Toxicity of arsenic and antimony in the area of Cu-Ag deposit Ľubietová

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Abstract

In the surroundings of the Ľubietová deposit the As and Sb contamination of the landscape components, i.e. sediments (both technogenous sediments and soils) and as well groundwater and surface water was described. As(V) and Sb(V) species are predominant species in the sediments while in the water As(III) and Sb(III) are dominant. The utilization of Eh-pH stability diagrams is complemented by the classic determination of As and Sb species by means of HG AAS method.

The presence of very toxic As(III) and Sb(III) species encourages the increased aspect during the estimation of the environmental risk within the studied area.

Key words: arsenic, antimony, speciation, toxicity, technogenous sediments, groundwater, surface water

Introduction

The decrease of pH and changes of oxidation–reduction potential (Eh) in sediments of the dump fields at the Ľubietová Cu-Ag deposit induces the release of toxic metal elements (mainly Cu, Fe, Cd, As, Sb, Pb, Zn, Mn, Ni, Co) from the solid phase where they are presented in the form of the less soluble minerals or in sorption complex into the groundwater and surface water. Concerning the environmental risk, toxic metals As and Sb represent the highest risk at the studied locality (according to Andráš et al., 2008).

Arsenic belongs among nerve poisons with cumulative character (Pitter, 1990). Elementary As0 is insoluble in the water and is not considered as toxic. In a matter of fact, after its consummation its transition to various toxic compounds occurs. Arsenic begins to be toxic (arsenious oxide – As2O3) in the dose above 10 mg (1 to 2 mg per 1 kg of weight). Average fatal dose is 180 mg for grown-up man. Generally, 99 % of As is imported into the human organism by the water and food consummation. The arsenic compounds have mutagenic, cancerous and teratogenic effects. Arsenic penetrates through the placenta into the breast milk. It binds on erythrocytes, deposits in the liver, kidney, skin, hair, nails, and cerebrum. As acts as capillary and cytostatic poison (Kafka and Punčochářová, 2002). It inhibits or blocks SH-group in enzymes by biochemical effect on human organism. It causes change of their effects, disconnects oxidation phosphorylations running in mitochondria whereby causing the destruction of respiration function of tissues. Arsenic replaces very often phosphorus and inhibits corresponding enzymes. It has an impact on capillary epithelium, causes destruction of blood vessels and increases their fragility. It accumulates in liver, bones, nails and hairs where it is mainly bound to S-S bridging of keratin (Benbrahim-Talla and Waalkes, 2008).

As toxicity increases in the order: organic compounds As(V) – arsenate, inorganic compounds containing As(V), organic compounds As(III) – arsenite, inorganic compounds As(III) – arsan. As(III) compounds are about 5 or 10 times more toxic than As(V) compounds (Lin and Puls, 2000) but As(V) has stronger cancerous effects. As(III) and As(V) can create methyl compounds (mono – di – trimethylarsenic) whereby causing the transition to less toxic forms (Matschullat, 2000). Majority of mammals methyl inorganic arsenic to dimethylarsenic acid. This substance is causing organ-specified toxicity and is promoting the formation of tumors in many organs (Benbrahim-Talla and Waalkes, 2008).

Acute poisoning by As is evident as gastro-intestinal disease accompanied by vomiting and diarrhea. As(III) inorganic compounds cause cancer of prostate, skin, blood vessels and kidney (Benbrahim-Talla and Waalkes, 2008). Chronic poisoning causes neurological difficulties, faint paralysis of hands and legs whereas gastro-intestinal symptoms are weaker. There can be observed formation of stains on the skin, decrease of potency, salivation, weight loss, central damage of visual and acoustic analyzer, painful peripheral polyneuritis, anemia, damage of bone...
marrow and spleen and neurological and hematological changes (Melicherčík and Melicherčíková, 1997). The most serious chronic effect is cancer of skin and lungs. Poisoning by As can be identified by horny skin with characteristic glaucous chromatosis, white stripes on nails and garlic-smelling breath (Kafka and Punčochářová, 2002).

In the fields treated by pesticides, arsenic is built into the soil and causes drop in productivity of arable crops and damage of trees (Kafka and Punčochářová, 2002).

The main source of As at the locality of Ľubietová is tetrahedrite, less important and more rare is arsenopyrite. During weathering, arsenic ore minerals are easy oxidized and As is transformed from forms with lower oxidation number to As(V) creating compounds of arsenic acid (Lin and Puls, 2000). It is soluble in the water but rarely can migrate to greater distances due to the fast reaction with metal cations and As and is bounded in the form of various arsenates.

Antimony compounds are less toxic than arsenic compounds. It is similar to arsenic with its impacts but poisoning by antimony is easier due to slower adsorption of its compounds. Soluble compounds in digestive tract hydrolyze, insoluble are less toxic. The most toxic compound of Sb is antimony potassium tartrate which is equally toxic as arsenious oxide and has similar disease effects.

Antimony causes temporary state reminding heart-attack. It inhibits some enzymes, influences metabolism of proteins and sugars, prevents the formation of glycogen in liver, and raises hypoglycemic states (Cejpek, 2000). Acute poisoning is evident as irritation of digestive tract, capillary dilatation, bloody diarrhea, persistent vomiting causing dehydration. There is observed the blood pressure drop causing collapse. There can be also observed bronchial spasm and persistent cough. Blood sugar level is decreasing and acute poisoning can be followed by symptoms of the liver damage.
During the long-term exposition the formation of stains on the skin on uncovered parts of the body can be observed as well as the degenerative changes on nails, formation of abscesses on nose septum, early loss teeth, chronic bagassosis, dyspepsia, vertigo, weight loss, cardiac-vessel diseases, failure of menstruation cycle and a retardation of the children’s growth up to 1 year. Sb can enter into the human organism by inhalation or by direct skin contact. Toxic dose is 150 mg (Marhold, 1980).

Elementary Sb is more toxic than its salts. Sb(III) compounds are 10 times more toxic than Sb(V) compounds (Smichowska, 2008) and methyl forms of Sb are less toxic than its inorganic salts. Sb(III) is markedly carcinogenic. Antimony in waters is usually presented as Sb(III), Sb(V), CH$_3$SbO(OH)$_2$ and (CH$_3$)$_2$Sb(OH).

Antimony is presented in nature mainly in the form of sulphides or oxides of Sb(III) and Sb(V), most frequently as antimonious oxide Sb$_2$O$_3$, antimonic sulphide Sb$_2$S$_5$ and antimony chloride SbCl$_3$ (Bencko et al., 1995). Oxidation mechanism of Sb(III) to Sb(V) is controlled by pH. This process is slower than by oxidation of many other metals (for instance Mn, Fe, etc.). Sb(III) can be stabilized by the formation of complex compounds (Leus and Johnson, 2005). It can bind very strongly on particles containing Fe, Mn or Al in the soils. From soils it gets into the food web (Smichowska, 2008).

Knowledge on various levels of toxic effects and on quality of different impacts of individual compounds of toxic metals on living organisms led to the efforts to specify the forms of toxic metals. From the point of environment, As and Sb present serious danger due to highly toxic character of their compounds.

Methodology

For characterization of contamination of the landscape components there were collected samples of technogenous sediments (dump material, Fig. 1) and samples of the groundwater and surface water (water from wells, mine water and mineral water from the Linhart Spring). Reference site A-12 (Fig. 1) is situated outside of geochemical anomalies of heavy metals to represent similar rock environment (Permian greywacke) as on dump field. It enables the comparison with territories polluted with toxic metals due to the mine activities.

pH of sediments was determined in the water and 1 M KCl leachate according to guidelines described by Lintnerová and Majerčík (2005). Samples of the groundwater and surface water were collected 3 times: in December (drought period), on 31 March 2008 (rain period) and on 27 May 2008 (drought period).

Samples of technogenous sediments were analyzed in the ACME Analytical Laboratories in Vancouver (Canada) by the ICP/MS analysis. Fe content was in the water samples determined by AAS and As and Sb contents by means of hydride method (HG AAS) at the Water Research Institute in Bratislava. Determination of As speciation in the water was realized by the connection of hydride generator Labtech HG-2 and electrothermic automizer Perkin-Elmer HGA-500 with the aim to overconcentrate arsenic volatile compounds on modified surface of graphite cuvette (analysed by Ing. Adriana Shearman, CSc.).

Results

As and Sb distribution in the landscape components in the surroundings of the Ľubietová deposit

Distribution of toxic metals on the dump field is unequal and reflects their primary concentration in individual parts of dump field and geochemical relations of which migration capabilities are very important (Andráš et al., 2009).

Maximum concentrations of theoretical extractable As (7 – 289 ppm) and Sb (71 – 61.6 ppm) can be considered as relatively high (Tab. 1).

It is possible to divide samples of the groundwater (Tab. 2) into 2 classes: a) crude waters, b) drinking waters. It is possible to assign samples T-1, LH-8 and LH-9 to crude waters and water samples from the wells of the houses No. 423 and No. 470 (under the dump field Podlipa) to drinking waters where as well sample LH-1 of the mineral water from the Linhart Spring belongs. First group of samples was compared with the Regulation of the Ministry of Environment of the Slovak Republic No. 636/2004 Coll. – The public water-supply systems – where individual categories of standard methods of crude water treatment to drinking water are established. Second group of samples was compared with the Resolution of the Government of the Slovak Republic No. 354/2006 Coll., establishing requirements on water intended for human consumption (drinking water) and on monitoring of drinking water.

Crude water: Except As content in the samples LH-8 and LH-9 (limit value established by the Regulation No. 636/2004 Coll. is < 0.05 mg · l$^{-1}$) all samples were in accordance with requirements of the Regulation No. 636/2004 Coll.

Drinking water: Water samples from the wells of the houses No. 423 and No. 470 did not exceed limit values for indicators of heavy metals established by the Resolution

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>Fe</th>
<th>As</th>
<th>Sb</th>
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<td>77</td>
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<td>63</td>
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<td>4.87</td>
<td>94</td>
<td>4.21</td>
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<td>1.94</td>
<td>71</td>
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<td>59</td>
<td>5.33</td>
<td>66</td>
<td>2.64</td>
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<td>64</td>
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<td>60</td>
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<td>–84</td>
<td>7.34</td>
<td>–58</td>
<td>1.32</td>
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No. 354/2006 Coll., only water sample from the well of the house No. 470 exceeded limit values for Zn (3 mg \(\text{L}^{-1}\)) and has high content of Cu (41.1 mg \(\text{L}^{-1}\), limit value is 30 mg \(\text{L}^{-1}\)). The most polluted was the water sample from the mineral spring Linhart. It exceeded limit values for Mn (55 \(\mu\text{g} \cdot \text{L}^{-1}\), limit value is 0.05 mg \(\text{L}^{-1}\)) and Cd (6 \(\mu\text{g} \cdot \text{L}^{-1}\), limit value is 0.003 mg \(\text{L}^{-1}\)).

Surface water (including drainage water) had generally moderately acid character at the Podlipa Locality (pH 6.1).
to 7.5) whereas water from the areas Kolba and Svätodušná had neutral or moderately alkalic character with pH values within the range of 7.0 (only in one case 6.4) to 7.7 (Tab. 3). Water pH was not influenced by the seasonal changer (summer vs. winter) at any from the studied localities.

With utilization of comparison of the concentration values of toxic metals in the surface water from the studied localities with the recommended limit values pursuant to the Resolution of the Government of the Slovak Republic No. 296/2005 Coll. it is possible to state that recommended limit values were exceeded in the case of Cu (recommended limit value is 20 μg - l⁻¹) and As (recommended limit value is 30 μg - l⁻¹). Concentrations of individual studied metals were in the drought period generally about 3 times higher than in the rain period (Tabs. 2 and 3).

**As and Sb speciation**

Application of results of thermodynamic studies of various authors enabled to determine Fe, As and Sb speciation in the samples. The Eh-pH stability diagrams of the As-Fe-O-S system (Figs. 2 and 3) displaying stability fields of arsenic calculated according to thermodynamic data published by Vink (1996) and Pokrovski et al. (1996, 2000) were adjusted by Lalínska (2009). Arsenic data of analysed samples of the technogenous sediments from Ľubietová falling within these diagrams mainly into the stability fields of complexes Fe(OH)₃ and As(V)(aq) or to mineral scorodite (Fe₃AsO₄·2H₂O). Probably, most of As occurs in solution in the less toxic oxidation level as As(V).

Similarly as in the previous paragraph, Eh-pH stability diagrams of the As-H₂O-S system (Figs. 4 and 5) published by Ryu et al. (2002) and Ferguson and Gavis (1972) point at As occurrence in the oxidation level (V) in the technogenous sediments of the dump field and soil. Most of As occurs mobile in the solution in the form of complex H₃AsO₄.

The study of As speciation in the groundwater with utilization of Eh-pH stability diagrams points out that within the stability diagrams by Vink (1996) and Pokrovski et al. (1996, 2000) most of samples fall within the stability fields of As(III) (Figs. 2 and 3). According to stability diagrams of Ryu et al. (2002) and Ferguson and Gavis (1972) As occurs in the form of complex H₃AsO₄ (Figs. 4 and 5) or in the form of mineral orpiment As₂S₃ (Fig. 4) and complex HAsO₄²⁻ (Fig. 5).

Arsenic in the surface water is presented as As(III) (aq) (Figs. 2 – 5), in the form of finely dispersed arsenopyrite (FeAsS; Figs. 2 and 3) or in the form of H₃AsO₄, As₂S₃, HAsO₄²⁻, AsS² or in the elementary form (Figs. 4 and 5).

Antimony is according to Vink (1996) in the supergene oxidation conditions mobile and behaves as arsenic. Eh-pH stability diagram by Brookes (1988) and Vink (1996) enables to specify Sb speciation (Fig. 6). Samples of technogenous sediments from Lubietová are falling within the stability field of complex SbO₄²⁻. Similar Sb form in the water with nearly neutral pH was described as well by Ashley et al. (2003).

In the groundwater antimony occurs mainly in the form of oxides Sb₂O₅. In one sample antimony occurs in the elementary form and in the other sample occurs on the
boundary line of the stability fields of solution and stibnite $\text{Sb}_2\text{S}_3$ (Fig. 6).

In the surface water the predominant forms of antimony occurrence are oxides $\text{Sb}_4\text{O}_6$. The occurrence of antimony in the form of complex $\text{SbO}_3^-$ and elementary $\text{Sb}$ is marginal (Fig. 6).

Determination of As speciation by the method described by Hagarová et al. (2004) pointed at predominant the occurrence of $\text{As(V)}$ in the surface water in the hypergenic conditions of the dump fields. About one third of samples showed certain portion of $\text{As(III)}$ not exceeding 30 % and the remaining part should have been $\text{As(V)}$. The highest portion of $\text{As(III)}$ was determined in the samples of the mine water V-7 (30 %), in the samples of water from the mountain stream by the mine water inflow V-8 (45 %), in the samples of surface water from the Peklo valley V-9 (20 %) and in the sample of water from the stream of the reference site V-12 (15 %) where total contents of As and Sb were very low.

**Discussion**

Arsenic occurs in the water mostly in the following forms: $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$ and $\text{HAsO}_2^0$ (Greenwood and Earnshaw, 1990) whereby $\text{As(III)}$ is in the oxidation weathering zone more mobile than $\text{As(V)}$ (Manning and Goldberg, 1997). The high As content in the water is connected with the decomposition of tetrahedrite (and arsenopyrite). It is controlled by the As sorption on amorphous Fe oxides and oxyhydroxides, clay minerals and hydro-goethite and by the decomposition of these secondary phases during changes of conditions (Andráš et al., 2009).

It is generally stated that in the reductive conditions As mobility is intended by bond of arsenates and arsenites on the surface of minerals, mainly on Fe oxyhydroxides. In the sulphide waters and in the systems containing sulphides, great part of dissolved As occurs in the form of As-S compounds playing important part during the dissolving of As sulphide minerals in alkalic conditions (Wallschläger and Stadey, 2004).

Sorption capacity of clay minerals, hydro-goethite and Fe oxyhydroxides against As is very high (up to 76 mg · l$^{-1}$ of As in Fe oxyhydroxides under pH 5). As sorption depends on pH, time, As concentration in solution and temperature (Mohapatra et al., 2007). The most intense sorption is under pH 4 (García-Sanchez et al., 2002; Lombi et al., 2000). According to Mohapatra et al. (2007) the kaolinite

![Fig. 6. Eh-pH stability diagram of Sb species (Brookins, 1988; Vink, 1996).](image-url)
is the best sorbent of As(V) from clay minerals presented in the dump field Lubietová-Podliпa. Less toxic As(V) sorbs on clay minerals more easier and quantitatively than more toxic As(III). During this process As(III) is oxidized on As(V) (Lin and Puls, 2000). Low oxidation–reduction potential causes arsenic precipitation and therefore clay shale with content of organic matter or sulphides are richer in arsenic.

The greatest portion of As(III) was determined in the samples of the groundwater and the surface water with high negative values of Eh. Sb speciation was not verified by the hydride method HG AAS. Sb(III) and Sb(V) exist in natural conditions in soluble forms: Sb(V) as Sb(OH)$_4^{2–}$ and Sb(III) in the form of Sb(OH)$_3^{−}$ (Filella et al., 2002). Hydrogoethite and Fe oxyhydroxides are important sorbents of Sb. Sb(III) and Sb(V) create on the surface of hydrogoethite and Fe oxyhydroxides complex compounds. Sb(III) can best sorb under pH 3 – 12 while maximum sorption of Sb(V) occurs under pH < 7. On the surface of hydrogoethite and Fe oxyhydroxides can occur during several days Sb(III) oxidation mainly under pH 3 – 5.9. Under pH ~ 9 its mobilization and release into the solution occurs while under pH < 7 it remains bounded on the surface of Fe oxides (Leus et al., 2006).

As Sb sorbs relative well on the surface of Fe oxides and oxyhydroxides it is possible to assume that part of Sb occurs in the water solution in the form of Sb$_4$O$_6$ and SbO$_3$– particles < 0.4 μm (Lalinska, 2009). It is suggested from relatively high level of Fe : Sb correlation (Tabs. 1 – 3).

Andráš et al. (2008) found out that cementation process known at the Špania Dolina deposit occurs as well as at the Lubietová deposit. It would be possible to use this process for construction of the Fe$^0$ – barrier to remove heavy metals (mostly Cu, As, Sb and Cd) from the drainage water.

Conclusions

Techkinson sediments and water at the locality of Lubietová are contaminated by arsenic and antimony. In the sediments (and soils) there is predominant arsenic in the less toxic oxidation level as As(V) and occurs in the form of FeAsO$_4$ · 2H$_2$O or in the forms of H$_2$AsO$_4$ and HAsO$_2^{2–}$. The study of antimony speciation pointed out at the occurrence of SbO$_3^{2–}$ species corresponding to minerals senarmontite and tripuhyite.

In the groundwater there is predominant As(III) in various forms as H$_3$AsO$_3^{3–}$, HAsO$_3^{2–}$ and As$_2$S$_3$. Antimony is predominant as Sb$_2$O$_3$ which is identical with the valentinite. In the surface water As was determined in both oxidation levels as As(III) and As (V). There are predominant forms of H$_3$AsO$_3^{0}$ and As$_2$S$_2$.

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