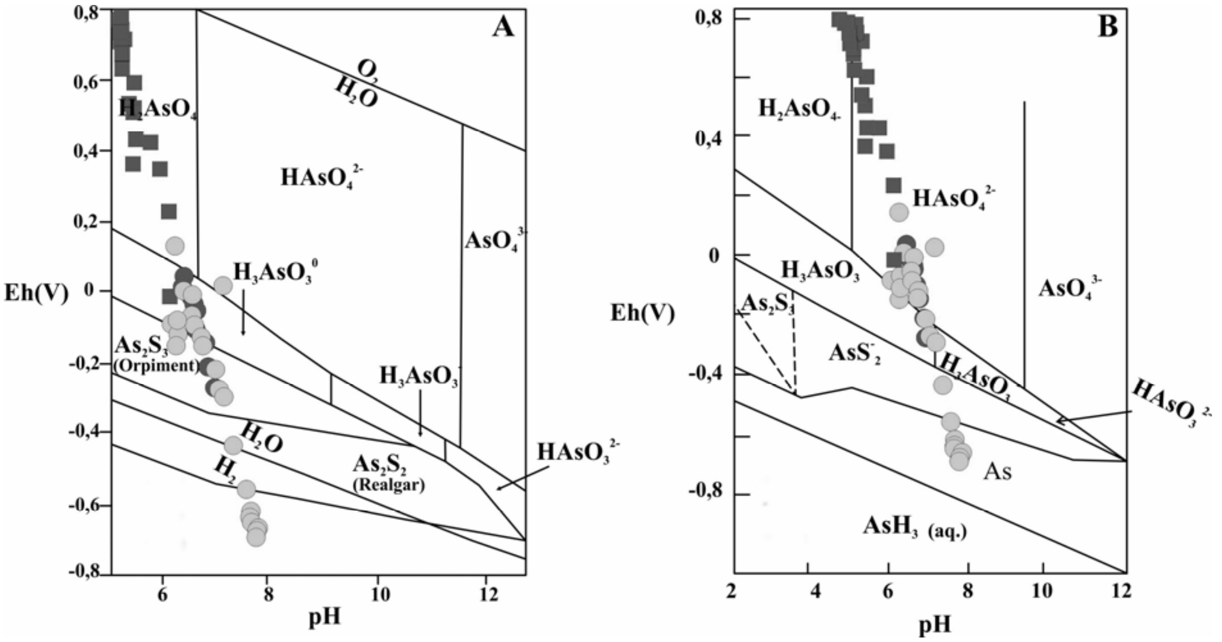

Figure 4. Eh/pH stability diagram for the system As-Fe-O-S; A - Vink (1996); B - Pokrovski et al., (2002); Ľubietová, dump fields Podlipa and Reiner.

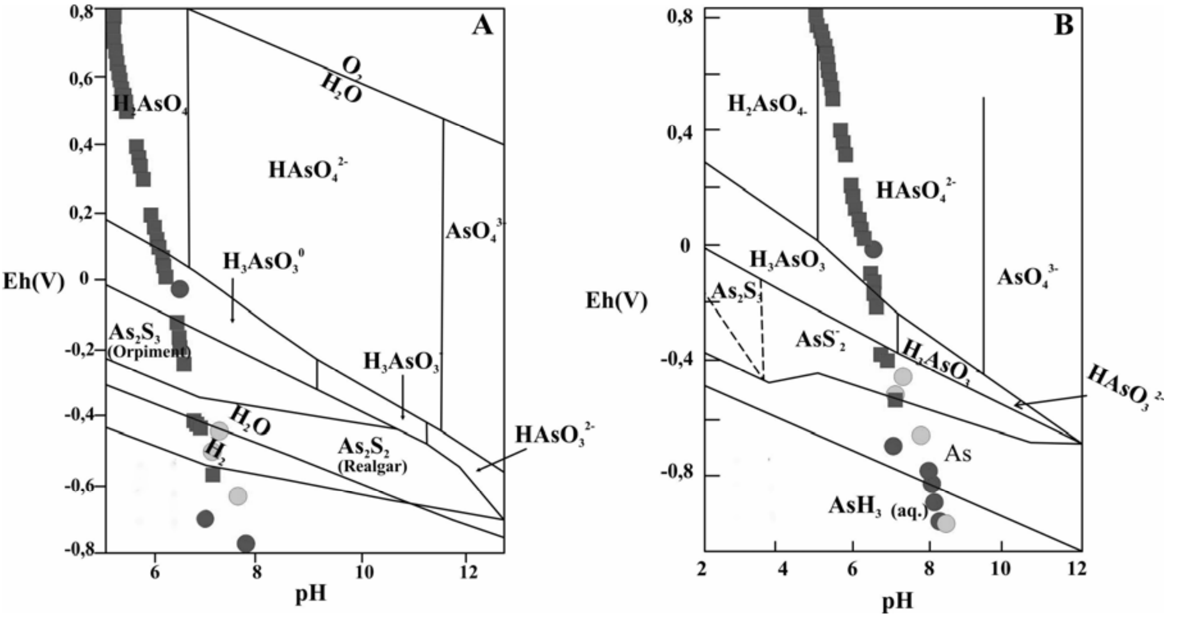

Figure 5. Application Eh/pH stability diagram for the system As-Fe-O-S
A - Vink (1996); B - Pokrovski et al., (2002) for locality Špania Dolina.

The surface water samples from Ľubietová belong predominantly to the field of H_3AsO_3(aq). As_2S_3 (Fig. 4 A), or more precisely to the fields of $HAsO_4^{2-}$ (As^{5+}) and H_3AsO_3(As^{3+}). Several samples belong also to the stability field of elementary As^0 (Fig. 4 B). Situation in Špania Dolina is different. As from the surface waters belongs to the field of AsS_2, As and AsH_3(aq) (Fig. 5 B).

In case we apply the results of groundwater Eh and pH specifications to the Eh-pH stability diagrams of the system of As-Fe-O-S as elaborated by (Ryu et al., 2002; Fig. 6), we can see that As in samples of technogenous sediments and soil in Ľubietová almost entirely comes under the most stable field of $Fe(OH)_4{\cdot}As^{5+}$(aq) from the point of view of thermodynamics (Fig. 6 A), and in Špania Dolina is comes to the most stable field of $Fe(OH)_4{\cdot}As^{5+}$(aq) from the point of thermodynamics in most cases (Fig. 6 B).

In Špania Dolina contrary to Ľubietová the occurrence of As in speciation As^{3+} was also recorded in several few samples both in the form of As^{3+}(aq) and in the form of arsenopyrite *FeAsS* (Fig. 6 B).

Most of water samples from Ľubietová belong to the stability fields of As^{3+} (Fig. 6 A). Arsenic in oxidation degree of As^{5+} can be found only in two surface water samples.

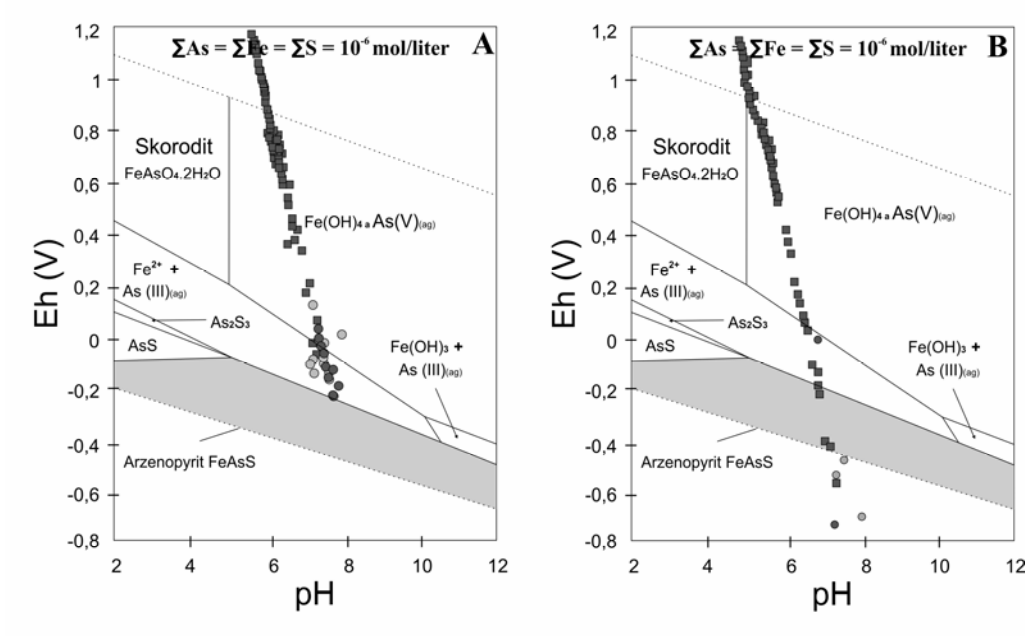

Figure 6. Eh/pH stability diagram for the system Fe-H_2O-S (Ryu et al., 2002);
A - Ľubietová, dump-fields Podlipa a Reiner, B - Špania Dolina.

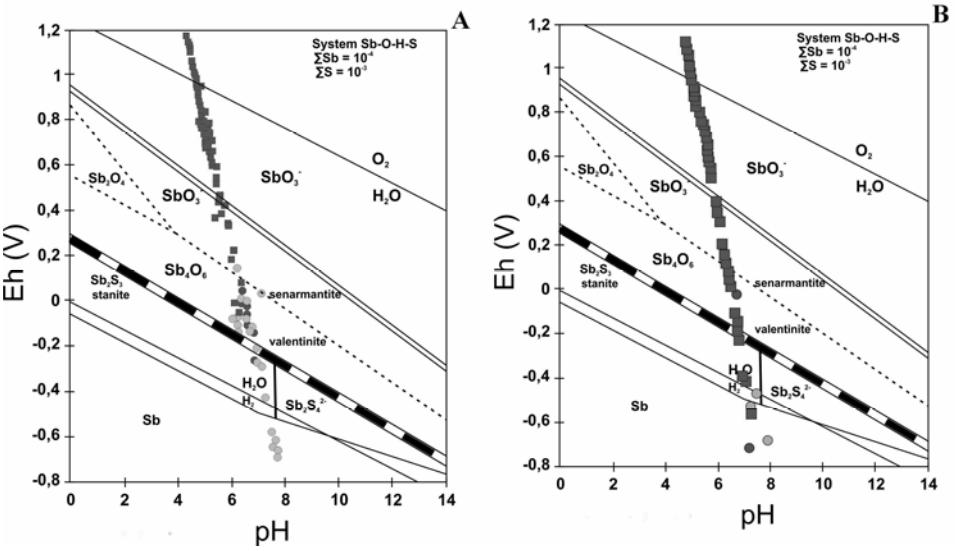

Figure 7. Eh/pH stability diagram for the system Sb-O-H-S (Vink, 1996);
A – Ľubietová, B – Špania Dolina.

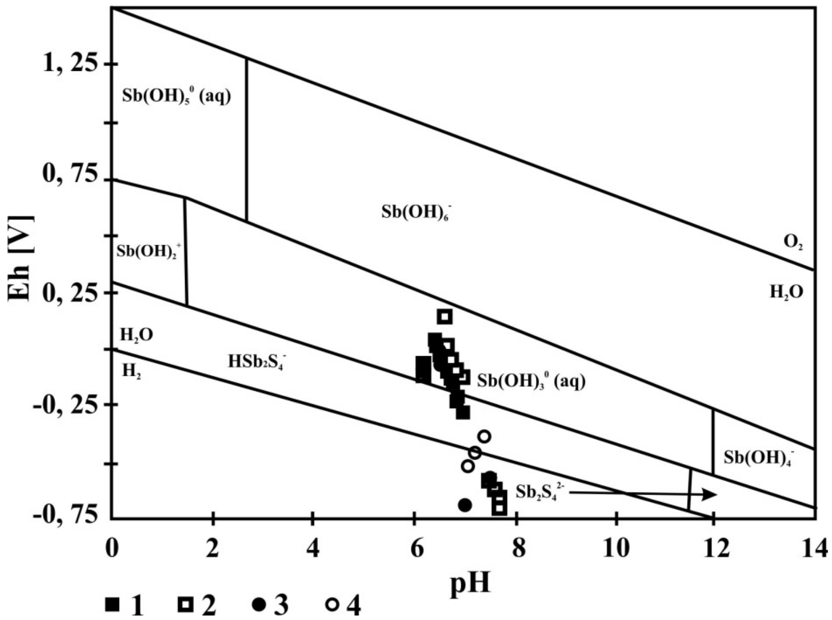

Figure 8. Eh/pH diagram for dominant forms of Sb in aqueous medium at 25°C and at concentration of dissolved Sb $2{,}9.10^{-10}$mg.l^{-1} (Krupka & Serne, 2002).
Explanatory notes: Ľubietová 1 – groundwater, 2 – surface water, Špania Dolina 3 – groundwater, 4 – surface water.

Most of water samples from Špania Dolina are characterized by lower values of Eh (pod -0.4) and alike the samples from Ľubietová they belong beyond the range of pH-Eh diagram (Fig. 6 B). In Ľubietová and Špania Dolina (Fig 7 A, B), most of Sb in sediments and soils is also present in the form of Sb^{5+} (SbO_3^-), but a smaller part of samples characterized by values of Eh <-0.1 belong to the stability fields of Sb^{3+}, i.e. the fields of valentinite and stibnite. Only one sample from Špania Dolina is situated into the stability field of elementary Sb (Fig. 7 B).

Conditions of groundwater and surface waters at study localities mostly indicate presence of Sb_4O_6 and Sb_2O_3 (Fig. 7 A, B) and Sb $(OH)_3^0$(Aq), $HSb_2S_4^-$ and Sb_2S_4 forms (Fig. 8; Krupka & Serne, 2002), thus more toxic Sb^{3+}, whereas the samples from Špania Dolina are in relation to the samples from Ľubietová (especially on the Vink´s diagram, Fig. 7) moved towards more negative values of Eh (Figs. 7, 8).

4. DISCUSSION

Copper belongs to elements that are essential for human on one side, and on the other side they are potentially toxic (Cu is hindering/blocking the membrane process, (Kafka & Punčochárová, 2002). In nature it can be found in the form of sulphides: covelite *CuS*, chalkocite *Cu₂S*, chalcopyrite *CuFeS₂*, bornite $CuFeS_3$, in the form of oxides and hydroxide-carbonates: tenorite CuO, kuprite Cu_2O, malachite $Cu_2CO_3(OH)_2$, azurite $Cu_3(CO_3)_2(OH)_2$ (Bencko et al., 1995).

According to Pitter (1990) the elementary hydrated ion Cu^{2+}, carbonate complexes $[CuCO_3(aq)]^0$, $[Cu(CO_3)_2]^{2-}$ and hydro-complexes $[CuOH]$, $[Cu(OH)_2(aq)]^0$, $[Cu(OH)]^{3-}$ and $[Cu(OH)_4]^{2-}$ can be found in natural waters from soluble forms of Cu. Study of speciation of Cu at Ľubietová and Špania Dolina localities investigated pointed out to presence of Cu especially in oxidation degree of Cu^{2+} in co-existence with oxides of Fe (limonite Fe_2O_3) in technogenous sediments and soils, then less in the oxidation degree of Cu^{3+} (Cu_2O_3), or as elementary Cu^0 as the case may be. Occurrence of all above-mentioned mineral forms was also confirmed by the mineralogical research (Andráš et al., 2008).

Copper in the waters on Ľubietová deposit is prevailing in the form of $Cu_2SFe_2O_3$, and its fewer amounts are also in the form of Cu^0 (with limonite Fe_2O_3) and Cu_2S (with pyrite FeS_2). Occurrence of limonite (hydrogoethite $Fe_2O_3{\cdot}nH_2O$) in the groundwater and surface waters was identified by X-ray diffraction analysis of water evaporates (Andráš et al., 2008). Occurrence of pyrite was not confirmed; however its presence is also possible with respect to mineral composition of ores.

Arsenic in its pure form can be found out rarely, and in natural conditions it appears in oxidation degree As^{-3} As^0, As^{3+} and As^{5+}. Among As inorganic forms we can find arsenates and arsenites in the nature most often, whereas arsenites present more dangerous form since they are more toxic and more mobile (Lin & Puls, 2000). Both of the above-mentioned forms can form methyl-compounds, due to which they change over to less toxic forms (Matschullat, 2000). Arsenic can be found out most frequently in the form of complex ions (Prundeanu & Buzgar, 2011; Fergusson, 1990). The most mobile form is As^{3+}. In the form of cation As^{3+} it often represents Fe^{3+} or Al^{3+} in crystal lattice of silicates or in ferrous oxides (Marsina, 1999). It can oxidize into less mobile form of As^{5+} (Bowel, 1994; Inskeep et al., 2002).

The main source of As is in the form of sulphide minerals in which it is present in elementary form or in the form of alloys, in arsenides of Cu, Ni, Pb, Fe and above all, in sulphides (arsenopyrite, cobaltite, proustite, enargite, tennantite), sulphosalts of metals such as Cu, Pb, Fe, Ag, Ti, in oxides (e.g. arsenolite As_2O_3), arsenites, arsenates, but marginally in silicates, too. According to traditional opinions the arsenic/arsenical ore minerals are easy to oxidize in the process of weathering/disintegration while As changes over from the forms with a lower oxidation degree (As^0, As^+, As^{3+}) to As^{5+}, forming compounds of arsenic acid. This acid is water-soluble but only very seldom it can migrate for longer distances because it rapidly reacts with metal cations and As bonds in the form of various arsenates (Lin & Puls, 2000). New thermodynamic data (Pokrovski et al., 2002) refer to a higher stability of arsenopyrite in surface conditions as anticipated in the past.

Through its oxidation in presence of water the following elements come into existence: As^+, As^{3+}, As^{5+}, sulphates, tio-sulphates, and polysulphides (Nesbitt et al., 1995). The most stable product of arsenopyrite oxidation is arsenate Fe^{3+} scorodite $FeAsO_4{\cdot}2H_2O$ (Dove & Rimstib, 1985).

The O'Neill´s data (1990) telling that As does not form separate cations in soils and sediments, but it appears in the form of arsenates (As^{5+}) and partially also in the form of more mobile and more toxic arsenates (As^{3+}), is in compliance with the results from Ľubietová and Špania Dolina. As^{5+} is also present in the form of $(H_2AsO_4)^-$ and As^{3+} in the form of $(H_3A_3O_3)^0$, whereas $(H_3AsO_3)^0$ is dominant at low pH and low Eh, and the arsenic mobility is directly proportional to As concentration and inversely related to time and concentrations of Fe and Al.

If we take theoretical grounds of Vink ´s work (Vink, 1996) into account, and if we apply them for conditions of dump fields at surrounding of Ľubietová and Špania Dolina, we can express a presumption that a considerable part of As in draining waters percolating technogenous sediments of mining landfills relates with oxidation of minerals containing As, especially however tetrahedrite and arsenopyrite. It is however regulated by As sorption to hydrogoethite and probably Fe oxyhydroxides as well (compare Andráš et al., 2008) and decomposition of secondary phases on changes of pH-Eh conditions.

Arsenic toxicity increases in the sequence as follows: organic compounds of As^{5+} - arsenates, inorganic compounds containing As^{5+}, organic compounds of As^{3+} – arsenites, inorganic compounds of As^{3+}, whereas compounds of As^{3+} are approximately five times even ten times more toxic than the compounds of As^{5+} (Virčíková & Pálfy, 1997; Lin & Puls, 2000), but As^{5+} has stronger carcinogenic effects. Both As^{3+} and As^{5+} may form methylic compounds (mono- di- and trimethyl-arsenic) both in the terrestrial and marine environment, through which they change over to less toxic forms, (Matschullat, 2000; Marin et al., 2010). Since pH-Eh diagrams indicate possibility of occurrence of more toxic speciation of As^{3+} at most of water samples from both study localities, i.e. of the surface and groundwater, it will be necessary to pay an increased attention to this issue in the future.

Antimony can be found in the nature in particular in the form of sulphides or oxides Sb^{3+} and Sb^{5+} as the case may be, and most frequently as antimonious oxide Sb_2O_3, Sb_2S_5 (golden sulphur) and antimonious chloride $SbCl_3$ (Bencko et al., 1995). Mechanism of oxidation of Sb^{3+} to Sb^{5+} is regulated/controlled by pH. This process is slower than in oxidation of numerous other metals (e.g. Mn, Fe...). Sb^{3+} can be also stabilized as a result of origin of complex compounds (Leus & Johnson, 2005). In the soil it is able of strong bonding to particles containing Fe, Mg or Al. It gets from soil even to the food chain, (Smichowskia, 2008).

Antimony compounds are a little less toxic than As compounds. Due to effects Sb is similar to As but Sb poisoning symptoms are milder especially due to the fact that its compounds are being absorbed more slowly. The compounds soluble in digestive tract hydrolyze, and insoluble compounds are little toxic. Elementary Sb is more toxic than its salts. Antimony compounds of Sb^{3+} are ten times more toxic than antimonic compounds of Sb^{5+} (Smichowskia, 2008), and methyl forms of Sb are less toxic than its inorganic salts. Sb^{3+} is strongly carcinogenic (Melicherčík & Melicherčíková, 1997).

In natural conditions, both Sb^{3+} and Sb^{5+} exist in soluble forms: Sb^{5+} as $Sb(OH)_6^-$ and Sb^{3+} in the form of $Sb(OH)_3$ (Filella et al., 2002). Vink (1996), on the contrary, states the hydroxide form of $Sb(OH)_3$ occurrence is metastable and that is why he does not take it into consideration in his study. SbO_3^- prevails over the solid Sb_2O_5, which is not a natural material and it is a metastable compound. A considerably extensive field of SbO_3^- explains both origin of numerous minerals (tripuhyite $FeSbO_4$, bindheimite $Pb_2Sb_2O_6(O,OH)$, romeite $(Ca,Fe,Mn,Na)_2(Sb,Ti)_2O_6(O,OH,F)$, melanostibite $MnSb_{0.6}Fe_{0.4}O_3$ and bystromite $MgSb_2O_6$), but also relative mobility of Sb.

Antimony in waters usually appears as Sb^{3+}, Sb^{5+}, $CH_3SbO(OH)_2$ and $(CH_3)_2Sb(OH)$. According to Roddick-Lanzilott et al., (2002), Smedley & Kinniburgh (2002) as well as according to Vink (1996) Sb is in aquatic environment less mobile than As, and at low pH it is quickly eliminated from solution as a result of adsorption to hydrogoethite, Fe-oxyhydroxides, or it enters scorodite in Fe-rich systems (Filella et al., 2002), as the case may be. Both Sb^{3+} and Sb^{5+} create complex compounds on the surface of hydrogoethite and Fe-hydroxides, due to which it can be supposed), that a part of Sb is present in the aqueous solution in the form of Sb_4O_6 and SbO_3^- particles < 0,4 μm. This effect was described also by Andráš et al., (2010) on the localities investigated. The best absorption of Sb^{3+} takes place at pH 3 – 12, while the maximal sorption of Sb^{5+} takes place at pH < 7. In the course of several days oxidation of Sb^{3+} can take place on the surface of hydrogoethite and Fe-hydroxides especially within the pH values ranging from pH 3 to 5.9. At pH ~ 9 it mobilizes and releases to the solution while at pH < 7 it stays bonded on the surface of Fe-oxides (Leus et al., 2006).

In both Ľubietová and Špania Dolina the major part of Sb in sediments and soils is present in the form of less toxic speciation of Sb^{5+} (SbO_3^-). On the basis of pH-Eh diagrams, the more toxic form of Sb^{3+} is prevailing in waters. This form of Sb can be anticipated especially in groundwater and in waters with lower values of Eh (<0.1), whereas the samples from Špania Dolina are moved towards more negative Eh values against the samples from Ľubietová.

Brookins (1986) presumes that Sb is non-mobile in oxidation conditions and it precipitates in the form of Sb_2O_4 (cervantite) and/or Sb_2O_5. If Sb is able of relatively good sorption onto the surface of Fe oxides and oxyhydroxides, it can be presumed that part of Sb in the aqueous solution is present in the form of particles of goethite < 0.4 μm. Even Andráš et al., (2008) has pointed out to the fact that antimony precipitates relatively fast on the deposits in question and is immobilized.

However, it is necessary to state that results of pH-Eh diagrams have only informative character since they are elaborated for ideal conditions of closed systems that cannot be found in nature. Therefore it is necessary to specify the above-mentioned preliminary results through further study.

At present the subject of justifiability of the total arsenic and antimony limit values in water for human consumption is much discussed both in the European Union and in the USA. For As the limit value is determined on the level of 10 $\mu g.L^{-1}$ and for Sb the limit value has been currently is missing. Various epidemiologic researches the goal of which is to obtain a sufficient number of high-quality data are taking place. These data should confirm or disprove justifiability of this value, (Kafka & Punčochářová, 2002).

Speciation of Cu, As and Sb on the basis of data obtained from pH-Eh diagrams have only an orientation character since they are applicable only for closed systems for which they have been elaborated. Despite the orientation character of data they however enable to trace tendencies/trends of the speciation of the element monitored/observed in nature and to deduce the toxicity risk.

5. CONCLUSIONS

Eh/pH diagrams enable to provide an informative indication of the speciation of Cu, As and Sb in sediments and water in the surrounding of abandoned Cu-mines.

Copper can be found in technogenous

sediments and soils predominantly in the form of Cu^{2+} and only marginally as Cu^{3+} (Cu_2O_3) and Cu^0. In groundwater and surface waters most of samples belong to the stability field of $Cu_2SFe_2O_3$ (and to the stability field of Cu^0 only in isolated cases).

The most frequent speciation of As in technogenous sediments of both ore districts of Ľubietová and Špania Dolina investigated is less toxic As^{5+}, while pH-Eh stability diagrams mainly indicate occurrence of forms of $Fe(OH)_4As$, $H_2AsO_4^-$, $HAsO_4^{2-}$. Arsenic in the samples of soils and technogenous sediments belongs to the stability field of more toxic form of As^{3+} (e.g. to the field of Fe^{2+} + As^{3+}aq) only very seldom.

The content of As in water is related to decomposition of arsenopyrite and tetrahedrite. Its re-deposition is realized through adsorption on the surface of Fe-oxyhydroxides. The As content is also checked by subsequent of secondary phases of As on changing the conditions.

In the groundwater both speciation of As (As^{3+}, As^{5+}) are represented approximately in the same portion/part. The samples especially belong to the stability fields of $H_2As^{5+}O_3^-$ $HAs^{5+}O_4^{2-}$ and $H_3As^{3+}O_3^0$. Speciation of As in the surface waters on both localities is moved (in relation to the groundwater) to less toxic form of As^{5+} (H_2AsO_3, $HAsO_4^{2-}$, $H_3AsO_3^0$).

Both the technogenous sediments and waters in localities of Ľubietová and Špania Dolina are contaminated also by Sb. In sediments and soils at the Ľubietová locality Sb is prevailing in the less toxic degree of Sb^{5+} and appears in the form of SbO_3^-, while on the dump field and sludge bed on Špania Dolina the smaller part of samples characterized by values of Eh < 0,1 belong to the stability fields of Sb^{3+}, i.e. fields of valentinite and stibnite.

In the groundwater and surface waters on both localities pH-Eh stability diagrams predominantly indicate occurrence of Sb in the forms of Sb_4O_6 and Sb_2O_3, thus more toxic Sb^{3+}.

The forms of Cu, As and Sb are moved relatively markedly towards lower values of Eh on the locality of Špania Dolina against the locality of Ľubietová.

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REFERENCES

Andráš, P., Lichý, A., Rusková, J.& Matúšková, L., 2008. *Heavy metal contamination of the landscape Ľubietová deposit (Slovakia).* Proceedings of World Academy of Science, Engineering and Technology, 34, ISSN 2070 – 3740, Venice, Italy, 97-100.

Andráš, P., Lichý, A., Kušnierová, M., Križáni, I., Ladomerský, J. Rusková, J. & Hroncová, E., 2009. *Heavy metal distribution at dump-field Lubietova - Podlipa and possibilities of clay fraction natural sorbent utilisation.* Acta Montanistica Slovaca. ISSN 1335-1788, 14, 2, 127-142.

Andráš, P., Rusko, M., Rusková, J., Lichý, A., 2010. *Arsen and antimony as the environmental risk in the surrounding of Ľubietová Cu-Ag deposit.* Průmyslová Ekologie, Jehla, Zďár nad Sázavou, Chrudim: Vodní zdroje Ekomonitor spol., ISBN 978-80-86832-50-0, 151-161 (in Slovak).

Ashley, P. M., Craw, D., Graham, B. P. & Chappell, D. A., 2003. *Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand.* Journal of Geochemical Exploration, 77, 1–14.

Bencko, V., Cikrt M., Lener J., 1995. *Toxic metals in environment and their influence on population.* Avicenum, Grada, Praha. ISBN 80-7169-150-X, 254 p.

Bowel, R. J., 1994. *Sorption of arsenic by iron oxides and oxyhydroxides in soils.* Applied Geochemistry 9, 279–286 (in Slovak).

Brookins, D. G., 1986. *Geochemical behavior of antimony, arsenic, cadmium and thallium: Eh-pH diagrams for 25°C, 1-bar pressure.* Chemical Geology, 54, no. 3-4, 271-278.

Dove, P. M.. & Rimstib, J. D., 1985. *The solubility and stability of scorodite, $FeAsO_4.2H_2O$.* American Mineralogist, 70, 825-844.

Fairthorne, D., Fornasiero G. & Ralston, J., 1997. *Effect of oxidation on the collectorless flotation of chalcopyrite.* International Journal of the Processes, 49 (1-2), 31-48.

Fergusson, J. E., 1990. *The heavy metals, chemistry. Environmental impact and health effect.* Pergamon Press, New Zealand, 614 p.

Filella, M., Belzile, N. & Chen, Y. W., 2002. *Antimony in the environment: a review focused on natural waters II. Relevant solution chemistry.* Earth Science Reviews, 59, 1-4, 265-285.

Inskeep W. P., McDermott T. R.. & Fendorf S., 2002. *Arsenic (V)/(III) cycling in soils and natural waters: Chemical and microbiological processes.* In: Frankenberger WT Jr. (ed.) Environmental Chemistry of Arsenic, Marcel Dekker, New York, p. 183-215.

Kafka, Z. & Punčochářová, J., 2002. *Heavy metals in nature and their toxicity.* Chemické listy 96, 611-617 (in Slovak).

Krupka, F. M. & Serne, R. J., 2002. *Geochemical* *factors affecting the behavior of antimony, cobalt, europium, technetium and uranium in vadose sediments.* Technical Reports, Pacific Northwest National Laboratory, Richland, Washington, 95 p.

Leus, A. K., Mönch, H. & Johnson, C. A., 2006. *Sorption of Sb(III) and Sb(V) to goethite: influence on Sb(III) oxidation and mobilization.* Environmental Science & Technology, 40, 23, 7277-7282.

Leus, A. K. & Johnson, C. A., 2005. *Oxidation of Sb(III) to Sb(V) by O_2 and H_2O_2 in aqueous solutions.* Geochimica et Cosmochimica Acta, 69, 5, 1, 1165-1172.

Lin, Z. & Puls, R. V., 2000. *Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process.* Environmental Geology, 39, 7, 753-759.

Marin, C., Tudorache, A., Moldovan, O. T., Povară, I.. & Rajka, G., 2010. *Assessing the contents of arsenic and of some heavy metals in surface flows and in the hyporheic zone of the Arieş stream catchment area, Romania.* Carpathian Journal of Earth and Environmental Sciences, 5, 1, ISSN 1842-4090, 13-24.

Marsina, K., (ed.) 1999. *Geochemical Atlas of Slovak Republic. III: Horniny.* Ministery of environment of Slovak Republic, 106 p. (in Slovak).

Matschullat, Jörg, 2000. *Arsenic in the geosphere; A review.* The Science of the Total Environment, 249, 297–312.

Melicherčík, M. & Melicherčíková, D., 1997. *Bioanorganic chemistry –Chemical elements and human organism.* Príroda, Bratislava, 188 p. (in Slovak).

Nesbitt, H. W., Muir, I. J. & Pratt, A. R., 1995. *Oxidation of arsenopyrite by air and air-saturated, distilled water, and implications for mechanism of oxidation.* Geochimica et Cosmochimica Acta, Vol. 59, No. 9, 1773-1786.

O´Neill, P. 1990. *Arsenic.* In: Heavy metals in soil. Edited by B. J. Alloway. Glasgow and London, Blackie and Son, p. 83–99.

Pitter, P., 1990. *Hydrochemie.* STNL, Praha, 211 p.

Pokrovski, G. S., Kara, S. & Roux, J., 2002. *Stability and solubility of arsenopyrite, FeAsS, in crustal fluids.* Geochimica et Cosmochimica Acta, 66, 13, 1, July 2361-2378.

Prundeanu, I. M. & Buzgar, N., 2011. *The distribution of heavy metals and As in soils of the Fălticeni municipality and its surrounding.* Carpathian Journal of Earth and Environmental Sciences, 6, 1, ISSN 1842-4090, 51-64.

Roddick-Lanzilotta, A. J., McQillan, A. J. & Craw, D., 2002. *Infrared spectroscopic characterization of As^{5+} ion adsorption from mine waters, Macraes mine, New Zealand.* Applied Geochemistry, 17, 445–454.

Ryu, J., Gao, S., Dahlgren, R. A. & Ziernberg, R. A., 2002. *Arsenic distribution, speciation and solubility in shallow groundwater of Owens Dry Lake, California.* Geochimica et Cosmochimica Acta, 66, 17, 2981-2994.

Smedley, P. L. & Kinniburgh, D.G., 2002. *A review of the source, behaviour and distribution of arsenic in natural waters.* Applied Geochemistry, 17, 517–568.

Smichowskia, P., 2008. *„Antimony in the environment as a global pollutant: A review on analytical methodologies for its determination in atmospheric aerosols".* Talanta Vol. 75, No.1, March15, p. 2-14.

VanReeuwijk, L. P., 1995. *Procedures for soil analysis.* International soil reference and information centre (ISRIC) a FAO OSN. Technical report, 9. Zubkova, N. V., Pushcharovsky, 87 p.

Virčíková, E. & Pálfy, P., 1997. *Review of dangerous wastes scotching containing arsenic, cadmium and mercury. Aktuálne ekologické otázky E 97, Nebezpečné odpady.* BIJO Slovensko, Košice 25. 3, 87-103 (in Slovak).

Vink, B. W., 1996. *Stability relations of antimony and arsenic compounds in the light of revised and extended Eh-pH diagrams.* Chemical Geology, 130, No. 1, p. 21-30.

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