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Dissolved matter and suspended solids in the Smolník Creek polluted by acid mine drainage (Slovakia)

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Abstract: The impact of acid mine drainage on the Smolník Creek catchment was evaluated approximately 10 years after the closure of the mining area. Water and suspended solids (particles >0.45 μm) were collected five times from June 2002 to July 2003. The water chemistry of 44 samples and Fe, Al, Mg, Ca, Na, K, Cu, Zn, Mn, Pb, As contents of 25 suspended solids sample HNO_3 leachates were analysed. Past reclamation effort decreased the volume of water effluent from the abandoned mine system and improved their quality, which is indicated by the decreased content of dissolved matter from 7–17 g/l to 5±1 g/l. However, from the new mine drainage 860 m^3/day of acid mine drainage water (pH 3.8±0.5) enter the creek and other polluted water is generated by tailings and old dumps. Elevated contents of Fe, SO_4^{2-}, Cu, Zn, Mn in comparison with the water limit (CD 98/83/EC) were detected in the creek water 16 km downstream the mine, near the confluence with the Hnilec River. The total mass of suspended solids seasonally increased 2–3 times under the mine because of iron oxyhydroxides generation in the mine-creek water-mixing zones. The suspended solids transported substantial doses of iron, Al, Cu, As and other elements, which can be the same or even higher than is removed in dissolved form. The suspended solids analyses documented the immediate impact and quantity of mine-derived pollution enlargement in the catchment and they increased objectivity of environmental impact assessment.

Key words: pollution, catchment, precipitates, acid mine drainage, iron oxyhydroxides.

Introduction

Abandoned sulphide ore mines are serious source of acid mine waters enriched with sulphate, iron and other toxic elements, which contaminate surface water, sediments and soils. The generation of this water is obviously the result of pyrite oxidation in mine waste, which is subject to intensive weathering (Nordstrom 1982; Gould et al. 1994; Bigham et al. 1996). The generated acid mine drainage (AMD) continually leaches the ore-bearing and rock minerals and mobilizes a number of potentially toxic elements. Pyrite as a waste mineral is deposited in gangue dumps and tailing heaps where AMD would be produced for tens of years (Jambor & Blowes 1994; Alpers & Blowes 1994).

The abandoned Smolník mine is regarded as a “hot spot” in the Central Europe region, where AMD is generated and discharged from a flooded mine and contaminated the Smolník Creek catchment (Lintnerová 1996; Šottník 2000; Rojkovič et al. 2003; Jordan & D’Alessandro 2004). The goal of this paper is to documented the environmental risk of an abandoned mine ten years after its flooding. The basis of the study is a series of water analyses collected irregularly in various time periods. Water analyses characterizing time intervals before (1986–1990) and after (1990–1994) the mine’s closure, the subsequent ecological accident on the Smolník Creek (1994–1995), the period of mine area remediation (1998–1999) and the 2002–2003 period are presented (Lintnerová 1996; Jaško et al. 1996, 1998; Lintnerová et al. 1999, 2003; Šottník 2000). The precipitates and suspended solids analyses were adapted into a methodology of environmental risk assessment (Pontér et al. 1992; Lintnerová et al. 1999; Brake et al. 2001; Hren et al. 2001; Rhoton et al. 2002; Miller et al. 2003). Sulphate, Fe^{2+} and other ions are transported as dissolved species in the mine groundwater. When exposed to air or mixed with freshwater, Fe^{2+} is readily oxidized to Fe^{3+} and secondary Fe precipitates are formed producing even more acidity (Stumm & Sulzberger 1992; Cornell & Schwertmann 1996). During rapid precipitation and neutralization of iron oxyhydroxides they scavenge and remove dissolved elements (Lintnerová et al. 1999; Rosse & Elliot 2000; Lee et al. 2002). However, these fine-grained solids are common by transported in suspended form (Ingri & Widerlund 1994; Brake et al. 2001; Lee et al. 2002). Ochre-iron compounds coated the creek and the Hnilec River sediments for 2–3 kilometers from the confluence. The aim of this study is to evaluate the amount and chemical and mineral composition of suspended solids in creek water and indicate its importance for the mine-derived pollution spreading in the catchment area.

Geology of deposit and environmental risk of the mining area

The abandoned Smolník ore deposit is situated in the Slovenské rudohorie Mts in the SE of Slovakia (Fig. 1).

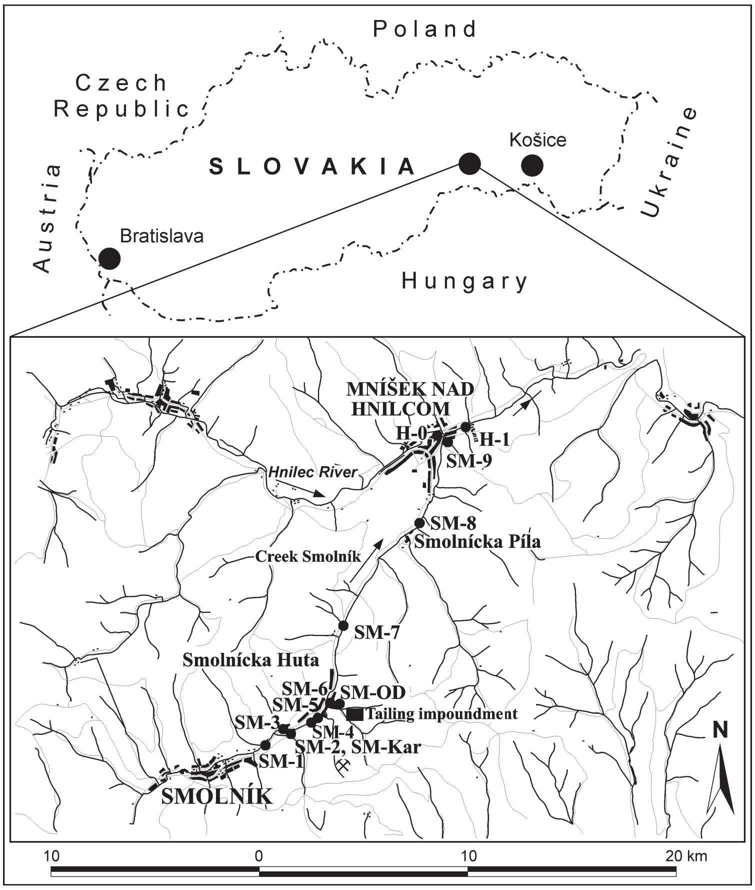

Fig. 1. Location of the Smolník mine (SM-2) and the monitoring points in the Smolník Creek selected in 2002–2003.

The volcano-sedimentary ore complex consists of concentrated pyrite beds and lenses in graphitic and mica-chlorite schist. Pyrite and chalcopyrite were dominant ore minerals (Bartalský 1993).

Smolník was a copper-ore deposit of European importance in the Middle Ages. It was exploited for centuries until 1990 (Bartalský 1993). AMD in the mining area were generated by the more than 6 million tones of abandoned pyrite ore in deposits and disseminated pyrite in surrounding rocks. As a result of flooding between 1991 and 1994, acid mine waters discharged from the flooded mine and contaminated the Smolník Creek and the Hnilec River (Lintnerová 1996; Jaško et al. 1996; Šottník 2000). Approximately 3 million tones of tailings were removed from the Smolník mine (Bartalský 1993). The tailing impoundment located near the abandoned mine increases the environmental risk of the mining area (Fig. 1). The tailings were covered with wood waste. The average 30 cm layer was not able to prevent the air oxygen diffusion and pyrite oxidation. Drainage water discharging on the impoundment base is neutral and iron oxyhydroxides precipitated from ferrous waters in open drainages (Lintnerová et al. 1999). Mine dumps, covering about 5 km^2 in the vicinity of the abandoned mine area and other waste, like wall rocks, metallurgic slag and tailings were disposed in the area during the various mining periods. The remediation of the mine area and technical improvement of the surface drainage system, the reinforcement of the creek bottom and the filling of the mine shaft (by andesite and limestone crush) decreased the potential amount of water infiltrating to the underground in the abandoned mine area. However, acid mine water enriched with metals and sulphate continuously contaminates surface waters, sediments and soils in the mine area (Lintnerová et al. 2003; Šoltés et al. 2003).

Materials and methods

Effluent mine water, the Smolník Creek water and suspended solid samples were collected at nine sites (Fig. 1). The creek water quality was evaluated from the time of active mining in 1989 until 2003. The available data from the hydrological and chemical database of the Slovak Hydrometeorological Institute (SHMI) and other unpublished data were used (Jaško et al. 1996, 1998; Šottník 2000; Rojkovič et al. 2003).

Waters

Mine water samples were collected from the new drainage of the abandoned mine (SM-2), waste dump channels (SM-3, SM-5), tailing drainage (SM-OD) and from the Smolník Creek. SM-1 is uncontaminated water. SM-4 and SM-6 are samples from zones of the mine and tailings drainage water mixing with creek water (mixing zone 1 and 2). The sample points SM-8 and SM-9 were located about 11 and 16 km respectively downstream from the abandoned mine. Two samples from Hnilec River water were taken to monitor changes in its water composition. Sample H-0 was located upstream from the confluence and H-1 at the confluence with Smolník Creek (Fig. 1).

Water samples were collected in five sampling periods from June 2002 to July 2003 in variable hydrological conditions. August 2002 was a period with the high precipitation in the whole Central European region and the creek water runoff was about 2.5 times higher than average. In the remaining four sampling periods (June 2002, October 2002, April 2003, July 2003) flow in the Smolník Creek were close to the average amount of 1 m^3/s.

Conductivity, Eh and pH values of each 44 samples were measured in the field. The collected water samples were filtered on site through 0.45 μm pore diameter cellulose nitrate membrane. Total Fe, Al, Mn, Ca, Mg, K, Na, Ba, Hg, Zn, Pb, Ag, As, Sb, Se, Co, Ni, Cr, V, Cu, and Cd were analysed in the first acidified (pH = 2) aliquot by AAS and ICP-AES methods. The second un-acidified aliquot was used to determine major anion concentrations (SO_4^{2-}, Cl^-, F^-, HCO_3^-) by standard colorimetric, volumetric and gravimetric methods. Fe^{2+} was determined in the third stabilized aliquot by redox titration ($KMnO_4$). The values of total dissolved solids (TDS) were expressed as a sum of analysed ions.

Suspended solids and precipitates

The preliminary distribution of two grain-size fractions of suspended solids was determined. Weight suspension was captured by continual filtration of creek and river water in June 2002. Waters were pumped and filtered through 1 µm cellulose filters and through standard 0.45 µm membrane at the SM-4, SM-6, SM-8, H-1 and H-3 sites. Samples H-1 and H-3 were taken from the Hnilec River at the creek confluence (H-1) and near the point where the Hnilec River flows into the water reservoir Ružín (H-3). The pre-weighed filters with captured solids were dried at 105 °C and were weighed again. The first result was used to find out the two effective methods — decantation for suspended solids collection in large volume and membrane filtration for quantitative evaluation (Pontér et al. 1992; Brake et al. 2001; Hren et al. 2001; Rhoton et al. 2002; Miller et al. 2003).

Depending on suspension quantity, 30 to 140 l of water was taken from the creek. The suspension was decanted for 24 hours. The obtained samples were dried at 40 °C (for mineralogical characterization) or at 105 °C (for chemical analyses) and homogenized. Besides the mass content, the mineral composition, organic matter content and acid insoluble residue (IR) of suspended solids were determined. This method was applied in August and October to check different hydrological conditions and two sets of the creek site samples (SM-1, SM-4, SM-6, SM-8, SM-9) were collected.

Amounts of suspended solids were evaluated by 0.45 µm membrane filtration simultaneously with water sampling. Because of very low total mass the cumulative suspended solid samples were collected in 3–5 days by filtration of 10 to 20 l of water depending on the suspended amounts. Wet samples were stored in acid leached plastic bottles and transported to the laboratory. The accumulated samples were dried at 105 °C and used for chemical analyses.

Fe oxyhydroxide precipitates were collected in the Smolník Creek (in the vicinity of the mine water effluent) and in tailings channels. Mineralogical analyses were performed on samples dried at room temperature and on samples dialysed in de-ionized water. The same precipitate samples dried at 105 °C were used for chemical analyses.

The mineralogical analyses of suspended solids and precipitates were carried out by X-ray diffraction technique on the Philips powder diffractometer (model PW 1710, using Ni-filtered CuKα radiation at 20 mA and 40 kV). Phase mineral analyses and chemical composition of precipitated particles were determined using transmission electron microscope (TEM) Jeol JSM equipped with an energy disspersive X-ray detector (LINK 1060).

The total content of organic carbon (TOC) was determined using C-MAT 550 Ströhlein equipment. The standard EGME (ethyleneglycol monomethylether) method was used to determine the specific surface area of suspended solids and precipitates.

For chemical analyses, dry samples of suspended solids and precipitates were digested in concentrated HNO_3 at 85 °C for two hours (Pontér et al. 1992; Rhoton et al. 2002 and others). The contents Fe, Al, Ca, Mg, Na, K, Cu, Mn, Zn, Pb, As in the supernatant were determined by the standard AAS and ICP AES methods. IR was determined in both cumulative and decanted samples by standard gravimetric method. IR determination allows recalculation of metal concentrations on acid dissolved base (ADB) and identification of the amount of metals released from the mine in different sampling periods.

Results and discussion

Water

The Smolník Creek water from 1986 to 2000

Mining activity has decreased water quality in the Smolník Creek, as is documented by analyses taken at the monitoring point B-68 (SHMU monitoring net) (Table 1).

Table 1: Average, minimum and maximum (in brackets) values of water collected in B-68 (SM-9), data in period 1986–2000 provided by the Slovak Hydrometeorological Institute (SHMI).

		Active mine Jan. 1986–May 1990		**Mine flooding June 1991–May 1994**		**AMD inflow to stream June 1994–Nov. 2000**		**Limit — 98/83/EC**
Nubmer of analyses		**60**		**41**		**78**		–
pH		5.0	(4.0–7.0)	7.5	(7.0–8.0)	4.8	(3.2–7.1)	6.0–8.5
Fe	mg/l	4.9	(0.6–16.0)	1.4	(0.3–15.4)	16.4	(2.4–95.6)	0.2
SO_4^{2-}	mg/l	159	(28–488)	51	(20–130)	186	(39–596)	250
Cd	µg/l	–		1.9	(0–21)	4.7	(0.3–39.6)	5
Pb	µg/l	–		7.1	(0.05–33)	18.8	(1–127)	25
As	µg/l	–		35	(0–425)	43	(1–634)	10
Cu	µg/l	228	(10–900)	35	(0–450)	260	(3–2360)	50
Cr	µg/l	–		–		7.8	(1.7–19.6)	50
Zn	µg/l	232	(10–750)	51	(0–166)	511	(57–1500)	40
Al	µg/l	–		–		1606	(304–5296)	200

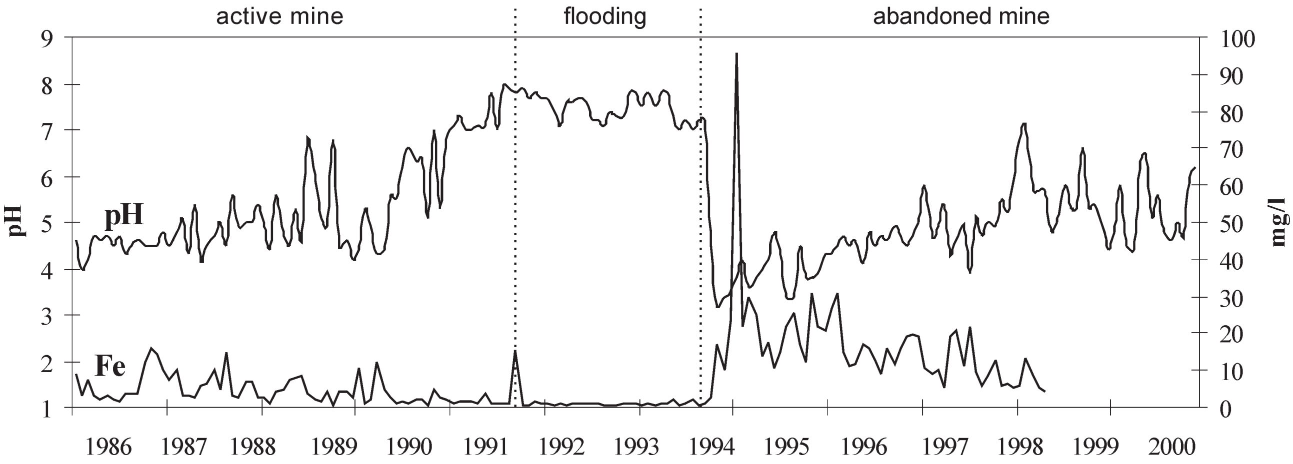

Fig. 2. Variation in concentration of Fe and pH values in the Smolník Creek in 1986–2000 (monthly data) according to the SHMI (Slovak Hydrometeorological Institute) data.

This point is identical with the point SM-9 (Fig. 1) and is situated approximately 16 km downstream from the mine close to the confluence of the Smolník Creek and the Hnilec River. The water effluent from the exploited mine seriously polluted the creek water by permanently adding metals (Cu, Zn, Fe) and sulphate (Table 1, Fig. 2).

The analyses of water that characterize the period flooding of the mine between 1991 and 1994 are shown in Table 1, when AMD did not discharge from the mine into the Smolník Creek. The data illustrate relative improvement of the Smolník Creek water quality. In the flooding period pH of stream water increased to 7.0–8.0 and concentrations of metals and sulphate decreased. In comparison with the previous period the average concentration of Fe, Cu, Zn and sulphate ions decreased several times. However, Fe and Zn contents were still higher than the limit (CD 98/83/EC). It is possible, that these and the other metals could be extensively released from polluted bank sediments or leached from mine wastes located in the vicinity of the mine.

AMD from the mine started to penetrate into the Smolník Creek again, after total mine flooding. A rapid decline of water quality recorded from May 30th to August 10th 1994 resulted in the death of fish and the breakdown of the creek's ecosystem (Table 2, Fig. 2). Strong acid water mobilized Al and other metals toxic to biota (Jaško et al. 1996; Lintnerová et al. 1999; Šottník 2000). The metal pollution of the creek water increased suddenly in 1994 and it was comparable to the pollution observed during the time of active mining (Table 1). Acidity and metal contamination of the creek water remained high during the following two years (1994–1995). The chemical composition of the creek water relatively improved in the next six years (1996–2001) and only the Fe and Zn contents were higher than the EC limit. Generally, two processes, spontaneous change in the mine water-rock system after mine flooding and the mine area remediation (1997–1998) improved water quality to the observed level.

Table 2: Water pH, sulphate and metal concentration at site B-68 (SM-9) during 1994.

B-68 **(SM-9)**	**pH**	**Fe** mg/l	**SO_4^{2-}** mg/l	**Cd** µg/l	**Pb** µg/l	**As** µg/l	**Cu** µg/l	**Zn** µg/l
May 4	7.2	0.7	35	0.1	2.9	9	43	41
May 30	7.2	1.2	41	2.3	5.5	6	50	37
Jun 6	4.5	2.4	50	3.8	4.1	7	111	57
August 10	3.2	17.2	450	14.6	81.1	634	2340	1200

Abandoned Smolník mine

The composition of discharged AMD from June 1994 to July 2000 is shown in the Table 3. In June 1994 water in the Pech shaft was strongly acidic (pH = 2.94) and had high contents of Fe, Mg, Al, sulphate and other metals (Jaško et al. 1996). Increased contents of Cu and Zn (Table 3) occurred at the beginning of the "first flush" (June–July 1994). High concentrations of sulphate increased total dissolved solids (TDS) from 7 to 17 g/l in effluent AMD in October 1995 probably because the AMD was pushed out from the mine depth. This can be suggested on the basis of the water composition from Pech shaft sampled in 1995, where the 41 g/l TDS in depth 105 m and 46 g/l in depth 265 m were determined.

The shaft was filled in 1997 and after that it was not possible to sample deep parts of the abandoned mine. At the same time, new drainage (SM-2) was constructed to capture the generated AMD. TDS concentration of water effluent from the new drainage was approximately 5 g/l and its acidity was buffered to pH 3.8 (Table 4). Decreasing contents of dissolved ions in comparison with 1994–1995 levels could result not only from stabilization of chemical processes in the flooded mine but probably also from reduced volume and rate of movement of waters flowing into the mine system. The improvement of the creek bottom and decline of its permeability and the channelling of meteoric water away from the mine area decreased a volume of infiltrating water. On the other hand, the abandoned mine produced approximately 860 m^3 water per day and it was a stable source of AMD in the area. Con-

Table 3: Values of mine water analysis in 1994–2000 (Jaško et al. 1996, 1998, and authors and other unpublished data). For 1999 and 2000 average values were used.

Number of analyses		June '94 shaft Pech n = 1	July '94 shaft Pech n = 1	Oct. '95 shaft Pech n = 1	Feb. '97 n = 1	May '99 Oct. '99 n = 10	Apr. '00 Sept. '00 n = 7
Al	mg/l	–	1 250	583	147	103 (87–112)	118 (99–165)
Fe (tot.)	mg/l	456	1 070	1 583	437	513 (427–580)	490 (408–617)
Mn	mg/l	80	141	147	37	38 (31–44)	34 (28–47)
Ca	mg/l	75	166	230	181	196 (183–215)	197 (176–266)
Mg	mg/l	1 338	9	1 510	524	333 (242–384)	330 (260–485)
SO_4^{2-}	mg/l	5 919	4 170	12 189	4 122	3 308 (2900–3600)	3 274 (2730–4300)
Zn	µg/l	43 210	100 000	61 650	18 690	13 860 (11300–16900)	13 350 (8950–23900)
Pb	µg/l	< 4	< 4	20	53	221	80
As	µg/l	0.001	23	330	79	37 (10–65)	13
Ni	µg/l	–	322	–	–	146 (133–160)	159
Cu	µg/l	36 790	89 980	10 580	3 850	2 700 (2240–3170)	4 860 (2910–8160)
Cd	µg/l	0.09	67	29	12	8	13
TDS	mg/l	–	7 092	17 108.5	5 556	4 769 (3884–5530)	4 966 (3716–6780)
pH		2.9	3.4	3.9	2.9	3.8 (3.5–4.0)	3.7 (2.8–4.1)

Table 4: Average, minimum and maximum (in brackets) values of mine water from abandoned mine (SM-2), tailings (SM-OD) and other AMD (SM-3, SM-5, SM-Kar) contaminated sites from the Smolník Creek collected in 2002–2003.

Number of analyses		SM-2 n = 5	SM-OD n = 5	SM-3 n = 1	SM-5 n = 1	SM-Kar. n = 1
Al	mg/l	82.7 (70.2–92.5)	0.2 (0.1–0.3)	474.0	58.6	159.5
Fe (total)	mg/l	542 (434–659)	5 (2–8)	3 229	321	1 091
Fe^{2+}	mg/l	356 (239–551)	2 (1–3)	421	166	222
Mn	mg/l	35.5 (32.6–38.5)	3.4 (1.2–5.7)	25.3	10.1	170.5
Ca	mg/l	190 (125–249)	44 (19–71)	304	160	2 539
Mg	mg/l	328 (246–385)	37 (15–60)	442	101	1 004
SO_4^{2-}	mg/l	3 642 (3125–4085)	253 (106–405)	14 800	2 220	9 058
Zn	µg/l	9 599 (6850–12040)	45 (31–55)	43 000	7 070	24 405
Pb	µg/l	81 (68–99)	< 4	156	18	42.5
As	µg/l	108 (29–380)	46 (14–90)	16 800	140	13
Co	µg/l	697 (483–914)	15 (7–26)	1 810	353	1 524
Ni	µg/l	207 (147–247)	24 (20–29)	625	179	771
Cu	µg/l	1 880 (1470–2120)	9 (6–15)	108 000	7 130	13 665
Cd	µg/l	9.2 (7.4–11.1)	3.1 (< 0.3–700)	101.3	14.5	21.4
TDS	mg/l	5 127 (4290–5990)	467 (228–752)	23 740	3 040	12 401
pH		3.83 (3.27–4.12)	6.76 (6.35–7.38)	2.20	2.95	2.92

sidering the water composition, AMD discharged from the new drainage (SM-2) is generated in the near-surface part of the mine and/or in mine waste. It is possible that the new drainage reclaimed a large area probably mine dumps too. Strongly acid water with high concentration of dissolved metals was formed in the mine adit Karitas (SM-Kar) as well as in other old works (SM-3 and SM-5) (Table 4).

Tailing impoundment

Tailing impoundment is the second important source of pollution connected with mining located in the mine vicinity. The major part of tailings is milled rock material from the deep part of the deposit where pyrite was enriched with As. The high As-content is a typical feature of the discharging water and precipitates formed in tailing drainages (Lintnerová et al. 1999). Mobilization of the redox sensitive elements Fe, S, As, Mn, partially Co are observed at SM-OD (Table 4). Higher contents of elements in water and relatively low Eh (4–50 mV) were observed especially in one tailing channel. This can explained increased contents of the mentioned elements as well as Ni and Zn in water, over the 2002–2003 monitoring periods (Fig. 3). The major portion of mobilized iron is accumulated (due to air oxidation) in drainage channel sediments and in mud reservoirs under the impoundment. The dissolved iron content (1.55 to 8.41 mg/l) which enters the Smolník Creek may be a fraction of iron mobilized by tailing pore water (Table 4). The relatively high sulphate-content in the drainage water (106 to 405 mg/l) is the result of primary pyrite oxidation in tailing and secondary anion/sulphate desorption from or iron oxide phases transformation in near-neutral conditions (Rosse & Elliot 2000; Lintnerová & Šefčíková 2002). Acid water (pH 3.4–3.9) with high sulphate content (1380 to 2080 mg/l) and metal concentrations (Al 14.6–72.8 mg/l, Cu 2.1–16.8 mg/l, Mn 4.9–19.4 mg/l) flow out continuously in small volumes from some parts of the dam and indicate pyrite oxidation in the tailings. The oxidation of sulphide minerals and leached, acid and cemented zones were recognized in the upper layer of tailing material in the depth of 40 to 110 cm (Lintnerová 2000).

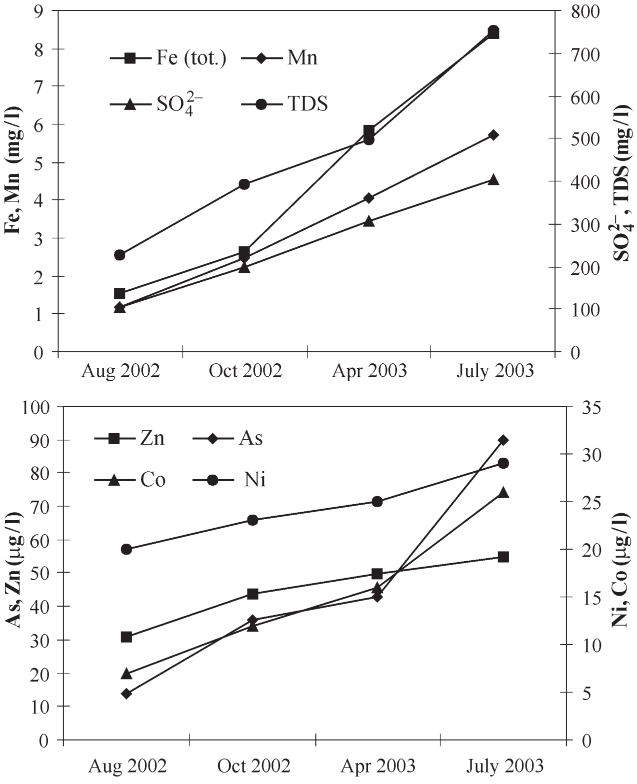

Fig. 3. Metals and sulphate concentrations in tailing water (SM-OD) in the 2002–2003 period.

The Smolník Creek water in 2002–2003

The composition of creek water from five monitoring points according to observation in periods from June 2002 to July 2003 are presented in Table 5 and are plotted in Fig. 4.

The point SM-4 is situated about 200 m downstream from the site where AMD enters the creek water and is homogenized with creek water — this is the first mixing zone. Increased contents of Fe, Al, Cu, Zn, Mn, Cd, Co, Ni and sulphate ion in water result from this AMD effluent running into the Smolník Creek. SM-2/SM-4 ratios of water concentrations were used to illustrate the relative dilution of the AMD elements in mixing zone. The concentration of Al decreased more than 100 times and despite this fact the Al exceeds the 0.2 mg/l concentration lethal to fish in waters (EC limit; Croman & Schofield 1979). The contents of iron (both Fe^{2+}, Fe^{3+}) decreased about 90 times, Mn, As, Co and Zn decreased 38–54 times and concentrations of other elements (Ca, Mg, Cu, Ni, Cd) were reduced less than 30 times. The comparison of water analyses in SM-4 during a nine year period (1995–2003) shows substantial lowering of dissolved solid concentration or water pollution over time (Jaško et al. 1996; Lintnerová et al. 1999; Šottník 2000). The volume of effluent water (30 l/s and more) decreased to the present level (10 l/s) approximately one year after the improvement of the drainage system in 1997–1998.

It is typical that the concentration of As, Ca, Mg, K, Na, sulphate as well as some other metals (Cd, Zn, Ni and Mn) increased in the second mixing zone (SM-6) below the site where tailing drainage flows into the Smolník Creek water (Table 5 and Fig. 4). The decrease of the water element concentrations can be seen between SM-6 and SM-8. These points are 10 km apart. Changes in the creek bottom morphology, small tributaries and leaching of old mine wastes can affect the creek water composition. It was found that redox conditions in the water changed from point SM-6, and more reducing condition in the downstream water could result in the higher mobilization of redox sensitive elements and increased relative contents of dissolved metals ob-

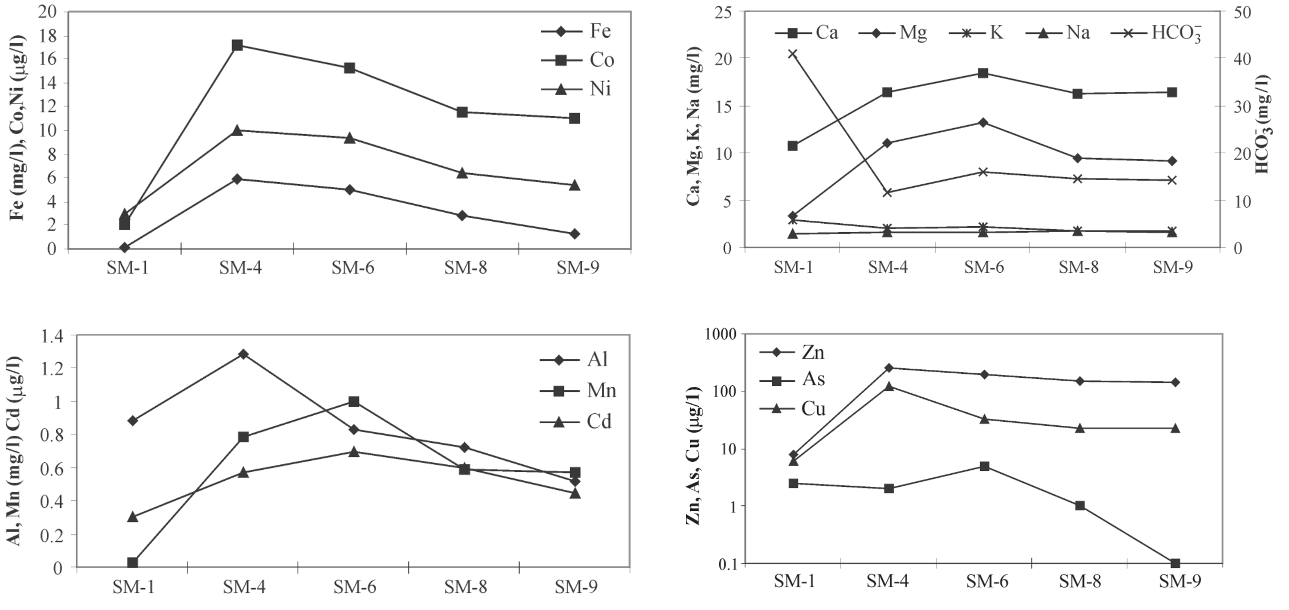

Fig. 4. The average values of metals in the Smolník Creek water in 2002–2003 calculated from analyses obtained during the five monitoring periods.

Table 5: Non-contaminated (SM-1) and contaminated creek water substantiate as the average, minimal and maximal (in brackets) values performed in 2002–2003 in five sampling periods.

Comp.	Unit	SM-1	SM-4	SM-6	SM-8	SM-9	H-0	H-1	Limit
Al	mg/l	0.07 (0.03–0.12)	0.73 (0.07–2.01)	0.12 (0.05–0.26)	0.22 (<0.30–0.40)	0.17 (0.05–0.30)	0.04	0.70	0.2
Fe (tot.)	mg/l	0.17 (0.10–0.27)	5.89 (2.13–13.90)	5.02 (1.35–8.56)	2.76 (1.46–4.10)	1.27 (0.68–2.93)	0.11	2.45	0.2
Fe^{2+}	mg/l	<0.1	5.04 (1.79–11.60)	4.06 (1.05–6.13)	2.08 (0.34–3.00)	1.78 (<0.1–2.28)	<0.1	0.69	–
Mn	mg/l	0.03 (0.01–0.04)	0.79 (0.24–1.70)	1.00 (0.24–2.05)	0.60 (0.20–1.25)	0.57 (0.18–1.19)	0.03	0.30	0.5
Ca	mg/l	10.8 (8.5–12.3)	16.0 (10.4–22.7)	18.4 (12.4–25.6)	16.3 (12.9–21.4)	16.5 (13.2–21.5)	21.2	21.8	50
Mg	mg/l	3.27 (3.05–3.58)	11.11 (5.05–19.40)	13.25 (5.24–23.20)	9.50 (5.18–16.20)	9.20 (5.00–15.20)	5.34	8.40	50
SO_4^{2-}	mg/l	18.4 (16.6–21.1)	90.1 (38.2–166.0)	108.9 (40.5–194.0)	79.6 (42.3–135.0)	77.7 (40.4–132.0)	22.5	49.9	250
HCO_3^-	mg/l	40.9 (21.4–82.4)	11.6 (3.1–24.4)	15.9 (3.1–30.5)	14.4 (3.1–23.2)	14.2 (3.1–23.2)	58.0	42.95	–
Zn	µg/l	8 (5–13)	253 (67–480)	197 (48–445)	151 (45–335)	143 (35–336)	6	69	40
Pb	µg/l	<4	5 (<4–5)	4 (<4–4)	<4	<4	<4	<4	25
As	µg/l	3 (<1–4)	2 (<1–3)	5 (<1–10)	1 (<1–1)	<1	1	3	10
Co	µg/l	<2	17 (5–29)	15 (4–30)	12 (3–23)	11 (3–22)	<2	5	20
Ni	µg/l	3 (<2–3)	10 (<2–14)	9 (4–16)	6 (4–11)	5 (3–10)	<2	3	20
Cu	µg/l	6 (4–11)	120 (21–408)	33 (8–85)	23 (6–51)	23 (5–66)	10	19	50
Cd	µg/l	<0.3	0.6 (<0.3–0.7)	0.7 (<0.3–0.7)	0.6 (<0.3–0.6)	0.5 (<0.3–0.6)	<0.3	<0.3	5
TDS	mg/l	81 (44–108)	188 (118–324)	218 (126–368)	166 (130–242)	164 (130–242)	136	158	50
pH		7.01 (6.00–7.63)	5.48 (3.53–6.27)	5.68 (3.63–6.61)	5.89 (4.70–6.29)	5.93 (4.87–6.43)	–	7.38	6.0–8.5
Eh	mV	127 (127–127)	138 (129–147)	69 (48–91)	77 (61–93)	77 (61–93)	88	–	–

served at SM-8 and SM-9 (Cornnell & Schwertmann 1996; Nickson et al. 2000). Old rock-wall dumps and weathered piles of metallurgic slag can be another potential source of toxic elements (Cu, As, Cd, Se) (Šoltés et al. 2003). Sample H-0 was taken from the River Hnilec above the confluence. Water samples from the third mixing zone (H-1, below the confluence of Hnilec River and Smolník Creek) documented an overall decrease in metals concentrations and their variations below the river and creek confluence. Only Fe and Zn exceed the limit in the river. However, the water in the confluence is not mixed enough, which is clearly visible, and metal contents change within a small distance.

Mine and tailing precipitates

The typical ochre iron oxyhydroxides were accumulated in drainage channelling water from the mine and tailing and they coat the bottom of the Smolník Creek. Jarosite ($KFe_3(OH)_6(SO_4)_2$), schwertmannite ($Fe_8O_8(OH)_6SO_4$) and goethite (FeOOH) were the principal phases identified in the precipitates generated from the effluent AMD (Lintnerová 1996; Lintnerová et al. 1999). These mineral phases were identified in samples collected at SM-2 and SM-5 sites in 2002–2003 (Fig. 5). The white precipitates occurred in narrow parts of the first mixing zone near the abandoned mine. Basaluminite ($Al_4SO_4(OH)_{10}{\cdot}5H_20$) was identified in precipitates sampled in a white strip earlier (Šottník 2000). In spite of this and theoretical calculations (not presented in this paper) no Al-oxyhydroxide phases were identified in the white precipitates by TEM/LINK analyses. Phases were unstable, released sulphate ions and changed to (low-crystalline) goethite in a 4–6 month span of time. Transformation could be followed by increase of specific surface area. Ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$) and goethite are common phases identified in tailing precipitates, occasionally found with gypsum (Lintnerová et al. 1999; Lintnerová 2000). Two X-ray bands of ferrihydrites were seen in low crystalline solids collected in various periods (Fig. 5; Bigham et al. 1990, 1996; Rhoton et al. 2002). The specific surface area values of the ferrihydrite/goethite precipitates were in the range 500 to 700 m^2/g. However, the highest values were determined in dialysed samples. The specific surface areas of AMD-precipitates (schwertmannite, jarosite, goethite) were in the range 150 to 400 m^2/g with a tendency to increase with decrease of sulphate content (Lintnerová & Šefčíková 2002).

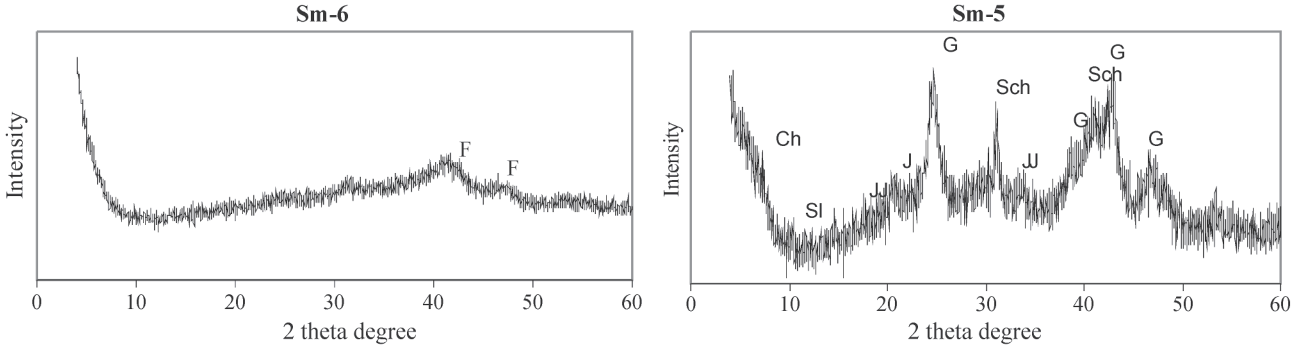

Fig. 5. X-ray diffraction patterns of the mine and tailing precipitates collected in June 2002. **J** — jarosite, **Sch** — schwertmannite, **G** — goethite, **F** — ferrihydrite, **Q** — quartz, **Ch** — chlorite, **Sl** — mica.

The ochre accumulations were sometimes observed in various distances downstream from the mine and at the creek-river confluence. The intermittent precipitation of solids indicated dependence on changes in water pH-Eh and temperature conditions in various climatic and hydrological seasons. Low crystalline ferrihydrite and goethite were identified in the X-ray profile of samples collected in SM-8 and SM-9 and indicated decreases of acidity and sulphate content.

Tailing precipitates were enriched with Zn, Cu, Mn, Ca and especially with As. Processing additives, like lime or alkali salts changed the neutralization potential of tailings, which could be extensively leached. It is typical that increased Ca content in water indicate a generation of acid sulphate pore water (Jambor 1994; Blowes & Ptacek 1994). Both, generated acidity and redox condition enhanced mobilization of Fe^{2+}, As^{3+} and other redox sensitive ions. This indicated composition of precipitates enriched in As and Mn, generated within open channels. The precipitation of dissolved elements, complexation with or sorption on the iron oxyhydroxide phases is pH dependent. High content of sulphate and other inorganic and organic ligands can play an important role in mineral phases stability and possible release of bounded elements (Ingri & Widerlund 1994; Lintnerová et al. 1999; Nickson et al. 2000; Lee et al. 2002; Munk et al. 2002; Lintnerová & Šefčíková 2003). Iron precipitates originating from abandoned mine water accumulated Al, Mg, Pb, As and Cu at a higher rate than tailing precipitates. Se, Sb, Co and Cr were also detected in the precipitates generated from water, which had leached old mine dumps and works (SM-5, SM-Kar) (Table 6).

Suspended solids

Suspended solids composed of particles above 0.45 μm grain size were captured on the membrane when water was

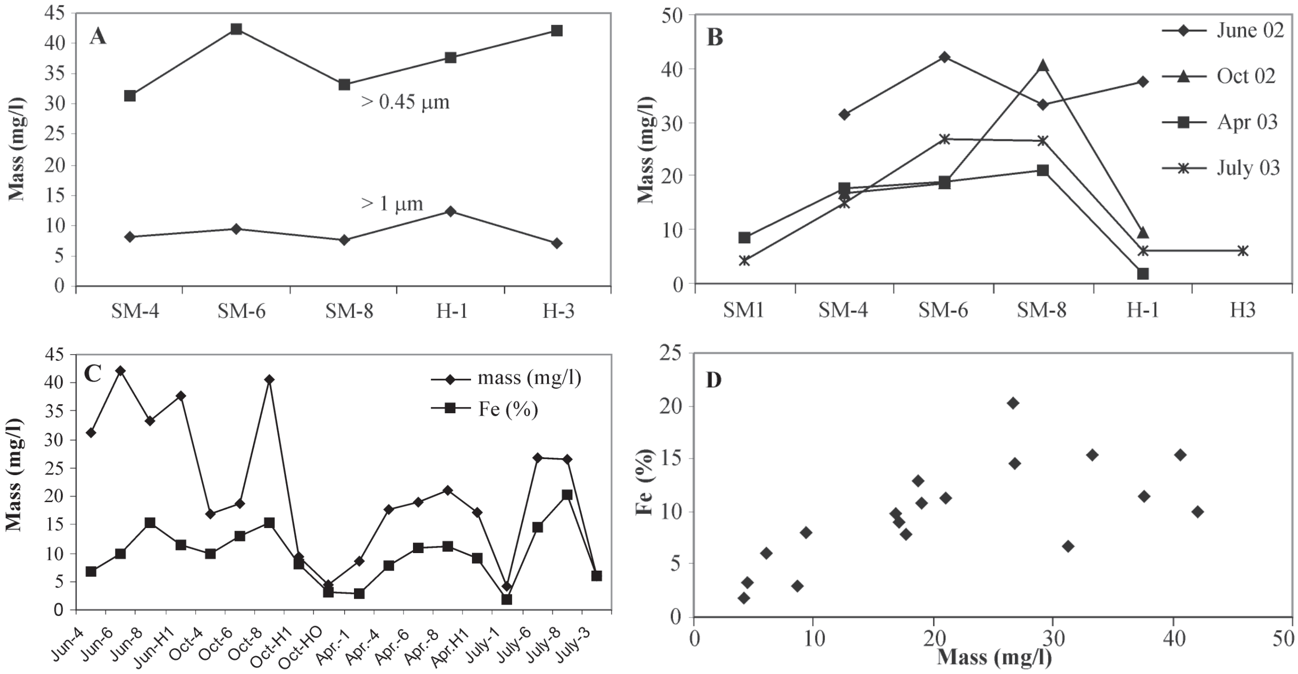

Fig. 6. Grain size distribution of water suspended solids sampled in June 2002. **B** — Mass distribution of suspended solids captured on 0.45 μm membrane. **C** — Mass and Fe content distribution. (e.g. Jun-4 = SM-4 sampled in June 2002, etc.) **D** — Mass and Fe co-relation (anomalous August 2002 values were omitted).

Table 6: Chemical analysis of mine drainage precipitates — not detected.

	Precipitates from mine waters				Precipitates from Smolník Creek		
	SM-2	**SM-5**	**SM-Kar.**	**SM-OD**	**SM-4**	**SM-8**	**SM-9**
	mg/kg						
Fe	42 700	44 900	35 210	33 150	35 130	40 900	20 650
Al	10 000	1 203	500	1 116	nd	nd	nd
As	2 523	842	38.46	10 724	59	14.25	119.33
Pb	459	41	–	78	55	50	188
Zn	77	45	76	1 052	164	345	854
Cu	270	302	68	731	217	1 057	2 164
Mg	1 696	616	–	3 398	–	–	–
Ca	27	77	–	21 031	–	–	–
K	272	551	–	1 978	–	–	–
Na	226	157	–	5 237	–	–	–
Mn	103	35	403	606	168	124	1 973
SO_4^{2-}	8 450	842	–	10 724	–	–	–
Se	–	0.52	0.06	–	0.22	0.02	–
Cr	–	3.75	–	8	14.24	–	7.8
Co	–	4.8	8.2	49	7.2	9.4	39.6
Sb	–	3.24	0.57	–	7.15	29.1	6.52

Table 7: Characteristics of suspended solid samples collected by sedimentation and decantation in two periods (August (SM-4/Aug) and October (SM-1/Oct) 2002). **nd** — not detected.

Samples decanted	Total mass g	Amount in water mg/l	IR (HNO_3) %	Organic Carbon %	Specific surface area m^2/g
SM-4/Aug	5.03	71.9	68.3	nd	223
SM-6/Aug	4.36	62.3	70.3	4.51	247
SM-8/Aug	4.42	63.1	69.2	4.32	248
SM-9/Aug	2.45	35.0	65.2	5.61	287
SM-1/Oct	1.04	7.4	55.7	nd	nd
SM-6/Oct	1.69	12.1	28.7	9.06	468
SM-8/Oct	5.35	38.2	47.8	7.25	448
SM-9/Oct	1.87	13.4	23.0	7.16	694

filtered or were accumulated from water in the sediment pots. Preliminary results have shown, that the particles from 1 to 0.45 μm in size constitute a considerable mass of suspended matter in comparison with the particles > 1 μm. These large particles were not evaluated separately (Fig. 6). The fraction passing through 0.45 μm membrane filter was taken as dissolved matter although it also includes a colloidal component.

The total mass of suspended solids obtained from one litre of the Smolník Creek water varied from 7 to 72 mg/l (Tables 7 and 8, Fig. 6). The amount of suspended solids in the non-contaminated part < 10 mg/l can increase up to 70 mg/l downstream from the mine site. However, seasonal change of water volume in the creek is the main factor influ-

Table 8: Chemical composition of suspended solid samples (captured on > 0.45 μm membrane) in the Smolník Creek in 2002–2003.

	Sample	Amount mg/l	IR %	Fe %	Mn mg/kg	Al %	As mg/kg	Pb mg/kg	Zn mg/kg	Cu mg/kg	Mg mg/kg	Ca mg/kg	K mg/kg	Na mg/kg
June 2002	**SM-4**	31.3		6.72	389	5.36	46	88	395	903	169	28	2 181	3 115
	SM-6	42.1		9.93	561	5.14	109	119	447	1 207	373	31	2 444	1 902
	SM-8	33.3		15.29	301	4.75	79	345	721	1 379	329	46	7 999	2 354
	H-1	37.6		11.36	501	2.36	38	137	1 440	890	450	125	1 693	2 634
	H-3	42.0		1.99	783	0.57	13	38	314	143	439	451	898	2 565
August 2002	**SM-4**	61.0	68.33	5.09	666	2.22	56	73	211	654	4 307	2 622	1 290	672
	SM-6	71.7	70.34	5.45	623	2.14	93	72	214	887	3 991	3 135	1 218	1 081
	SM-8	67.3	69.22	5.68	645	1.96	66	95	1 080	960	4 376	4 071	1 587	1 521
	H-1	89.3	72.67	3.70	1 220	1.31	16	54	401	514	4 457	7 484	2 016	1 315
	H-0	47.7	73.94	2.60	1 731	1.16	37	39	204	177	5 280	8 269	1 387	1 283
October 2002	**SM-4**	16.9	17.61	9.82	279	9.05	79	95	502	1 618	2 577	15 020	2 153	3 849
	SM-6	18.7	22.50	12.92	367	6.94	154	90	1 442	1 821	2 690	25 580	1 352	1 830
	SM-8	40.7	43.18	15.32	897	5.46	96	108	642	1 917	4 239	5 478	1 497	1 320
	H-1	9.4	34.34	8.03	779	2.36	36	53	1 377	994	4 392	17 470	5 548	6 836
	H-0	4.4	53.02	3.23	1 930	1.39	47	<0.1	645	305	7 466	16 946	5 587	6 653
April 2003	**SM-1**	8.6	61.00	2.91	1 422	1.12	57	76	373	277	3 498	6 422	2 313	1 976
	SM-4	17.7	29.26	7.78	267	7.71	107	118	184	1 011	1 454	1 509	872	1 058
	SM-6	19.0	17.61	10.82	318	6.57	211	111	256	1 459	1 163	2 343	840	704
	SM-8	21.0	37.52	11.30	314	4.80	98	101	289	1 847	750	1 616	779	759
	H-1	17.2	47.08	9.00	896	2.08	80	70	987	1 164	1 524	6 164	1 826	3 584
July 2003	**SM-1**	4.2	40.30	1.83	851	0.62	46	–	655	283	2 830	10 456	10 384	6 523
	SM-6	26.8	15.70	14.49	97	8.91	200	135	253	1 281	771	2 073	746	3 507
	SM-8	26.6	17.40	20.28	125	6.76	92	106	488	2 003	860	1 811	1 803	1 331
	H3	6.1	2.70	6.01	3 158	1.23	77	–	1 322	525	3 541	13 497	6 667	10 492

encing the total amount of suspended solids transported by the creek waters. Ignoring the high water outflow values in August 2002, the contents of suspended solids increase 2–3 times below the mine and the largest amount was captured at SM-6 and SM-8 sites during each monitoring period (Fig. 6B,C). Increased content in the SM-6 site recorded the inflow of the partitioned tailing precipitates into the creek. The interpretation of the SM-8 maximum is not simple because various old mining wastes could be leached and iron and other metals would supply the stream water. Regardless of that, the increased amount of suspended solids enriched by iron at distances of 11 km to 16 km from the mine shows that suspended solids could transport a comparable mass of mine-derived elements as was transported in water dissolved form (Tables 5, 7, Fig. 7). If 30 mg/l of suspended solids contained approximately 10 % of mine-derived Fe, then each litre of water transported 3 mg of Fe in suspended solids at the SM-8 site. The mine-derived content is the Fe content at SM-8 reduced to the SM-1 value.

Seasonal changes of creek outflow affected not only the amount but also the quality of suspended solids The decanted samples accumulated in August and October 2002 were used to estimate, mineral composition, organic carbon and insoluble residue (IR) in samples (Table 7). Seasonal changes caused IR values in the range 17 to 74 % of a sample. If the August 2002 values are omitted, IR is in the range 17 to 40 % (Tables 7 and 8). The identical mineral association, chlorite, mica/illite, feldspar and quartz, was identified in all decanted samples. No well-crystallized iron oxyhydroxide phases were found in the X-ray pattern of "fresh" suspended solid samples. The fine particles and the aggregate grains (50–100 nm) of iron oxide phases were distinguished by means of TEM investigation, on the basis of extensive Fe content and typical acicular flocks to needle like and short lath grains. Sulphur content was obviously low, frequently in the range of the analytical error. We suggest that amorphous aggregates of hydrated iron oxide species (like fine crystalline ferrihydrite to goethite phases in precipitates) dominate in the suspended solid. However, a lot of individual particles were so fine that they passed through 0.45 μm pores in the membrane filter. On the other hand, the high "salinity" of the creek water continually supplied by AMD could elevate flocculation of hydrated iron oxide nano-particles or colloidal matter which explained occurrence of the typical aggregate of iron oxyhydroxides in suspended solids. High content of mineral phases in suspended solid could increase sedimentation rate of solids and direct various sorption or dissolution processes in the water-sediment interface.

The values generally above 200 m^2/g documented a high specific surface area of the suspended solid samples (Table 7). Observed variance in specific surface area values and organic carbon contents is connected to some extent with seasonal creek outflow changes (Table 7). The samples enriched with organic matter (7.2 to 9.1 %) were collected in the moderate creek runoff season (October 2002). The higher content of organic carbon may be a result of sorption on enlarged (due to hydrated iron oxide precipitation) specific surface area of suspended solids. On the other hand, organic species with high molecular weight like humid acids

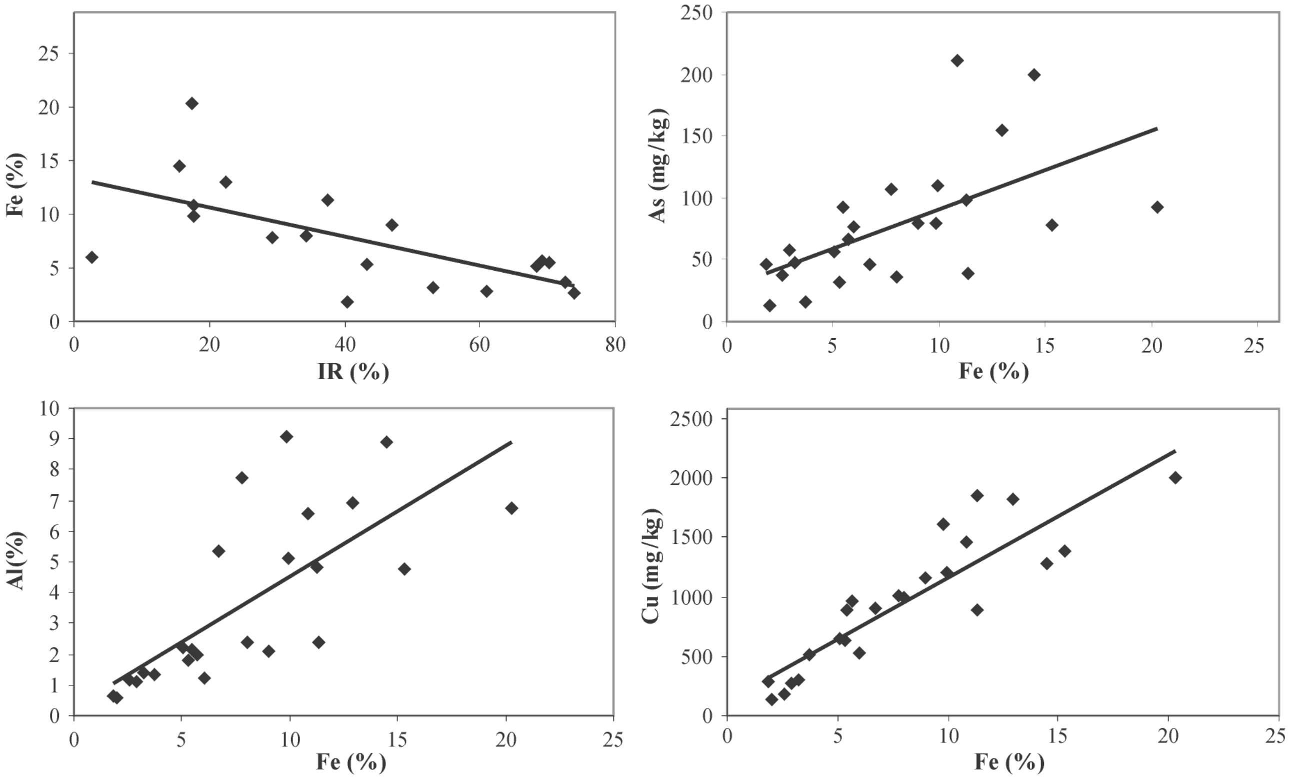

Fig. 7. Geochemical co-variation in Fe, IR and selected metals in the suspended solids.

could stabilize hydrated iron (III) oxides in dissolved or colloidal form in river water and prolonged iron transport (Boyle et al. 1977; Ingri & Widerlund 1994; Zuyi et al. 2000). The organic content in precipitates could be connected with microbial activity in AMD system, which substantially increased the rate of pyrite oxidation (Gould et al. 1994). However, a municipal pollution and leached organic species from soil would be a more probable important source of organic matter in suspended solids.

Element distributions

The results of chemical analyses documented the increased content of Fe, Al, As, Pb, Cu in suspended solids in the contaminated part of the creek (Table 8). The samples collected in the medium creek runoff have higher than 50 % of acid (HNO_3) dissolved phases of suspended solids mass (Tables 8 and 9). The iron oxyhydroxide phases composed a substantial part of the acid soluble part of the suspended solids, which document the different Fe contents of suspended solids in contaminated and uncontaminated (SM-1 and H-0) streams (Fig. 7). The content of Fe increased from 2–3 % in SM-1 to 6–20 % downstream from the mine (SM-4, SM-8). Various factors, mainly the pH dependence of precipitation of Fe oxyhydroxides, the composition of water from individual mine-derived sources, organic carbon, sulphate and alkali ion (ionic strength — salinity) can change element contents and reduce geochemical correlation of Fe with other elements (Fig. 7). However, the typical feature of systems influ-

Table 9: The chemical composition of suspended solids figured on acid dissolved base (ADB), average values.

		SM-1	SM-4	SM-6	SM-8	H-0	H-1
Number of samples		**2**	**3**	**4**	**4**	**2**	**3**
Fe	%	5.26	12.99	16.34	17.61	8.43	14.60
Al	%	1.96	7.96	8.68	6.36	3.71	3.76
As	mg/kg	112	142	251	135	124	103
Pb	mg/kg	196	171	163	166	150	106
Zn	mg/kg	1 026	512	798	1 235	1 079	1 979
Cu	mg/kg	592	1 818	2 157	2 407	665	1 856
Mg	mg/kg	6 854	6 261	4 812	4 738	18 089	4 778
Ca	mg/kg	16 990	9 531	12 217	5 306	33 924	19 101
K	mg/kg	11 662	2 638	1 938	2 366	8 613	5 942
Na	mg/kg	7 997	2 759	2 755	2 136	9 549	8 582
Mn	mg/kg	2 536	940	769	819	5 379	1 439

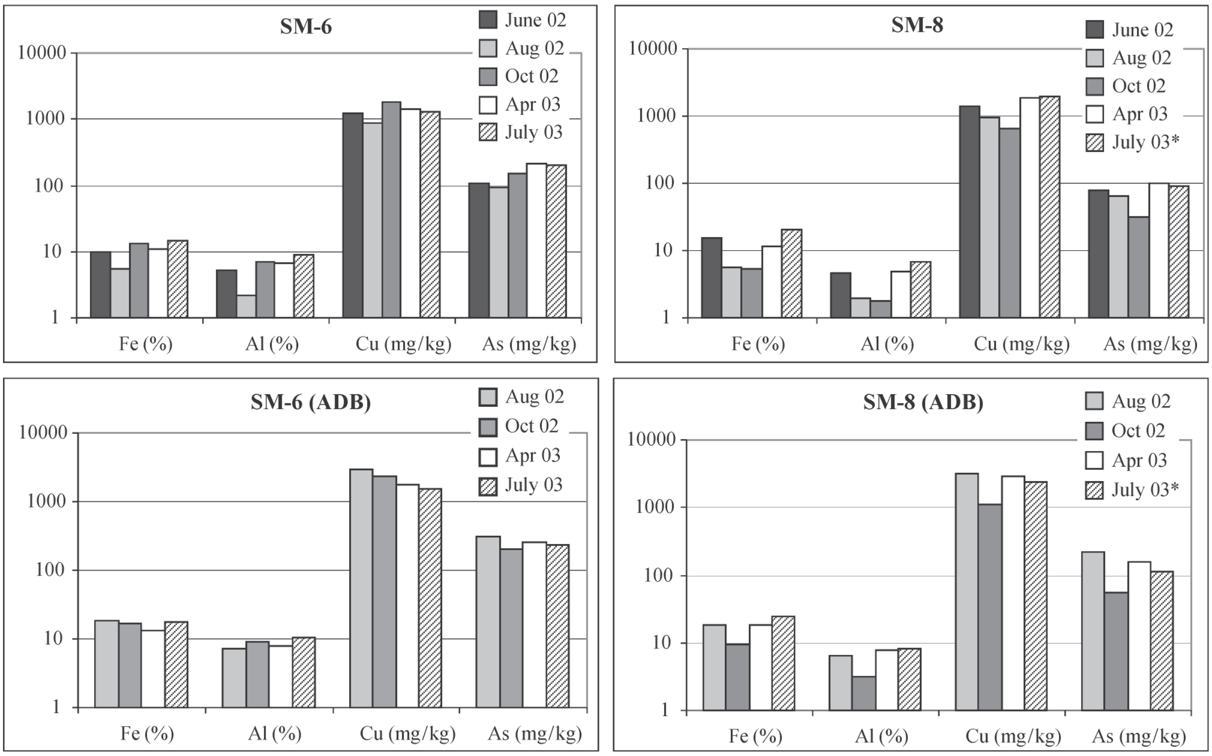

Fig. 8. Comparison of Fe, Al, Cu and As concentration in SM-6 and SM-8 samples of suspended solids and values recalculated on acid dissolved basis (ADB). July 03* — analyse from SM-9 was added.

enced by AMD is clearly visible. The increased content of Al in the dissolved part of all suspended solids samples is evidence that dissolved Al is removed either via Fe oxides precipitation and/or sorption on re-suspended sediments or organic matter or via flocculation into colloids (Sholkowitz 1978; Chester 2003). The samples collected in the mine-creek (SM-4) and the tailing-creek (SM-6) water mixing zones have similar microelement contents of fresh drainage precipitates and prime mine water composition (Table 8). Some enrichment with Mg and Pb could be distinguished precisely in this mixing zone below the mine. Analogously, increased contents of As and Ca in suspended solids from the second mixing zone (SM-6) signalized partitioned tailing precipitates transported by drainage water and potential change in water composition. The contents of Ca but also of K, Na, Mn, Zn in suspended solids are depleted in comparison with SM-1 because of leaching and generation of dissolved species due to neutralization. The element concentrations recalculated on the acid dissolved basis (ADB) clearly eliminates seasonal outflow changes and show variance in the amount of mine-derived elements transported in suspended solids (Table 9). Results indicated that more turbulent (high runoff) water conditions diluted the content of potentially mine-derived metals, but the total yield of metals was not changed dramatically (Fig. 8, Table 9). The amount of main elements (Fe, Cu Al and As) is similar in samples collected in the same site of stream during the various outflow seasons. This could document stabilized input of the studied elements into the stream and assumed potentially stabilized solid flux into the river (Fig. 8).

The contents of Cu, Zn and Mn were higher in solids captured far downstream from the mine because of the pH-dependent metals co-precipitation with and sorption on the Fe oxyhydroxides or other suspended phases in more neutral creek water (Tables 8, 9, Fig. 8). Comparison of the H-0 and H-1 samples shows the relative content of the mine-derived elements transported by suspended solids into the Hnilec River. The elevated metals concentrations in solids (Zn, Mn) below the confluence could be a sum of metals derived from the mine and other areas transported by the Hnilec River water. Some depletion on K, Na, Ca, Mg and Mn was still apparent in suspended solids below the confluence. Due to imperfect mixing and/or dilution of the creek with river water along the creek site bank for 1 to 3 km below the confluence there was prolonged acid reaction (pH 5.6 to 6.8) in the water and the water-sediments interface. It can be assumed, that increased content of alkali and hydro-carbonate ions in the Hnilec River water admit flocculation of colloids (hydrated iron, Al, Mn oxides, and other mineral solids) and its sedimentation on the bottom (Boyle et al. 1977; Sholkowitz 1978; Chester 2003).

The amounts of metals, transported in a certain span of time were calculated from the obtained results (Table 8). To document the mass of metals transported to the river by average creek outflow (1 m^3/s) the sampling site SM-8 was situated near the confluence. If 30 mg/l (average amount) of suspended solids contained 10.79 % Fe, 0.136 % Cu and 0.055 % Zn, then it can be estimated that the creek transported 2.590 kg/day of suspended solids with 280 kg of Fe, 3.54 kg of Cu and 1.44 kg of Zn. If we calculate this for the dissolved forms of metals (Table 5) we can estimate that 238.5 kg of Fe, 13.05 kg of Zn and 1.99 kg of Cu were transported by water per day at the point SM-8.

Suspended solids in environmental risk assessment

The results indicated that precipitation of iron oxide phases in the mine-creek mixing zones and seasonal changes of water volume in the creek are major causes influencing the amount of suspended solids transported by water in the contaminated part of the creek. The suspended solids transported the substantial dose of iron and other elements, which can be the same or even higher than is removed in dissolved form. However, lot of questions concerning the suspended solids grain-size definition (particles above 0.45 μm) and importance of colloidal phase quantification, objectivity and reliability of quantitative determination by various methods and other problems arise. Only some aspects, such as the proportion of mineral and organic phase versus seasonal outflow and/or the mine flux of Fe and other typical mine derived elements into the creek catchment, were discussed. The results indicated that the water-suspended solids–precipitates–sediment system is compl icated and many processes at the water-solid interface must be understood in such a multiphase system (Boyle et al. 1977; Sholkovitz 1978; Ryan & Gschwend 1992; Brake et al. 2001; Hren et al. 2001). It is not optimal to use this method in broad environmental risk assessment, because simple and representative methods could be recommended. However, for the quantitative evaluation of suspended solids, it is inevitable to use various geochemical, transport or space-time models, generated according to obtained data. Separation and analyses of suspended solids can evaluate the immediate toxic element content in stream water (Rhyan & Gschwend 1992; Munk et al. 2002; Rhoton et al. 2002). Since it can be exactly selected at a relatively short distance from the sources, it can be more precise and cost less than sequence (river) sediment analyses. Iron oxides are common natural phases, which effectively attenuate (toxic) element concentrations of water. However, they occur not only in suspended solids, but also in colloids, which extend transport and thus catchment pollution. Mixing of concentrated AMD with creek water, or mixing of polluted creek water with river water, gradually changed its ionic strength and/or the composition of the water and precipitation and stability of particulate (and colloid) mineral phases (Ingri & Widerlund 1994; Zuyi et al. 2000; Chester 2003). Goethite as a widespread Fe oxide phase and end-member of various hydrated phase transformations can serve as a pollution signal in a potential risk area (Bigham et al. 1990; Cornell & Schwertmann 1996; Rhoton et al. 2002).

Conclusion

Two important conclusions concerning the composition of the water from the abandoned mine can be presented.

Firstly, the relative stabilization of AMD composition was observed in a relatively short time (approximately 9–10 years) after the mine flooding. Secondly, the high pollution potential of medium acid and mineralized AMD (pH 4 and 5 g/l TDS) was documented. AMD effluent from the mine is relatively low (830 m^3/day) in comparison with the Smolník Creek outflow, which dilutes AMD at least one hundred times. The dilution is not sufficient, because unacceptable contents of metals (Fe, Cu, Zn) in the creek water were detected 16 km downstream from the mine at the confluence with the river and the metal pollution can rise seasonally especially during dry periods. The observed properties of water and the mine area indicated that such processes could pollute the creek catchment for a long time.

A natural mechanism of water cleaning precipitation of iron oxyhydroxide mineral phases was detected. Extremely fine-grained precipitates were transported by stream water as suspended solid. Two to 3 times higher contents of suspended solids were generated in the contaminated part of creek water and showed a definite tendency to increase over a distance of 11 to 16 km downstream from the mine. The suspended solids analyses documented the immediate impact and measure of mine-derived pollution enlargement in the catchment. Increased contents of metals and other toxic (redox and pH sensitive) elements, phase instability and enlarged specific surface of suspended solids can affect water quality and biota living conditions. The evaluation of suspended solids increases the objectivity of environmental impact assessment in the catchment area effected by AMD.

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