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OCCURRENCE OF ANTIMONY AND ARSENIC AT MINING SITES IN SLOVAKIA: IMPLICATIONS FOR THEIR MOBILITY

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Abstract: Antimony and arsenic are the main contaminants in surface and groundwater from mining activity in the ore deposit areas in Slovakia (Slovenské rudohorie Mts., Nízke Tatry Mts. and Malé Karpaty Mts.). The highest dissolved concentrations of antimony were found in outflow from the Samuel Adit (9.3 mg/L) in Dúbrava and from the Jozef Adit (3.54 mg/L) in Čučma. The highest dissolved concentrations of arsenic were found in the outflow from the Agnes Adit (2.4 mg/L) in Poproč and from the Gabriela Adit (1.35 mg/L) in Čučma. Dissolution of stibnite is faster, compared to arsenopyrite and the early coatings on arsenopyrite grains are enriched in antimony. Dissolved concentrations of antimony in Dúbrava site are probably the highest reported concentrations in mine drainage in the world. Principal attenuation process for both contaminants is their adsorption on hydrous ferric oxides (HFO) and arsenic shows stronger partitioning and higher contents in sediments than antimony. Mass flux calculations indicated much more significant input of both antimony and arsenic from mine adits, compared to ground water seepage. Remediation of mining sites should be therefore focused on capture and treatment of mine adits' water.

Keywords: Antimony, Arsenic, Mine Water, Mass Flux, Adsorption

1. INTRODUCTION

Under natural conditions, antimony and arsenic occur in surface water and groundwater only in trace concentrations. Antimony and arsenic are considered to be highly toxic for biota and humans (Filella et al., 2002; Smedley & Kinniburgh, 2002; Sracek et al., 2004a). In view of these adverse effects on human health, their concentrations in drinking water are strictly regulated. In 1993, the World Health Organization (WHO) established on the basis of the toxicological effects the limit concentration of antimony in drinking water equal to 0.005 mg/L. Arsenic has been in the focus of the World Health Organization since 1958, and since 1993 its limit concentration in the drinking water has been set to 0.01 mg/L. The Slovak legislation for drinking water has assessed the arsenic content since 1991 and antimony since 1998 (Government Regulation no. 496/2010 Coll). The presence of antimony and arsenic in surface water and groundwater, and associated stream sediments and soils are an issue of serious environmental concern. Mining activity, ore exploitation and processing, tailings ponds, and mine water are the sources of antimony and arsenic in surface and groundwater in Slovakia. The highest concentrations of these contaminants are present in the ore deposits areas (Slovenské Rudohorie Mts., Nízke Tatry Mts. and Malé Karpaty Mts.). They are considered as important sources of antimony in

Europe.

This study presents results of hydrogeological investigations in the frame of two multidisciplinary projects, whose goals were to evaluate the environmental impact of open adits, uncovered waste-rock piles and tailings left after the closing of former mining activities in Slovakia at the Pernek-Krížnica, Pezinok-Kolársky vrch, Dúbrava, Medzibrod, Poproč, and Čučma ore deposits (Fig. 1) (Chovan et al., 2006; Chovan et al., 2010; Flakova et al., 2012; Hiller et al., 2009; Ondrejkova et al., 2013).

The Pernek-Krížnica site is located in a metamorphosed volcano-sedimentary complex. The principal Sb mineral is stibnite (Sb_2S_3), which appears in association with carbonates and quartz; arsenopyrite (FeAsS) and pyrite (FeS_2) are also present. At Pezinok-Kolársky vrch site, stibnite and berthierite ($FeSb_2S_4$) are the principal Sb minerals and arsenopyrite is the principal As mineral. Quartz and carbonates are frequent gangue minerals. At Dúbrava, the most abundant minerals are stibnite and pyrite, while quartz, calcite, and Fe-dolomite appear as gangue minerals. At Medzibrod, the dominant ore minerals are stibnite, arsenopyrite and berthierite, and the gangue minerals are calcite, dolomite, and quartz. At Poproč, stibnite is the most abundant, but pyrite and arsenopyrite plus gangue minerals like Fe-dolomite and quartz are also common. Finally, at Čučma, stibnite is again prevalent, followed by pyrite, arsenopyrite and chalcopyrite. Principal gangue minerals are calcite and siderite.

2. MATERIAL AND METHODS

At the abandoned mining deposits Pernek-Krížnica, Dúbrava, Medzibrod, Poproč and Čučma, the sampling of mine drainage, surface waters and ground waters was carried out from 2006 to 2010 along with field measurement of physico-chemical parameters of water. The purpose of the study was to determine the extent of contamination of waters and identify the principal sources of contamination. In total, 110 samples of water were collected, 18 from the deposit Pernek-Krížnica, 30 from the deposit Dúbrava, 13 from the Medzibrod deposit, 27 from the deposit Poproč and 22 from the deposit Čučma. In the period 2003-2006 the impact of abandoned deposit Pezinok-Kolársky vrch on the environment was assessed and methods of remediation were proposed. In total, 26 sites were monitored and 75 water samples were analysed, (Chovan et al., 2006; Flakova et al., 2012), the data being included in the present study.

In the field, temperature of air, temperature of water, pH, and redox potential were measured. The pH was measured using a WTW Multi 350i equipped with an electrode Sentix 41; dissolved oxygen was measured with a WTW oxymeter 340i/SET using an electrode DurOx^{R}325-3 and the electrical conductivity was measured with a WTW Multi 350i using an electrode TetraCon^{R}325. Samples were filtered in the field using 0.45 μm filter and acidified by ultrapure HNO_3. All samples were kept at 4°C until analyses.

Figure 1. Studied sites.

Water chemical analyses were made in the Hydrogeochemical Laboratory of the Department of Hydrogeology, Comenius University in Bratislava, and in the Geoanalytical Laboratory of the Slovak Geological Institute of Dionýz Štúr. The following parameters were determined: COD_{Mn}, COD_{Cr}, BOD_5, Na, K, Ca, Mg, Fe, Mn, NH_4^+, Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}, HPO_4^{2-}. Sulphate was determined by gravimetry after precipitation with $BaCl_2$ and Cl^- by titration with $Hg(NO_3)_2$. Concentrations of NH_4^+, NO_3^-, and HPO_4^{3-} were determined by spectrophotometry using a PERKIN ELMER UV/VIS Lambda 11 apparatus. Na, K, Ca, Mg, Fe, Mn were analysed by AES-ICP (VISTA-MPX fy Varian).

The material from the tailings at the deposit Čučma (CU-1 borehole) and material from boreholes in the deposit Pezinok-Kolársky vrch underwent sequential extraction for arsenic and antimony by a standard procedure (Battacharya et al., 2006). The operationally defined fractions included (1) water-soluble fraction using de-ionized water, (2) exchangeable and carbonate fraction using 0.1 M $C_2H_3NaO_2$, (3) reducible fraction using 0.1 M hydroxylamine and HCl, (4) organic and sulfidic fraction using 8.8 M H_2O_2 and 1 M NH_4COOH, and finally (5) residual fraction using 7 M HNO_3.

At all mining adits discharge was measured using calibrated V-notch weirs and mass flux of contaminants M was calculated as a product of discharge Q and concentration C, M = Q x C.

3. RESULTS AND DISCUSSION

Principal ions are plotted in Piper diagram (Fig. 2), concentrations of antimony and arsenic in all sampled waters including mine adits, surface and ground waters are in Fig. 3 and Fig. 4, respectively.

In the formation of the chemical composition of mine water, processes of oxidation of sulphides, along with dissolution of carbonates and dissolution of silicates are involved, depending on the rock environment. Ion exchange processes and adsorption may play an important role in soil cover and the presence of ochres. In the studied mine waters sulphate anion is dominant; the dominant cations are calcium and magnesium (Fig. 2). Water has generally close to neutral or even alkaline pH due to the high content of carbonates, mainly calcite and dolomite, in the ore-hosting rock; only samples from Pernek, with relatively low Sb (Fig. 3) and As (Fig. 4) concentrations, make an exception.

Relevant water chemistry data only for the mine adits outflows are shown in Table 1. They are in a narrower range compared to the complete data set because some groundwater samples have low concentrations of antimony and arsenic. When comparing individual mine adit sites, there are some differences in chemical composition of mine adits waters. At the deposits Pernek-Krížnica and Pezinok-Kolársky vrch, there also are significant dissolved concentrations of iron and aluminium.

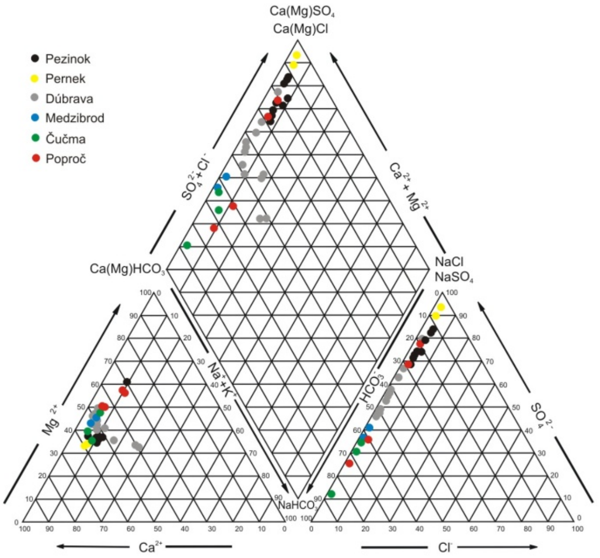

Figure 2. Piper's diagram of mine adit waters.

In terms of total water contamination, the deposit Dúbrava is important because of the highest concentrations of dissolved antimony and also high arsenic concentrations (Table 1). Due to the large discharge of effluent water from mine adits, relatively large amounts of these elements enter the environment. In the waters of the Dúbrava deposit, antimony concentrations ranged from 830 to 9,300 μg/L (Table 1). In the deposits Čučma and Poproč significant contamination of ground and surface waters and subsequent direct threat to the health of the local population of the communities in Čučma and Poproč were found. The concentration of antimony in waters in the deposit Čučma ranged from 17 μg/L to 7,130 μg/L, in the deposit Poproč from 180 to 750 μg/L, and in the deposit Medzibrod from 445 to 500 μg/L (Table 1).

The highest dissolved concentrations of arsenic (2,400 μg/L) in water were found at the deposit Poproč (Table 1). Significant concentrations of arsenic were also identified in the waters at the deposits Medzibrod (from 163-180 μg/L) and Čučma (1,350 μg/L). The deposit Pezinok-Kolársky vrch (not shown in figures) contained the largest concentrations of As (28,380 μg/L) and Sb (7,750 μg/L) in the leachate from the tailings pond (Flakova et al., 2012).

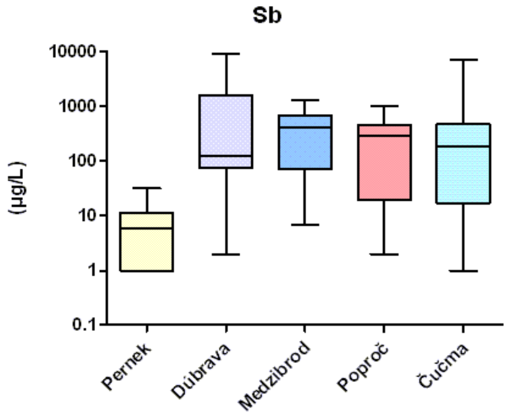

Figure 3. Concentration of Sb in all waters: mine adits, surface and ground waters.

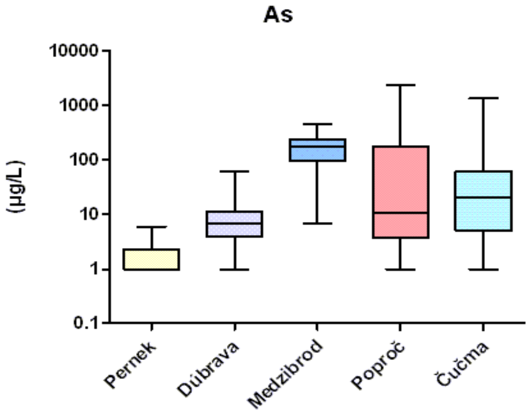

Figure 4. Concentration of As in all waters: mine adits, surface and ground waters.

The most important sources of contamination in all studied areas are the outflows from abandoned mining adits. The highest concentrations of antimony were found in the outflow from the Samuel Adit (9,300 µg/L) in Dúbrava and from the Jozef Adit (7,130 µg/L) in Čučma. The highest concentrations of arsenic were found in the outflow from the Agnes Adit (2,400 µg/L) in Poproč and from the Gabriela Adit (1,350 µg/L) in Čučma. These very high concentrations are linked to the convective oxygen supply into mining adits, where large sulphide bodies are exposed and convection caused by temperature and pressure gradients results in high sulphide oxidation rate (Sracek et al., 2004b, 2006). Similar conditions in Iron Mountain, California, produced the highest mine drainage As concentrations in the world and even negative pH values (Nordstrom et al., 2000).

The mine waters from adits pollute the surface waters in the studied areas. However, important sources of contamination are also the tailing ponds and waste rock piles. Concentrations of 1,450 µg/L Sb and 24,680 µg/L As were measured in the neutralized leakage water (pH from 6.6 to 7.0) from tailing pond at the abandoned deposit Pezinok-Kolársky vrch (Flakova et al., 2012). The high Sb and As contents in the solid phase are in reducible fraction of sequential extraction (e.g. linked to hydrous ferric oxides, HFO), but sulphidic fraction and especially residual fraction are also significant. Mineralogical study indicated a faster dissolution of stibnite (Sb_2S_3), compared to arsenopyrite (FeAsS), and early ferric oxyhydroxides coatings on the surface of primary sulphides are enriched in antimony compared to arsenic. For example, at Pezinok-Kolársky vrch mine tailings almost all stibnite and berthierite in the oxidation zone has already been dissolved, but arsenopyrite is still present (Flakova et al., 2012). In early stages of mining wastes evolution there is a higher concentration of antimony than arsenic in pore water and antimony dominates adsorption. Later, the situation changes and arsenic competes with antimony for the adsorption sites (Casiot et al., 2007). Both contaminants form oxyanionic species and their adsorption decreases at high pH values (Stumm & Morgan, 1996; Langmuir, 1997).

Mass fluxes of antimony and arsenic were calculated and compared for different periods of year. In August 2009, in Čučmiansky Brook, the monthly mass fluxes of antimony and arsenic were 0.61 kg and 0.05 kg, respectively, and in Laz Brook, below the tailings pond, they were 2.93 kg for antimony and 0.29 kg for arsenic (Table 2). In the Dúbrava deposit, the highest mass fluxes of Sb in surface waters were in spring from the HDP Adit (171.395 kg in April 2008) and Svätopluk Adit (159.482 kg in April 2008) as a consequence of extreme discharge in the period. The mass fluxes inputs are much higher than the contaminant input by groundwater seepage across hyporheic zone determined by groundwater flow modeling (Flakova et al., 2012); Ondrejkova et al., 2013), which accounts for less than 3.0 % of total antimony and arsenic input into surface streams.

The most important parameters affecting the speciation of antimony and arsenic in waters are pH and Eh. At the studied sites, waters have relatively high pH values, i.e., up to 8.24. From the Eh-pH diagram for Sb (Fig. 5), it follows that in the mine waters pentavalent antimony prevails, with $Sb(OH_6)^-$ as dominant species. Arsenic in water is present only as As(+V) and prevalent species are $HAsO_4^{2-}$ and $H_2AsO_4^-$ (Fig. 6). The presence of arsenic in the pentavalent form was confirmed by its analytical speciation in waters of the Pezinok-Kolársky vrch deposit (Flakova et al., 2012).

Most of the mine waters are well-neutralized and there is the formation of ferric minerals coatings on the surface of primary sulphides (Flakova et al., 2012), which limits their oxidation (Blowes et al., 1998; Vencelides et al., 2007).

Table 1. Selected parameters of mine waters from adits at studied abandoned mining sites; for each parameter, the range/average (n=4) is shown.

Mining sites	**TDS**[a]	**pH**	**Eh**	**SO_4^{2-}**	**Fe**	**Al**	**As**	**Sb**
adits	(mg/L)		(mV)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Pernek								
Pavol	642-932/804	3.18-6.26/5.51	297-357/327	403-611/531	4.2-12.5/4.64	<0.02-2.59	<0.001-0.007	0.005-0.016/0.011
Zubau	1,749-2,187/1,681	2.69-2,76/2,72	252-336/299	1,311-1,613/1,462	21.6-98.1/63.3	26.9-31.7/29.3	0.004-0.034/0.019	0.005-0.009/0.007
Pezinok								
Pyritová	950-1,730/1,327	7.60-7.99/7.79	252-334/596	478-883/713	0.14-0.90/0.48	<0.03-0.09	0.022-0.104/0.044	0.3-0.654/0.454
Budúcnosť	465-663/553	7.18-7.48/7.37	217-471/268	216-298/260	2.48-3.78/3.19	<0.03-0.04	0.013-0.027/0.022	0.087-0.150/0.112
Sirková	674-833/744	6.69-7.87/6.77	283-337/301	301-390/344	0.42-5.36/2.14	<0.03-0.03	0.004-0.033/0.018	0.014-0.046/0.026
Dúbrava								
HDP	282-293/287	7.96-7.98/7.97	484-503/495	93-101/99	0.027-0.051/0.039	<0.02-0.07	0.005-0.034/0.02	2.63-3.28/2.95
Samuel	382-448/415	8.24-8.30/8.27	454-464/461	142-171/155	0.042-0.046/0.044	<0.02-0.08	0.010-0.062/0.036	8.5-9.3/8.9
Svätopluk	157-173/165	7.59-7.85/7.72	415-457/432	48-49/49	0.020-0.504/0.262	0.08-0.18/0.13	0.008-0.057/0.033	1.58-1.65/1.61
Rakytová	332-395/363	7.94-8.10/7.99	463-504/483	137-179/157	0.023-0.039/0.031	0.02-0.06/0.04	0.008-0.039/0.023	1.30-1.74/1.52
Martin	323-334/328	8.15-8.40/8.27	472-504/486	93-102/97	0.034-0.145/0.089	<0.02-0.06	0.0011-0.034/0.023	0.83-0.90/0.86
Flotačná	340-351/345	8.15-8.28/8.18	470-483/475	119-129/124	0.030-0.041/0.036	<0.02-0.07	0.004-0.016/0.01	1.33-1.46/1.39
Ignác*	486	7.99		267	0.025	0.08	0.006	1.550
Medzibrod								
Murgaš	433-450/441	7.04-7.14/7.07	353-447/400	108-115/111	0.083-0.112/0.098	<0.02-0.07	0.163-0.18/0.172	0.445-0.5/0.472
Poproč								
Anna	230-343/286	6.90-7.04/6.97	206-354/280	48.7-49.8/49.3	0.245-4.4/2.32	<0.02	0.005-0.012/0.085	0.18-0.75/0.46
Agnes	540-564/552	6.29-6.56/6.42	212-214/213	240-272/256	32.7-51.5/42.1	<0.02-0.02	2.15-2.40/2.28	0.38-0.60/0.49
Čučma								
Jozef	324-362/343	7.67-7.95/7.81	398-470/434	70.8-77.3/74.2	0.065-0.183/0.124	< 0.02	0.051-0.084/0.068	3.54-7.13/5.34
Gabriela*	879	7.12		67	0.555	< 0.02	1.35	0.017
Matej*	274	7.33		48	0.083	< 0.02	0.027	0.170

*there was only one sample taken from some adits

Table 2. Mass flux of arsenic and antimony.

Sampling points	Q (L/s)	As (µg/L)	Sb (µg/L)	Flux As (µg/s)	Flux Sb (µg/s)	Flux As (kg/month)	Flux Sb (kg/month)
Čučma (August 2009) Čučmiansky Brook	1.60	12	147	19.2	235	0.050	0.610
Čučma (August 2009) Laz Brook	4.27	26	265	111	1,131	0.288	2.933
Dúbrava (April 2008) HDP Adit	20.16	34	3,280	685	66,124	1.777	171.395
Dúbrava (April 2008) Svätopluk Adit	37.29	57	1,650	2,125	61,528	5.509	159.482

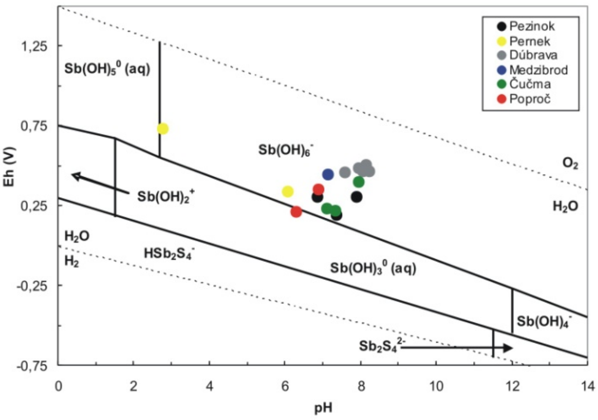

Figure 5. E_H-pH diagram for the dominant aqueous species of antimony in mine waters (diagram was calculated for 25 ºC and a concentration of $10^{-14.6}$ mol/L total dissolved antimony; according to Krupka & Serne (2002)

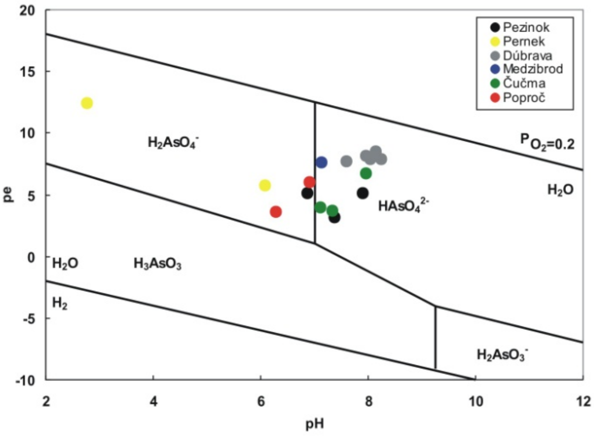

Figure 6. Partial *pe*-pH stability diagram for the soluble forms of arsenic in mine waters (according to Appelo & Postma (2005).

Principal attenuation process for both contaminants is the adsorption on hydrous ferric oxides (HFO), as reported in previous works (Wilson et al., 2004; Leuz et al., 2006). At the studied sites, antimony is more mobile compared to arsenic, i.e. it has a lower adsorption affinity, and less variability in antimony concentrations was observed in sampled waters (Hiller et al., 2009). This is consistent with the reported total HFO contents larger than 20 wt.% for arsenic and 1.5 wt.% for antimony (Hiller et al., 2012) and also with lower reported values of adsorption isotherm K_d for antimony (Krupka & Serne, 2002; Casiot et al., 2007).

Measured dissolved concentrations of antimony and arsenic are very high even in comparison with world sites; e.g. concentrations up to 55,000 µg/L Sb were reported at Hillgrove, Australia, by Ashley et al. (2003) and 52,000 µg/L As were reported at Prohibition Mill, New Zealand by Haffert & Craw (2008). However, these sites are not affected by mine drainage and the dissolved concentration of 9,300 µg/L Sb at Dúbrava site, linked to alkaline pH values, seems to be the highest reported mine drainage value in the world. Since the maximum contaminant load is from mining adits, it would be beneficial to capture and treat contaminated water at adits outflow and, thus, to avoid downstream contamination of water and sediments.

4. CONCLUSIONS

The study confirmed the behavior of antimony and arsenic observed in generally well-neutralized mine waters. Arsenic is adsorbed more strongly and, thus, antimony is more mobile, generally showing higher dissolved concentrations. However, at early stages of contamination, i.e. after deposition of mining wastes, adsorption of antimony prevails, probably due to faster dissolution kinetic rate of stibnite and berthierite compared to arsenopyrite and resulting extremely high dissolved antimony concentrations. At later period, dissolved arsenic concentrations reach higher levels and partitioning of arsenic into HFO ochres becomes more significant.

Dissolved concentrations of antimony at Dúbrava site are probably the highest reported concentrations in mine drainage in the world and most of dissolved antimony and arsenic input is from mining adits. It seems to be a consequence of high sulphide oxidation rate caused by convective oxygen supply into adits. Calculated mass fluxes from adits account for more than 90% of total input for both contaminants. This means that treatment of outflow from adits should be given a priority compared to other remediation options.

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REFERENCES

Appelo, C.A.J. & Postma, D., 2005. *Geochemistry, groundwater and pollution, 2nd ed.* A.A. Balkema, Rotterdam, Holland, 536.

Ashley, P.M., Craw, D., Graham, B.P. & Chapell, 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, 1-14.

Bhattacharya, P., Claesson, M., Bundschuh, J., Sracek, O., Fagerberg, J., Jacks, G., Martin, R.A., del Storniolo, A. & Thir, J.M., 2006. *Distribution and mobility of arsenic in the Río Dulce alluvial aquifers in Santiago del Estero Province, Argentina.* Science of Total Environment, 358, 1-3, 97-120.

Blowes D.W., Jambor J.L., Hanton-Fong C.J.& Lortie L., Gould W.D., 1998. *Geochemical, mineralogical and microbiological characterization of a sulphide-bearing, carbonate-rich gold-mine tailings impoundment, Joutel, Québec*, Applied Geochemistry 13, 6, 687-705.

Casiot, C., Ujevic, M., Munoz, M., Seidel, J.L. & Elbaz-Poulichet, F., 2007. *Antimony and arsenic in a creek draining an antimony mine abandoned 85 years ago (Upper Orb basin, France).* Applied Geochemistry, 22, 4, 788-798.

Chovan, M., Lalinska, B., Sottnik, P., Jurkovic, L., Zenisova, Z., Flakova, R., Krcmar, D., Lintnerova, O., Hiller, E., Klimko, T., Jankular, M., Hovoric, R., Ondrejkova, I., Lux, A., Vaculik, M., Michnová, J. & Petrak, M., 2010. *The assessment of the effects of mining activities on the environment around abandoned Sb deposits of Slovakia with remediation proposals (in Slovak), Final report of the project APVV-0268-06*. Comenius University Bratislava, Slovakia, 352.

Chovan, M., Andras, P., Cernansky, S., Dlapa, P., Flakova, R., Hudacek, M., Krcmar, D., Kusnierova, M., Lalinska, B., Lux, A., Majzlan, J., Milovska, S., Moravansky, D., Sevc, J., Simonicova, A., Slesarova, A., Sottnik, P., Uhlik, P., Urik, M. & Zenisova, Z., 2006. *Determination of the contamination risk by Sb, As, S around the Pezinok ore deposit and remediation proposal: toxicity of As and Sb, acidification (in Slovak), Final report of the project no. AV/901/2002 (VTP25).* Comenius University Bratislava, Slovakia, 225.

Filella, M., Belzile, N. & Chen, Y.W., 2002. *Antimony in the environment: a review focused on natural waters, I. Occurrence. Earth.* Earth-Science Reviews, 57, 1-2, 125-176.

Flakova, R., Zenisova, Z., Sracek, O., Krcmar, D., Ondrejkova, I., Chovan, M., Lalinska, B. & Fendekova, M., 2012. The behavior of arsenic and antimony at Pezinok mining site, southwestern part of the Slovak Republic. Environmental Earth Sciences, 66, 4, 1043-1057.

Haffert, L. & Craw, D., 2008. *Processes of attenuation of dissolved arsenic downstream from historic gold mine sites, New Zealand.* Science of the Total Environment, 405, 1-3, 286-300.

Hiller, E., Jurkovic, L., Kordik, J., Slaninka, I., Jankular, M., Majzlan, J., Göttlicherd, J. & Steiningerd, R., 2009. *Arsenic mobility from anthropogenic impoundment sediments – Consequences of contamination to biota, water and sediments, Posa, Eastern Slovakia.* Applied Geochemistry, 24, 11, 2175-2185.

Hiller, E., Lalinska, B., Chovan, M., Jurkovic, L., Klimko, T., Jankular, M., Hovoric, R., Sottnik, P., Flakova, R., Zenisova, Z. & Ondrejkova, I., 2012. *Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia.* Applied Geochemistry, 27, 3, 598-614.

Krupka, K.M. & Serne, R.J., 2002. *Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Sediments; Report PNNL-14126.* Pacific Northwest National Laboratory, Richmond, Washington, USA, 95.

Langmuir, D., 1997. *Aqueous Environmental Geochemistry.* Prentice Hall, Inc., New Jersey, USA, 600.

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

Nordstrom D.K., Alpers C.N., Ptacek C.J.& Blowes D.W., 2000. *Negative pH and extremely acidic mine waters from Iron Mountain, California,* Environmental Science & Technology, 34, 254-258.

Ondrejkova, I., Zenisova, Z., Flakova, R., Krcmar, D. & Sracek, O., 2013. *The distribution of Antimony and Arsenic in Waters of the Dúbrava Abandoned Mine Site, Slovak Republic.* Mine Water and the Environment, 32, 3, 207-221.

Smedley, P.L. & Kinniburgh, D.G., 2002. *A review of source, behaviour and distribution of arsenic in* *natural waters.* Applied Geochemistry, 17, 5, 517-568.

Sracek, O., Bhattacharya, P., Jacks, G., Gustafsson, J.P. & Brömssen von, M., 2004a. *Behavior of arsenic and geochemical modeling of arsenic enrichment in aqueous environments.* Applied Geochemistry, 19, 2, 169-190.

Sracek, O., Choquette, M., Gélinas, P., Lefebvre, R. & Nicholson, R.V., 2004b. *Geochemical characterization of mine drainage from a waste rock pile, Mine Doyon, Québec, Canada,* Journal of Contaminant Hydrology, 69, 1-2, 45-71.

Sracek, O., Gélinas, P., Lefebvre, R. & Nicholson, R.V., 2006. *Comparison of methods for the estimation of pyrite oxidation rate in a waste rock pile at Mine Doyon, Québec, Canada,* Journal of Geochemical Exploration, 91, 99-100.

Stumm, W. & Morgan, J.J., 1996. *Aquatic chemistry, 3rd ed.* John Wiley & Sons, Inc., New York, USA, 1022.

Vencelides, Z., Sracek, O. & Prommer, H., 2007. *Modeling of iron cycling and its impact on the electron balance at a petroleum hydrocarbon contaminated site at Hnevice, Czech Republic,* Journal of Contaminant Hydrology, 89, 3-4, 270-294.

Wilson, N.J., Craw, D. & Hunter, K., 2004. *Antimony distribution and environmental mobility at an historic antimony smelter site, New Zealand.* Environmental Pollution, 129, 2, 257-266.

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