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TECHNICAL ARTICLE

The Distribution of Antimony and Arsenic in Waters of the Dúbrava Abandoned Mine Site, Slovak Republic

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Abstract The abandoned Dúbrava Mine, situated in the northern part of the Nízke Tatry Mts in the middle of Slovakia, was the most significant producer of antimony (Sb) in the former Czechoslovakia. Mine drainage from adits (containing up to 9,300 μg/L of Sb), mine waste dumps, and the leachate from mine tailings contribute Sb and arsenic (As) into nearby Paludžanka Creek and groundwater. Some drinking water resources have been closed due to excessive Sb concentrations; the concentration of Sb in one household well (126 μg/L) far exceeds the Sb drinking water limit of 5 μg/L. Although Sb is attenuated by dilution and adsorption on ferric iron in stream sediment in the Paludžanka Creek, Sb concentrations increase downstream of the mine tailings and then remain almost constant, leading to concentrations of 128 μg/L at the northern boundary of the study area. The dissolved As concentrations in the mine drainage are much lower than Sb, ranging from 4 to 62 μg/L. Flow and transport modeling confirmed the observed contamination pattern and the major role of the mine adits. Results of this study indicate serious Sb contamination, which could be mitigated by treatment of the adit discharges.

Keywords Adits · Dúbrava deposit · Water contamination

Introduction

Antimony and arsenic are widely distributed; concentrations of antimony (Sb) in groundwater and surface water normally range from 0.1 to 0.2 μg/L (Bowen 1979). The concentration of arsenic (As) in natural waters is generally about 1 μg/L. Both elements can be toxic (Filella et al. 2002; Gebel 1997, 1999; Smedley and Kinniburgh 2002) and are strictly limited in drinking water by the EU, with an upper value of 0.005 mg/L for Sb and 0.01 mg/L for As.

Antimony is a chalcophile element, occurring with sulphur and metals such as copper, lead, silver and gold. Behavior of Sb is similar to As, but its higher atomic number makes it slightly more metallic than As. These elements enter the aquatic environment naturally by weathering of rocks, volcanic eruptions, and runoff from soils, but also due to mining and industrial and municipal leachate discharges (Smedley and Kinniburgh 2002; U.S. EPA 1980). Antimony, just like As, can exist in several oxidation states in natural environments and is normally found in aqueous solutions in trivalent and pentavalent forms (Filella et al. 2002).

Both Sb and As form oxyanions that are mobilized in alkaline environments due to desorption from negatively charged surfaces of Fe(III) phases. This contrasts with cationic contaminants, which are transported mostly in suspension in alkaline conditions (Sracek et al. 2011, 2012).

Antimony and As contamination presents a serious problem in many countries around the world (Naidu et al. 2006; Wilson et al. 2010). The most severe cases of groundwater contamination by As have been found in

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aquifers in Asia (e.g. Bangladesh, India; Nickson et al. 2000), China, Nepal, and Central and South America (e.g. Argentina, Mexico). The problems are mostly linked to *naturally occurring arsenic*. Extremely high levels of As (190,000 mg/L) were found in the pore water of a waste rock pile at the Berikul gold mine (Gieré et al. 2003), and Sb concentrations up to 55 mg/L were detected at the Hillgrove mining area in Australia (Ashley et al. 2003).

All Sb mines in the Slovak Republic (e.g. Pezinok, Dúbrava, Medzibrod, Poproč, Čučma) were abandoned in the early 1990s without remediation. The long-term exploitation produced large amounts of waste rock and tailings that contribute to the contamination of the adjacent environment (Fľaková et al. 2011a, b, 2012; Hiller et al. 2012; Jankulár et al. 2008; Majzlan et al. 2007; Trtíková et al. 1999; Ženišová et al. 2009).

The Dúbrava deposit, situated in the northern part of the Nízke Tatry Mountains, was the most significant producer of Sb in the former Czechoslovakia (Chovan et al. 1998). Many mine waste dumps, tailings, and closed mine adits can be found there. Elevated Sb contents up to 644 mg/kg and As contents up to 140 mg/kg have been detected in the Paludžanka Creek stream sediments (Hiller et al. 2012). The soils contain up to 9,619 mg/kg of Sb and up to 930 mg/kg of As, far exceeding average Slovak soil Sb and As levels (Čurlík and Šefčík 1999) and estimated global average soil contents (Reimann and de Caritat 1998). This paper presents the distribution of Sb and As in surface water and groundwater at the Dúbrava deposit and modeling that was undertaken to better understand the *existing situation and the potential benefits of capturing and treating the adit discharges*.

Geology and History of Mining at Dúbrava

The Dúbrava deposit is situated about 7 km south of the village of Dúbrava, on both sides of the Križianka valley. Ore mineralization in the Nízke Tatry Mountains is represented by vein-type hydrothermal deposits, locally substituted by veinlet and veinlet-impregnation types. Country rocks of the Dúbrava deposit consist predominantly of biotitic granodiorites and tonalites and, to a considerably lesser extent, granites, aplites, pegmatites, and subordinate diorites and basanites (Chovan 1990). Elongated bodies of migmatites and gneisses represent relics of crystalline cover.

The Dúbrava ore field is about 1 km wide and 4 km long, with a vertical extent up to 350 m. Quartz veins containing Sb-rich mineralization follow the N–S direction and are associated with numerous diagonal veinlets. The best ore bodies were located at intersection points of the main and diagonal veins (Chovan et al. 1994).

Two mineralization phases can be discerned at the Dúbrava deposit. The earlier, high-temperature phase is represented by lens-shaped quartz-pyrite veins containing impregnations of scheelite ($CaWO_4$). The later sulphidic assemblage is represented by Fe-dolomite [$FeCa(CO_3)_2 + MgCa(CO_3)_2$] and bismuthite [$(BiO_2)CO_3$], as well as tetradymite (Bi_2Te_2S), chalcopyrite ($CuFeS_2$), chalcostibite ($CuSbS_2$), and tetrahedrite ($Cu_{12}Sb_4S_{13}$) that infringe on the scheelite and pyrite grains.

The major ore minerals at this locality are stibnite (Sb_2S_3) and pyrite (FeS_2). Arsenopyrite (AsFeS), Pb, Sb, Bi-sulphosalts, sphalerite ((Zn,Fe)S), tetrahedrite ($Cu_{12}Sb_4S_{13}$), bournonite ($PbCuSbS_3$), chalcostibite ($CuSbS_2$), native gold, and scheelite are also present. Quartz (SiO_2), calcite ($CaCO_3$), Fe-dolomite and barite ($BaSO_4$) are the most frequent gangue minerals (Michálek and Chovan 1998).

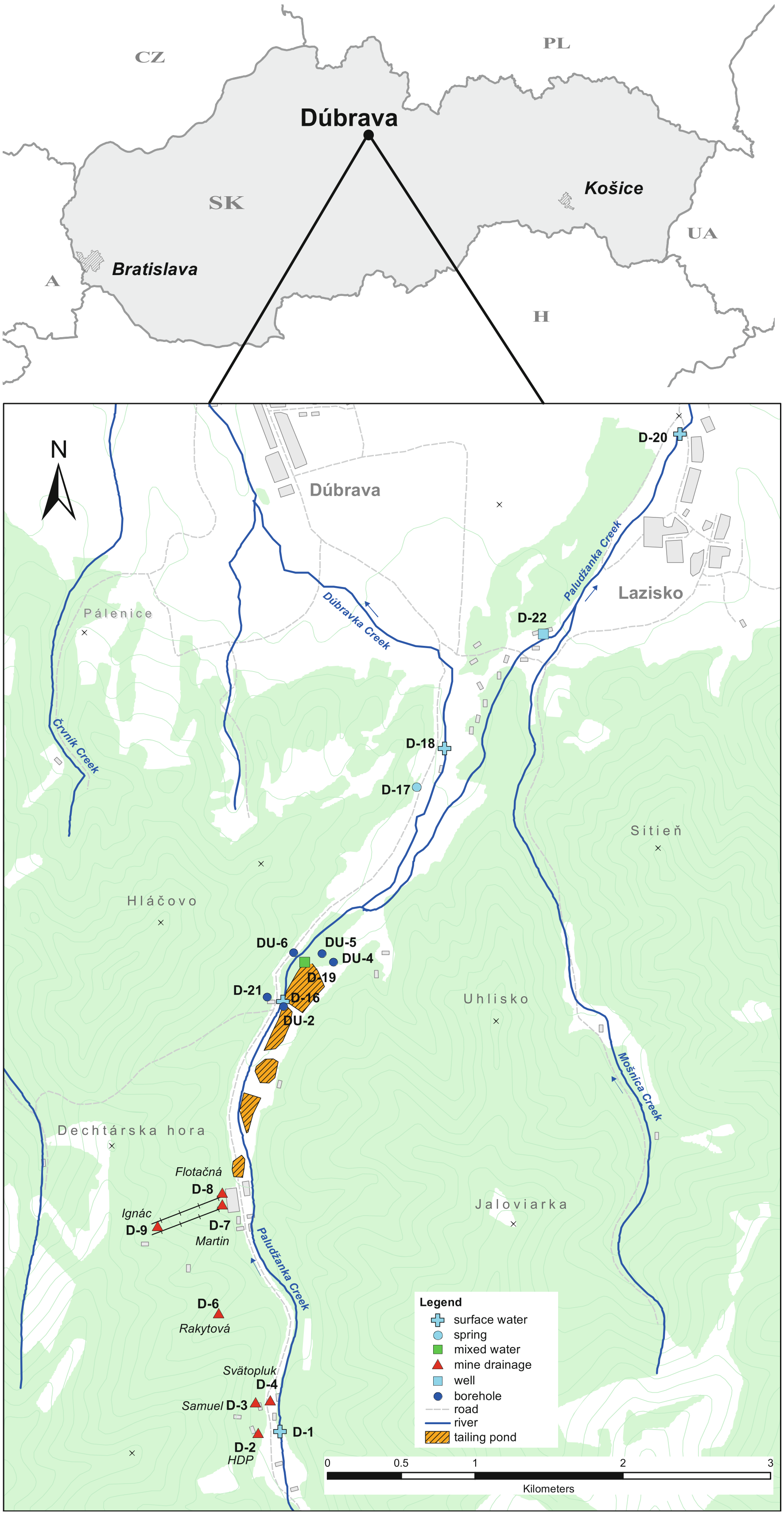
References to gold panning from alluvial sediments of the Nízke Tatry Mountains have been recorded from the thirteenth century. Stibnite exploitation in this region as a byproduct of Au and Ag ores commenced in the first half of the seventeenth century and continued, with some interuptions, until the end of the twentieth century. During the last four decades of the twentieth century, mining activities were concentrated on the Dúbrava deposit—the main Sb producer in former Czechoslovakia (Chovan et al. 1998).

Exploitation of Sb ore occurred in the Predpekelná and Dechtárka mine sections. The most productive period of the deposit was from 1943 to 1991. During this period, the antimony ore flotation processing plant was constructed. The waste produced by the processing plant was deposited as mine tailings in the Rudné Bane Banská Bystrica area, which became an environmental issue after the mine closed in 1991. Three mine tailings dam were constructed in total. The oldest one is situated at the highest altitude in the Križianka valley and occupies an area of 24,000 m^2, the second is situated just below the first and occupies an area of 27,000 m^2. The third tailings area, which only started operating in 1989, is situated north of the second tailings deposit, and occupies an area of 104,000 m^2 (Fig. 1) (Arvensis et al. 1994).

Materials and Methods

Sampling points (Fig. 1) included seven adit outlets (HDP D-2, Samuel D-3, Svätopluk D-4, Rakytová D-6, Martin D-7, Flotačná D-8, Ignác D-9). Groundwater has been monitored in five boreholes, D-21, DU-2, DU-4, DU-5, and DU-6 (Chovan et al. 2010). All the drilled boreholes were located in alluvial deposits of the Paludžanka Creek with average borehole depth 9 m and were equipped with PVC casing. Groundwater samples were also taken from the

Fig. 1 Map of monitoring sites at the Dúbrava abandoned deposit



Teplica spring (D-17) and one domestic well (D-22) associated with a cottage area called Pod Dobákom (Fig. 1).

Monitoring sites also included three profiles on Paludžanka Creek (D-1, D-16, D-20) and one profile on Dúbravka creek (D-18). Monitoring has also been performed at a ground water seep site (D-19) at the base of one of the tailings areas (Fig. 1).

Field parameters (water temperature, pH, redox potential (Eh), electrical conductivity (EC), and dissolved oxygen (DO) have been monitored since 2007. EC was measured with a WTW Multi 350i using a TetraCon^{R}325 electrode, the pH was measured using a WTW Multi 350i with a Sentix 41 electrode, and the Eh was measured with a WTW pH meter 340i using a SenTix^{R}ORP combined platinum electrode equipped with a calomel reference electrode. Field Eh measurements were corrected for the standard hydrogen electrode (SHE) (Pitter 2009). DO was measured with a WTW Oxi 340i/SET oxymeter using a DurOx 325-3 electrode.

Water samples were taken from the sampling points in Sept. 2007 (13 samples) and April 2008 (18 samples). There was good weather during the sampling, and discharges in the surface water bodies corresponded to a low flow period. Adits were sampled immediately at their outflow zone or a few meters downstream at places with limited access. Groundwater samples from boreholes were taken after renewing the well volume several times and waiting for stabilization of the EC and pH values. Samples selected for trace element analysis (Fe, Mn, Al, Co, Cu, Ni, Zn, and Pb, and in Sept. 2007, Cd, Cr, and Hg) were filtered through a 0.45 μm filter and preserved with ultrapure HNO_3. The samples for determination of Sb and As were filtered through a 0.45 μm filter and then preserved with ultrapure HCl. All samples were kept at 4 °C until analyses. Concentrations of As and Sb were determined by AAS (hydride generation, Spectr AA 220 fy Varian with a flame-heated silica atomizing tube and automatic hydride generator); Na, K, Ca, Mg, Cl^-, NO_3^-, SO_4^{2-}, Si, Fe, Mn, Al, Cr, Cu, Zn, Co, Ni, Pb, Cd, Hg were analysed by AES-ICP (VISTA-MPX fy Varian) in the Slovak Geological Survey's Geoanalytical Laboratory. The measured concentrations of trace elements in the certified and synthetic standards were within 10 % of their true values. Replicate analyses were carried out on selected samples and variations were also in the range of ±10 %.

Speciation modeling was performed using PHREEQC-2 (Parkhurst and Appelo 1999). Thermodynamic data for complexes and minerals of arsenic were compiled from the Minteq, Wateq, and Llnl databases available with PHREEQC-2. Data for Ca-bearing As complexes, As minerals, and Ca-arsenate minerals were taken from Bothe and Brown (1999), while data for Mg-bearing arsenic complexes were from Whiting (1992).

Cluster analysis was performed with STATGRAPHICS Centurion XVI using the Ward's method. The squared Euclidean distances method was used as a distance standard.

Groundwater flow was modeled with Groundwater Vistas v5 (GWV, based on Modflow) from Environmental Simulations, Inc. (ESI). Calibration of the flow model was performed in PEST (Doherty 2010). Transport modeling was performed with MT3DMS (Zheng and Wang 1999) software and was based on the Modflow flow modeling results. The main hydraulic parameters of the aquifer were evaluated using groundwater level measurements in six observation wells, surface water flow, and water level measurements at two observation points, pumping tests performed on two wells, and grain size analyses from six wells. The main parameters for transport model were taken from Zheng and Bennet (2002) and adjusted during calibration. Source concentrations of pollutants were based on chemical analyses of field samples.

Results

Water Chemistry

Surface water and groundwater are of the $Ca–Mg–HCO_3–SO_4$, $Ca–Mg–SO_4–HCO_3$, and $Ca–Mg–SO_4$ types (Fig. 2). Selected parameters of the studied waters are listed in Table 1. Based on pH, the groundwater is alkaline in character. The pH values in the mine drainage waters ranged from 7.43 to 8.55 as a consequence of carbonate dissolution. Values of Eh corrected with respect to SHE ranged from +231 to +517 mV. Concentrations of sulfate in the mine drainage were relatively low, from 48.3 to 179.0 mg/L, except for the outflow from Ignác Adit (D-9), where they reached 267 mg/L. Concentrations of Fe and Mn were also low.

Surface water pH values were above 6.89; Eh ranged up to 540 mV in Paludžanka Creek (D-1). Concentrations of sulfate in the stream were below 19.7 mg/L. The lowest pH in the study area was found in groundwater from wells in the alluvium below tailings area 3, with a minimum value of 6.4 (well DU-5). The Eh there ranged from 119 to 533 mV. The groundwater there also had slightly increased concentrations of Fe (0.95 mg/L) and Al (450 μg/L), but SO_4^{2-} concentrations were less than 196 mg/L (DU-2).

Dissolved Antimony and Arsenic Concentrations

Concentrations of Sb and As were the highest in the outflow from the adits (Table 1). The Sb concentrations consistently exceeded 830 μg/L (Fig. 3); the maximum Sb concentration was 9,300 μg/L and was found in the outflow

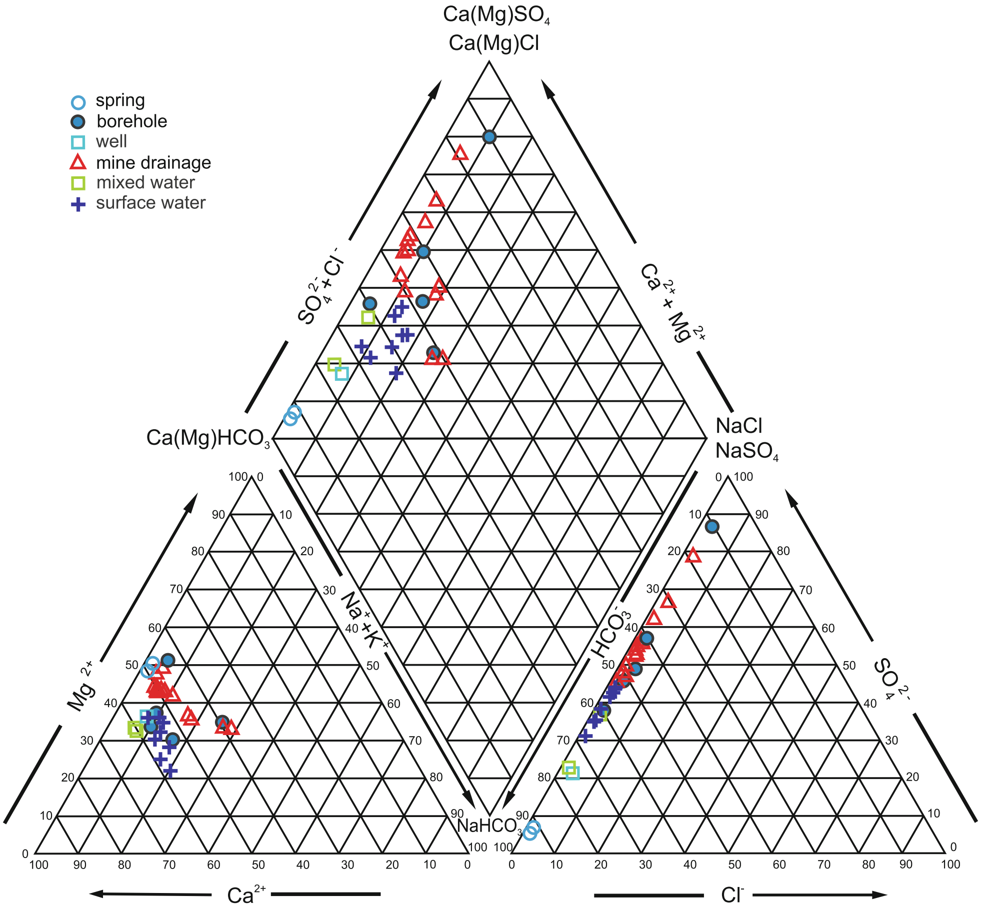


Fig. 2 Piper diagram of the chemistry of water samples at the Dúbrava mining site

from the Samuel Adit in April 2008. Concentrations of As in mine waters ranged from 4 μg/L (Flotačná Adit) to 62 μg/L (Samuel Adit), but were much lower than the Sb concentrations.

The leachate from the mine tailings also contained high contents of Sb, As, and other trace elements; 104 μg/L of Sb and 16 μg/L of As were found in seepage waters from mine tailings 3 (D-19).

Concentrations of Sb were low (8–10 μg/L) in the highest upstream profile on Paludžanka Creek (D-1). The concentrations increased downstream due to the input of mine water from the adits and drainage from the mine tailings, and then remained almost constant downstream of the tailings. Concentrations of Sb were 76–128 μg/L in the last sampled profile on Paludžanka Creek, downstream from the village of Lazisko (D-20). Concentrations of As in the creek did not increase downstream and remained almost constant (6–10 μg/L).

The concentration of Sb in a private well in the Pod Dobákom area (D-22) reached 126 μg/L, which is much higher than the Sb drinking water limit of 5 μg/L (Government of the Slovak Republic regulation no. 496/2010). Concentrations of As were below the detection limit.

Background surface water concentrations in the study area, i.e. in Paludžanka Creek, upstream of the mine site (D-1), were 10 μg/L for Sb (Fig. 3) and 9 μg/L for As. Background groundwater concentrations were represented by Teplica Spring, located on the left bank of Paludžanka Creek (DUH-17), where respective Sb and As concentrations were 2 and 4 μg/L.

Based on chemical analysis and discharge measurements, it is evident that outflows from mine adits are the principle source of Sb and As in Paludžanka Creek. This is linked not only to high concentrations of Sb and As in the outflows, but also to high discharge levels, which vary during the year. Table 2 provides the mass flux of Sb and As into the creek. The maximum mass flux of Sb was from the HDP Adit in spring, when 171.395 kg/month was discharged. The maximum mass flux of As was from the Svätopluk Adit (5.509 kg/month of As).

Stability diagrams for pe-pH were plotted for the dominant forms of Sb, As, and Fe (Fig. 4a–c) using data collected in Sept. 2007 and April 2008. Based on these diagrams, Sb is present as Sb(V) and its dominant species is $Sb(OH)_6^-$ (Fig. 4a). Similarly, As is present as As(V), dominantly as $HAsO_4^{2-}$ (Fig. 4b). Arsenic in

Table 1 Field parameters and concentrations of dissolved species of samples collected during Sept. 2007 (07) and April 2008 (08) at designated sampling points; temperature (t) is in °C, electrical conductivity is reported in mS/m, Eh is reported in mV, concentrations of Ca, Mg, Fe, Mn, HCO_3^-, and SO_4^{2-} are reported in mg/L, while the other concentrations are reported in μg/L

	Date	t	EC	pH	Eh	Ca	Mg	Fe	Mn	HCO_3^-	SO_4^{2-}	Al	As	Sb	Co	Cu	Ni	Pb	Zn
D-1	07	5.2	4.7	7.60	518	6.3	1.6	0.011	0.006	18.7	9.2	90	8	8	<2	<2	<2	<5	8
	08	3.0	4.3	7.30	530	5.4	1.2	0.040	0.020	12.3	5.3	<20	9	10	<2	<2	<2	<5	2
D-2	07	5.4	36.8	7.98	503	38.8	20.4	0.027	0.016	105.9	101.0	70	5	2,630	<2	<2	6	<5	8
	08	5.5	39.5	7.96	484	42.7	21.9	0.051	0.022	110.6	100.0	<20	34	3,280	<2	<2	<2	<5	5
D-3	07	5.8	55.7	8.30	466	59.3	38.6	0.042	0.014	165.2	171.0	80	10	8,500	<2	<2	4	<5	6
	08	4.9	50.5	8.24	464	52.2	33.1	0.046	0.004	141.4	142.0	<20	62	9,300	<2	<2	<2	<5	6
D-4	07	5.2	20.2	7.85	415	20.7	10.5	0.020	0.006	62.3	48.3	80	8	1,580	<2	<2	<2	<5	6
	08	5.0	22.6	7.59	457	23.3	12.2	0.504	0.024	67.7	48.8	180	57	1,650	<2	3	<2	11	6
D-6	07	6.5	50.8	7.94	504	55.3	29.6	0.023	0.012	112.1	179.0	60	8	1,740	<2	<2	<2	<5	7
	08	6.0	44.5	8.05	463	47.7	25.2	0.039	0.004	104.6	137.0	20	39	1,300	<2	<2	<2	<5	5
D-7	07	6.9	42.1	8.39	472	33.8	17.4	0.034	0.011	143.3	102.0	60	11	900	<2	<2	<2	<5	4
	08	6.4	42.1	8.15	504	35.6	17.9	0.145	0.008	141.4	93.1	<20	34	830	–	–	–	<5	2
D-8	07	7.2	44.8	8.22	470	44.8	20.9	0.030	0.010	127.8	129.0	70	4	1,460	<2	<2	<2	<5	<2
	08	6.5	44.3	8.15	483	44.1	20.2	0.041	0.005	126.0	119.0	<20	16	1,330	<2	<2	<2	<5	2
D-9	07	6.1	63.6	7.99	457	70.7	40.6	0.025	0.012	90.4	267.0	70	6	1,550	<2	<2	<2	<5	8
D-16	07	4.9	8.5	7.66	502	9.2	3.0	0.025	0.021	28.1	18.6	80	7	121	<2	<2	<2	<5	9
	08	3.9	6.4	7.62	466	7.3	2.4	0.034	0.003	18.4	11.1	<20	10	79	<2	<2	<2	<5	4
DU-2	08	6.2	53.2	6.43	375	63.6	26.1	0.695	0.129	36.2	196.0	450	3	107	3	4	<2	<5	15
DU-4	08	7.6	16.9	6.39	408	19.2	6.6	0.303	0.013	43.0	33.60	250	3	30	<2	<2	<2	<5	23
DU-5	08	7.6	51.3	6.39	415	66.5	24.2	0.306	0.070	138.3	144.0	240	3	4	<2	<2	<2	<5	5
DU-6	08	5.3	35.3	7.10	348	33.8	23.9	0.184	0.013	132.2	65.4	40	4	45	<2	<2	<2	<5	5
D-17	07	7.1	41.9	7.90	533	49.6	30.5	0.200	0.030	280.4	16.1	90	1	2	<2	<2	<2	<5	6
	08	6.9	42.9	8.02	448	48.2	28.6	0.038	0.003	267.4	12.8	<20	2	4	–	–	–	<5	6
D-18	07	5.0	9.2	7.75	537	11.1	4.3	0.023	0.015	31.1	18.4	80	7	125	<2	<2	4	<5	7
	08	4.2	6.6	7.44	496	8.6	2.6	0.036	0.003	18.4	10.5	<20	10	76	–	–	<2	<5	3
D-19	07	8.6	44.8	7.50	426	57.3	18.9	0.376	1.360	193.2	88.9	60	7	77	<2	<2	5	<5	37
	08	6.8	38.7	7.95	378	54.9	18.6	0.241	0.103	199.8	48.4	40	16	104	–	–	<2	<5	3
D-20	07	7.8	12.7	7.81	509	13.0	5.3	0.033	0.012	53.0	19.7	70	6	128	<2	<2	2	<5	9
	08	4.8	9.1	7.44	474	10.7	3.8	0.034	0.004	33.8	12.5	<20	7	76	–	–	<2	<5	<2
D-21	08	6.4	39.3	7.75	259	32.1	17.1	0.211	0.103	129.1	85.8	<20	7	20	<2	<2	<2	<5	<4
D-22	08	–	12.5	7.37	–	28.3	10.9	0.035	0.042	103.9	22.22	<20	<1	126	<2	<2	<2	<5	0.1

samples from wells in the Paludžanka Creek alluvium (DU-2, DU-4, DU-5) are in the $H_2AsO_4^-$ field due to the relatively low pH.

Oxides and oxihydroxides of Fe play an important role in attenuation of Sb and As. Based on the pe-pH diagram, the principal Fe phase at the Dúbrava site was $Fe(OH)_3$ (Fig. 4c).

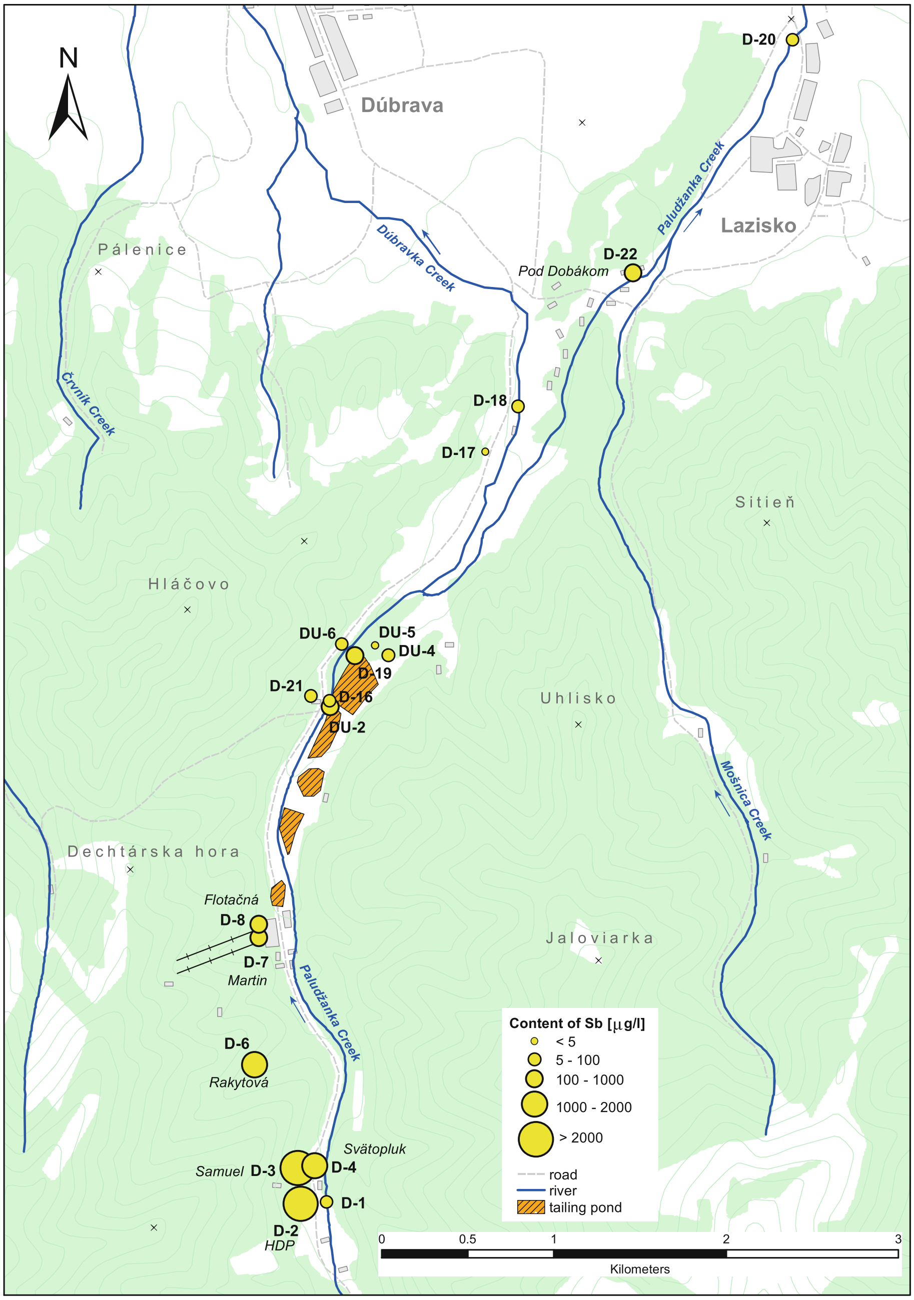
Speciation Calculation

PHREEQC-2 Interactive (Parkhurst and Appelo 1999) and a database for As minerals (Sracek et al. 2004) were used to calculate saturation indices (SI) for calcite ($CaCO_3$), rhodochrosite ($MnCO_3$), gypsum ($CaSO_4 \cdot 2H_2O$), amorphous $Al(OH)_3$ and $Fe(OH)_3$, goethite ($FeO(OH)$), siderite ($FeCO_3$), and scorodite [$(FeAsO_4) \cdot 2H_2O$] (Table 3). Calculations were performed using data from Sept. 2007 and April 2008.

In all samples, SI values were positive for amorphous $Fe(OH)_3$ and goethite. Based on mineralogical analyses of phases in Fe(III) ochres (Belzile et al. 2001; Trtíková et al. 1999), goethite is formed later during aging of less stable Fe(III) phases.

Negative SI values were calculated for rhodochrosite, gypsum, siderite, and also for amorphous $Al(OH)_3$ (except in samples from wells DU-2, DU-4, and DU-5 in April 2008), and in most samples for calcite (Table 3). All samples were undersaturated with respect to the only significant

Fig. 3 Concentrations of dissolved antimony (April 2008)



As(V) mineral, scorodite, probably due to the low concentrations of Fe(III). Supersaturation with respect to amorphous $Fe(OH)_3$ and goethite suggests that these phase might be adsorbents of dissolved As and Sb.

Cluster Analysis of Water Quality Data

Water chemistry data and results of field parameter measurements based on sampling in Sept. 2007 and April and Nov. 2008 were interpreted using hierarchical cluster analysis (HCA) in STATGRAPHICS Centurion XVI program. The total number of analyses was 30; selected parameters were TDS, Na^+, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, HCO_3^-, Si, Fe, As, and Sb. Field parameters were EC, pH, DO, and Eh. The HCA divided samples into two basic groups, A and B, which comprise four clusters (1–4) (Fig. 5).

The first group (A) is composed of clusters 1 and 2, which include all surface, ground, and seepage waters. Cluster 1 includes waters from Paludžanka and Dúbravka creeks, and also water from well DU-4. Groundwater from the spring, other wells, and seepage waters are in cluster 2 (Fig. 5).

Table 2 Flux of As and Sb of mine water collected during Sept. 2007 (07) and April 2008 (08) at designated sampling points

Mine adit	Date	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)
D-2	07	4.48	5	2,630	22.4	11,782.4	0.058	30.540
(HDP)	08	20.16	34	3,280	685.4	66,124.8	1.777	171.395
D-3	07	0.56	10	9,300	5.6	4,760.0	0.015	12.338
(Samuel)	08	1.60	62	8,500	99.2	14,880.0	0.257	38.569
D-4	07	13.52	8	1,580	108.1	21,361.6	0.208	55.369
(Svätopluk)	08	37.29	57	1,650	2,125.5	61,528.5	5.509	159.482
D-6	07	7.24	8	1,740	57.92	12,597.6	0.150	32.653
(Rakytová)	08	7.36	39	1,300	287.0	9,568	0.744	24.800
D-8	07	3.75	4	1,460	15.0	5,475	0.039	14.191
(Flotačná)	08	4.19	16	1,330	67.0	5,572.7	0.174	14.444

The second group (B) comprises mine water from all of the adits, confirming that their composition differs. This is caused by their much higher concentrations of Sb, As, and sulfate. Within the group, two clusters, 3 and 4, can be distinguished. Cluster 3 comprises waters from adits HDP, Svätopluk, and Samuel, which are all located in the Predpekelná mining zone. Cluster 4 comprises waters from the Dechtárka and Rakytová mining zones with adits Flotačná, Ignác, Martin, and Rakytová, where the Martin adit is the most different from the other adits. Difference between clusters 3 and 4 is probably caused by higher Sb concentrations in water from the Predpekelná mining zone, where the highest concentrations of Sb at the Dúbrava deposit were found.

Contaminant Transport Modeling

Based on water level monitoring and hydraulic data, a hydraulic model of the study area has been developed. The modeling domain begins at the outflow from Flotačná adit (D-8); its downgradient boundary is at the end of the valley close to Pod Dobákom (D-22). The model was prepared using Groundwater Vistas (GWV) v5, which comprises several packages including MODFLOW, MODPATH, PEST, and MT3DMS. The basic model characteristics are: 430 × 80 cells with dimensions 10 × 10 m, four layers, which cover the saturated zone (20–50 m thick), 59,880 active cells (remaining cells are not active, "no flow"), 278 cells with constant hydraulic head (H is constant), and 685 cells for the river (boundary condition based on water level in river, river bottom elevation, thickness of river sediments, and their hydraulic conductivity). Boundary conditions H = constant was imposed for groundwater at the southern inflow boundary with H = 890 m above sea level (asl) and at the northern outflow boundary with H = 695 m asl. Parameters for the river were: width = 3 m, conductance = 1.5×10^{-3} m^2/s. Concentration in the river was set to C = 100 µg/L. Cells out of the alluvium were not active (no flow). Parameters of the saturated layer were: hydraulic conductivity $k = 7.4 \times 10^{-4}$ m/s, specific storage $S_s = 0.01$, specific yield $S_y = 0.15$, porosity n = 0.3, and effective porosity $n_e = 0.2$. The digital elevation model was from 700 to 1,000 m asl, the thickness of the bottom layer was from 20 m at the valley margins to 50 m in the valley's central zone, and the initial water table elevation was from 660 to 890 m asl. In transport, longitudinal dispersivity was $\alpha_L = 20$ m and transversal dispersivity was $\alpha_T = 1$ m. Reaction barrier was simulated using distribution coefficient K_d, bulk density of dry sediment d, and half-life $t_{1/2}$.

The modeling domain was 3,800 m long, with an average width of 250 m, and an average hydraulic gradient of I = 0.043. Average specific discharge was 2.75 m/day and average linear velocity was 13.75 m/day (assuming an effective porosity of 20 %). For this length of modeling domain, the time of advective transport across the whole domain was 276 days (Krčmář et al. 2010).

First, the current state of contamination was modeled, based on monitoring data from 2007 and 2008. Concentrations of Sb were about 100 µg/L in the creek and about 40 µg/L in wells located in alluvium. Then the concentration of 100 µg/L in the creek was applied as a boundary condition. In the mine tailings areas, a constant concentration boundary condition was imposed. Transport parameters were taken from the literature (Zheng and Bennet 2002). Modeling indicates transport from the contaminated river into the alluvial sediments aquifer. The contamination is transported by dispersion from alluvium farther into the surrounding area. Spreading of contamination is more limited only in the zone where water flows from surrounding slopes (especially around well DU-4). Due to the sparse network of monitoring points, it is impossible to determine more reliable values of dispersivities and spreading of contamination in horizontal and

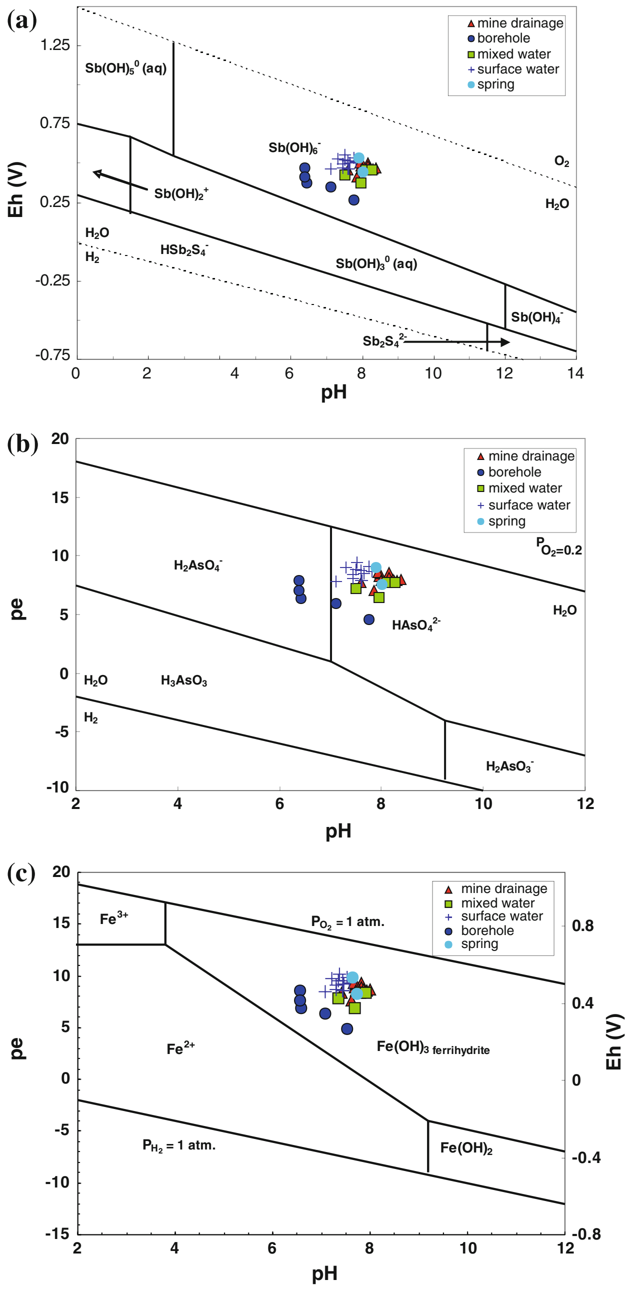


Fig. 4 pe–pH diagrams for dissolved: **a** antimony, **b** arsenic, **c** iron

vertical directions. However, data for the Pod Dobákom well (NE boundary of domain) from 2008, where the Sb concentration was 126 µg/L, show that the model solution is realistic (concentrations in model were 80–90 µg/L).

Based on monitoring results, the principal sources of Sb contamination are outflows from the mine adits. For example, in 2007, Sb concentrations in the mine adit discharges ranged from 1,460 to 9,300 µg/L and the total discharge was 60 L/s. This extremely contaminated water flows into surface streams and the surrounding groundwater aquifer. In our opinion, the area affected by this contamination can be relatively easily limited by capturing and treating this adit water.

For this reason, we next modeled the impact of treating the water flowing from the adits. In the model, the initial contaminant concentration in the creek, set as zero, was combined with the contamination of ground water modeled in stage 1. Time of modeling was 1,000 days and concentrations were modeled for consecutive time steps (Fig. 6). The improvement was evident; for example, in the Pod Dobákom well, Sb concentrations decreased from ca 85 to 15 µg/L after 1,000 days, when steady state had been reached. This concentration is still above the 5 µg/L limit for drinking water, but is much lower than the original concentration.

The impact of mine tailings on the spreading of contamination can also be observed in Fig. 6. However, it must be kept in mind that the modeled impact of mine tailings is questionable because the infiltration from mine tailings was only estimated. It is likely that this is a “worst case scenario” and that the real situation might be better. Also, the effect of sorption was not included in the model and real attenuation of contamination is probably more significant; this depends on the retardation coefficient R_f, which is difficult to estimate. However, the sorption capacity of alluvial sediments in the study area is very limited (Arvenzis et al. 1994; Letko 1992).

Discussion

The abandoned Dúbrava ore deposit is typical of mine sites in Slovakia, in that all compartments of the environment, including ground water and surface water, were affected by previous mining. Silicate minerals in the gangue rock play a major role in the water chemistry, as does oxidation of sulfidic minerals and dissolution of carbonates. Dissolution of carbonates and hydrolysis of silicates both produce neutral mine drainage (Nordstrom 2011). Vrana and Rapant (1991) interpreted the neutral pH values to be a consequence of carbonates present in the mineralized veins. A similar situation is observed at other ore deposits in Slovakia, such as Pezinok-Kolársky vrch (Fľaková et al. 2005, 2012), Čučma (Fľaková et al. 2011a), Poproč (Fľaková et al. 2009), and Medzibrod (Fľaková et al. 2011b; Ženišová et al. 2009). Šottník et al. (2011) interpreted pH values of 6.62–7.47 in river sediment at Dúbrava to be a consequence of the high neutralization capacity of the rocks there.

Intense contamination of Paludžanka Creek waters close to the Dúbrava mine tailings have been reported previously, with concentrations of Sb ranging from 130 to 140 µg/L in 1992 and 1993 (Arvensis et al. 1994) and 190 µg/L in 2003 (Vrana et al. 2005). Similar

Table 3 Values of saturation indices (SI) for selected minerals based on samples collected during Sept. 2007 (07) and April 2008 (08) at designated sampling points

	Date	Calcite	Rhodochrosite	Gypsum	Amorphous Al(OH)$_3$	Amorphous Fe(OH)$_3$	Goethite	Siderite	Scorodite
D-2	07	−0.17	−1.14	−1.76	−0.91	2.53	7.68	−6.14	−7.45
	08	−0.13	−1.00	−1.73	−1.74	2.80	7.95	−5.49	−6.31
D-3	07	0.46	−0.87	−1.45	−1.20	2.72	7.88	−5.79	−7.61
	08	0.29	−1.49	−1.55	−1.99	2.82	7.94	−5.59	−6.60
D-4	07	−0.75	−1.83	−2.25	−0.71	2.39	7.53	−4.74	−7.10
	08	−0.94	−1.45	−2.21	−0.09	3.74	8.87	−3.56	−4.41
D-6	07	−0.06	−1.30	−1.44	−0.99	2.38	7.57	−6.21	−7.32
	08	−0.03	−1.70	−1.58	−1.55	2.66	7.83	−5.49	−6.57
D-7	07	0.32	−0.91	−1.83	−1.45	2.55	7.76	−6.30	−7.87
	08	0.10	−1.21	−1.84	−1.97	3.21	8.40	−5.70	−6.26
D-8	07	0.21	−1.10	−1.63	−1.23	2.48	7.69	−6.05	−8.06
	08	0.13	−1.46	−1.66	−1.98	2.66	7.85	−5.95	−7.14
D-9	07	−0.05	−1.36	−1.22	−0.96	2.45	7.62	−5.72	−7.50
D-1	07	−1.97	−2.48	−3.35	−0.40	2.07	7.21	−6.83	−6.89
	08	−2.53	−3.45	−3.63	−0.98	2.64	7.69	−6.02	−5.75
D-16	07	−1.59	−1.73	−2.91	−0.50	2.47	7.59	−6.10	−6.69
	08	−1.90	−2.79	−3.21	−1.31	2.65	7.73	−5.39	−6.28
D-18	07	−1.38	−1.75	−2.85	−0.59	2.45	7.58	−6.85	−6.88
	08	−2.01	−2.96	−3.17	−1.16	2.59	7.68	−5.61	−6.00
D-20	07	−0.98	−1.55	−2.78	−0.84	2.44	7.68	−6.30	−7.05
	08	−1.65	−2.58	−3.02	−1.19	2.53	7.65	−5.04	−6.22
D-17	07	0.31	−0.63	−2.48	−0.80	3.28	8.49	−5.33	−7.24
	08	0.40	−1.56	−2.58	−1.86	2.59	7.79	−4.84	−7.86
D-21	08	−0.37	−0.44	−1.90	−1.57	3.19	8.37	−0.97	−6.19
DU-2	08	−2.02	−2.19	−1.34	0.66	2.09	7.27	−1.81	−5.44
DU-4	08	−2.35	−3.01	−2.42	0.42	2.53	7.76	−2.77	−4.89
DU-5	08	−1.41	−1.90	−1.45	0.36	2.15	7.38	−1.75	−5.31
DU-6	08	−1.00	−1.94	−1.99	−0.34	2.77	7.91	−1.41	−5.67
D-19	07	−0.18	0.61	−1.69	−0.66	3.35	8.63	−2.80	−5.53
	08	0.25	−0.14	−1.94	−1.19	3.38	8.59	−2.84	−6.02

concentrations (Fig. 3) were found near the village of Lazisko in 2008 (128 μg/L). The lowest Sb concentrations in surface water (8 μg/L) were found upgradient of the study area (D-1). In Paludžanka Creek, downstream from the mine tailings (D-16), Sb concentrations reach 79–121 μg/L, depending on the season and discharge levels in the creek. In the final monitored profile downstream of Lazisko (D-20), Sb concentrations (76–128 μg/L) were almost equal to those close to the mine tailings (Table 1; Fig. 7).

Previous studies also confirmed high concentrations of Sb in the mine adit outflows. Comparison of chemical analyses made during project APVV (Chovan et al. 2010) and older data indicate persistent contamination. Arvensis et al. (1994) and Vrana et al. (1984, 2005) reported Sb concentrations of 2,740 and 2,900 μg/L in 1982 and 1992, respectively, in HDP (D-2) adit, compared to concentrations of 2,630 μg/L in 2007 and 3,280 μg/L in 2008. In contrast, Sb concentrations in the discharge from the Samuel Adit (D-3) increased: in 1982, Sb concentration was 2,360 μg/L (Vrana et al. 1984), but in 2007 and 2008, concentrations were much higher (8,500 and 9,300 μg/L, respectively). Concentrations of Sb in outflow from the other adits have not changed very much from 1982 to 2008.

Despite the high As concentrations in the mine tailings, the principal contaminant sources are the adit outflows. It is evident that As concentrations are much lower than the Sb concentrations, which is probably due to the limited mobility of As bound to a solid phase (Ashley et al. 2003; Hiller et al. 2009). However, the opposite situation was found in Slovakia at the Pezinok-Kolársky vrch deposit,

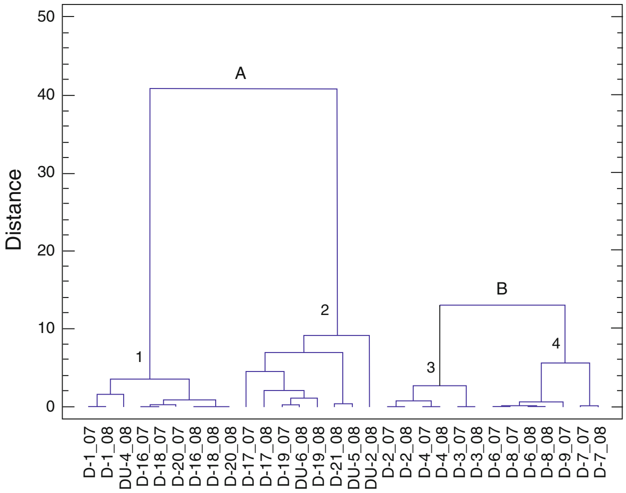


Fig. 5 Dendogram showing groups (*A* and *B*) and subgroups (*1–4*) of water samples examined in this study

where arsenic dominated, and the highest concentrations of As and Sb were in groundwater contaminated by mine tailings, which had respective concentrations 90,000 and 7,500 μg/L (Fľaková et al. 2012).

Speciation calculations at Dúbrava indicated that all samples were undersaturated with respect to scorodite. This was probably caused by low concentrations of Fe(III) in the pore water. Similar results have been reported for other mine sites in Slovakia; socrodite was found in only one sample at Poproč (Chovan et al. 2010; Klimko et al. 2011). Scorodite is a common product of arsenopyrite oxidation (Alpers et al. 1994 in Chovan et al. 2010), but is relatively unstable (Buckley and Walker 1988 in Chovan et al. 2010).

In contrast, saturation indices were generally positive for amorphous $Fe(OH)_3$ and also goethite (FeO(OH)). Results of speciation calculations are consistent with mineralogical analyses and with speciation calculations at other Slovak mine sites, such as Čučma (Fľaková et al. 2011a, b), Poproč (Fľaková et al. 2009), Medzibrod (Ženišová et al. 2009), and Pernek (Jašová et al. 2010). Due to the lack of secondary As and Sb phases, adsorption of Fe(III) phases is the principal attenuation mechanism. However, this process is limited at alkaline pH due to the oxyanionic nature of both contaminants.

Release of even limited amounts of Sb and As from soil and river sediments can significantly impact their dissolved

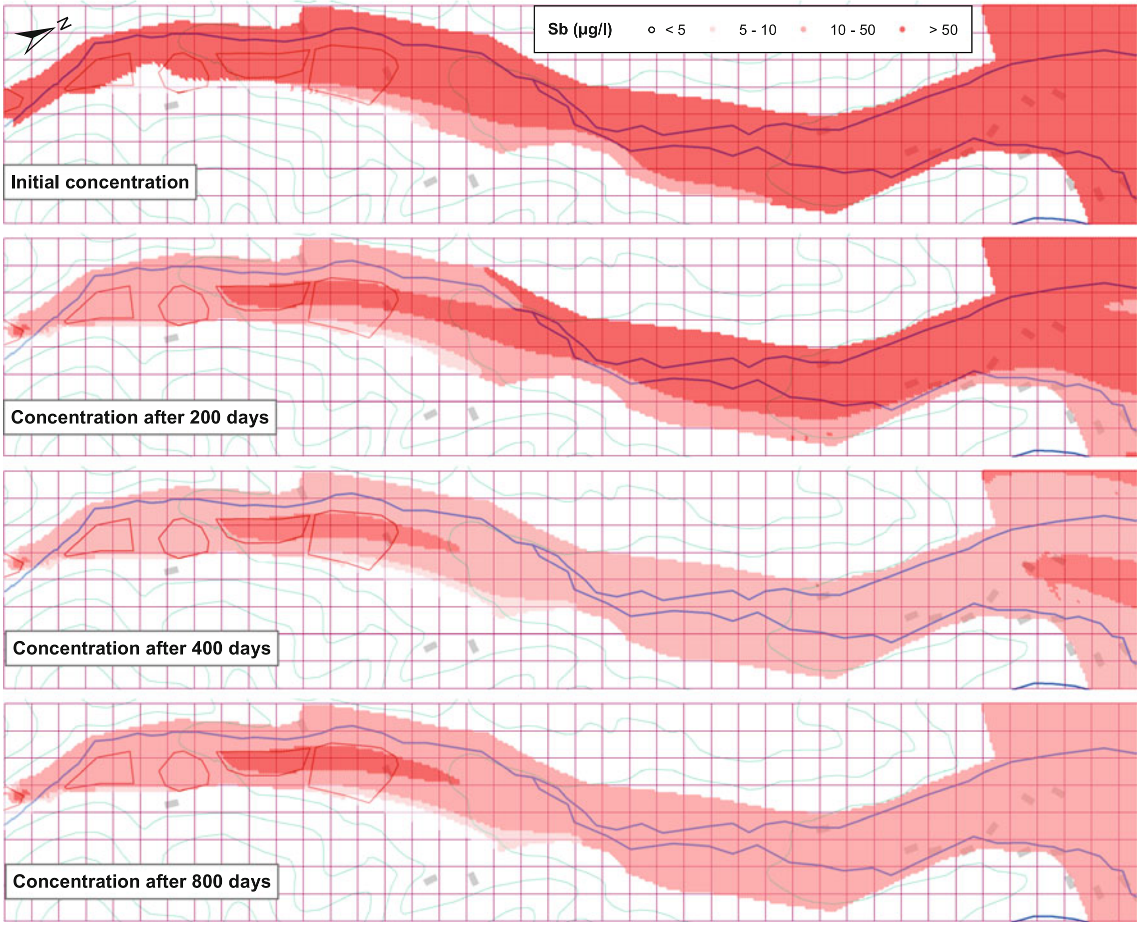


Fig. 6 Modeled concentrations of antimony in groundwater after 200, 400, and 800 days

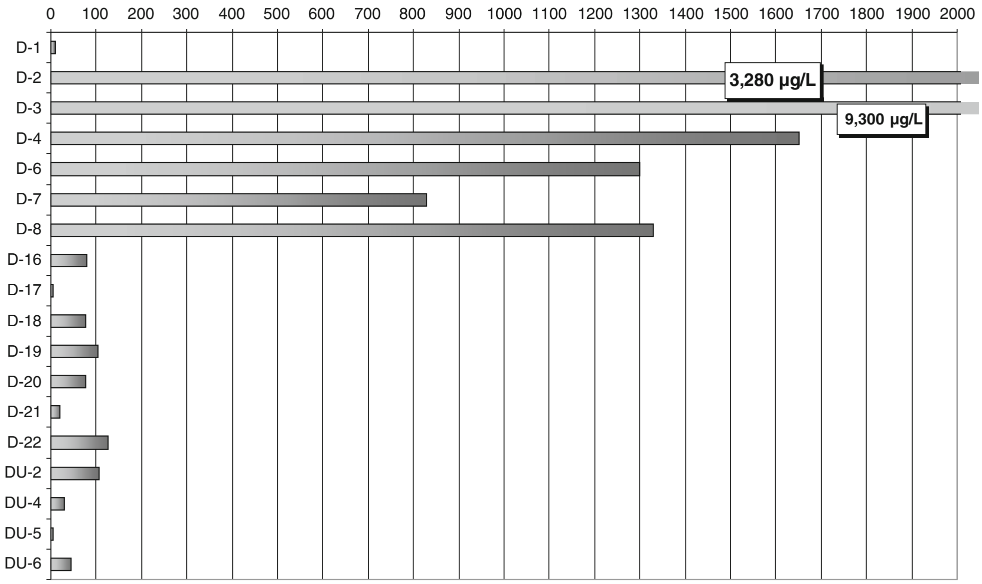


Fig. 7 Concentrations of Sb (µg/L) in surface water and groundwater around the abandoned Dúbrava ore deposit (April 2008, Chovan et al. 2010)

concentrations (Hiller and Šutriepka 2008; Hiller et al. 2009; Jankulár et al. 2010). Leaching of samples from the Pernek deposit showed higher mobility of Sb compared to As (Hiller et al. 2009), despite the generally higher observed mobility of As (Wilson et al. 2004; Wolfram et al. 2000).

The closed Dúbrava deposit is the most serious source of Sb contamination in Slovakia (Chovan et al. 2010) and is probably one of the most serious in the world. In addition to the adit outflows, seepage from waste rock piles and mine tailings contain several other potentially toxic contaminants (As and Sb, less Pb and Zn); this is demonstrated by high concentrations of Sb (104 µg/L) and As (16 µg/L) in seepage waters from tailings area 3 (D-19). The tailings contain enough carbonates to neutralize the acidity formed by the oxidation of sulfides (Chovan et al. 2010), which explains the relatively high pH (7.5–7.95) of the seepage waters. Similar neutralization by carbonates in mine tailings has been described at the Pezinok (Majzlan et al. 2007) and Medzibrod (Chovan et al. 2010) mine sites in Slovakia and at the Goesdorf mine in Luxembourg (Filella et al. 2009). High concentrations of Sb in seepage waters from mine tailings indicate fast oxidation of stibnite in unsaturated tailings, where stibnite is rare due to its fast dissolution rate (Ashley et al. 2003; Ženišová et al. 2009). Fast dissolution of stibnite has also been demonstrated in mineralogical studies (Chovan et al. 2010).

Stream sediments at Dúbrava reflect the multiple sources of contamination, including water rock piles, mine adits, and mine tailings (Chovan et al. 2010; Petrák et al. 2011). Principal contaminants are As and Sb, but high contents of Pb, Zn, and Cu were also found. The Sb and As levels in Paludžanka Creek alluvium ranged up to 9,616 and 844 mg/kg, respectively, downstream from tailings area 3. Soils around old mining works and especially fluviosols in alluvium of Paludžanka Creek are potential sources of mobilizable forms of As and Sb and other contaminants, which can be released and bioaccumulated in living organisms (Hiller et al. 2009; Jankulár et al. 2010; Ženišová et al. 2010).

The accumulated Fe ochre near the old mine works also has a high potential impact on the environment. The ochres have high As (up to 2 g/kg) and Sb (up to 1.6 g/kg) levels in low crystallinity phases (Lalinská et al. 2009, 2011). Selective extraction at the closed Medzibrod Sb deposit indicated the dominant presence of As and Sb in amorphous and low crystallinity Fe-oxihydroxides and their significant desorption from these phases (Chovan et al. 2010).

Based on local geology, there are high background Sb and As contents in rock environment, but they are relatively stable. Mining activities greatly accelerate Sb and As release because they disturb long-term equilibrium. Infiltration of precipitation into the abandoned mines, waste rock piles, and mine tailings has resulted in intense leaching of wastes and mobilization of contaminants. Mine wastes containing even low levels of potentially toxic contaminants, which are linked to unstable mineral phases, represent a more serious threat to the environment than wastes with high contents linked to relatively inert mineral phases (Lalinská et al. 2011). Also, mine adits allow easy penetration of oxygen and intense circulation and drainage of waters (Nordstrom et al. 2000), with resultant mobilization of Sb and As. It is evident that mining at the Dúbrava deposit has caused intense environmental contamination.

Conclusions

The abandoned Dúbrava deposit is highly contaminated by Sb. The principal source of contamination is outflow from the old mine adits. The highest Sb concentration, in the outflow from the Samuel Adit (9,300 μg/L) (Ženišová et al. 2009), is similar to the highest levels reported at other contaminated sites around the world. The lowest concentration, 830 μg/L, found in the outflow from the Martin Adit, is still quite significant. Other sources of contamination are the waste rock piles and mine tailings near the former processing plant. Background Sb concentrations in surface water are low (6–10 μg/L), but they increase to 128 μg/L downstream of the mine tailings. Antimony has also impacted groundwater previously used to supply water; concentrations ranged from 120 to 150 μg/L in exploited springs that had to be closed. High Sb concentrations (126 μg/L) were also found in domestic wells downgradient of the Dúbrava deposit. Contents of Sb reach 9,616 mg/kg in soils and 644 mg/kg in stream sediments. Similar contamination has been reported at other abandoned Sb deposits in Slovakia, such as Poproč, Čučma, Zlatá Idka, Medzibrod, Pernek-Križnica, and Pezinok-Kolársky vrch (Fľaková et al. 2005, 2012; Ženišová et al. 2009), but Sb concentrations are greatest at Dúbrava, where the situation requires some mitigation. Based on flow and transport modeling, collection and treatment of outflow from the abandoned mine adits seems to be a promising mitigation option.

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