

GEOCHEMICAL STUDY OF SURFACE WATER AND SEDIMENT AT THE ABANDONED PB-ZN MINING SITE AT GYÖNGYÖSOROSZI, HUNGARY

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ABSTRACT

A geochemical and mineralogical study of surface water and sediment was performed at an abandoned Pb-Zn mining site containing neutralised acidic mine drainage at Gyöngyösoroszi in Hungary to estimate the risk of the remobilisation of potentially toxic elements along the Toka Stream from the sediment as a secondary source of contamination. The study was performed in the dry season. The sediment of the discharge at the neutralised mine drainage contains primarily amorphous iron hydroxide; however, despite neutralisation, the concentrations of Zn, Cd, As and Pb are still above levels that could potentially cause environmental risk. In addition, the further presence of As, Cd, Cu, Hg, Pb, and Zn was identified in high concentrations at the abandoned mine tailing. The difference in the composition of the sediment in equilibrium with the water and that of the dried sediment suggest that Al, Mn, and Ni are released and transported primarily in solution. However, because the water quality of the Toka stream that has been affected by the abandoned mining site is under rehabilitation, the quantity of the potentially toxic element concentrations in the solution were low, with the exception of Cd and Zn, which were identified at high concentrations; this was particularly observed at the mine tailing discharge.

KEYWORDS:

abandoned mining site, heavy metal, surface water, sediment

1. INTRODUCTION

Along streams and rivers, neutralised acidic mine drainage and abandoned tailing sediments that are present downstream still represent the risk of heavy metal remobilisation as a secondary source of pollution. The oxidative

weathering of pyrite at the mining sites contributes to the formation of acid mine drainage (AMD) and is therefore the dominant process that controls heavy metal mobility and speciation [1-3]. Pyrite oxidation is a complex process because it involves numerous biogeochemical pathways. In the absence of buffering agents, the oxidative weathering of pyritic ores results in a decrease in pH, which increases the solubility of heavy metal-containing minerals [4-6]. In addition, along streams and rivers, tailing sediments and overbank sediments that are present downstream represent the risk of heavy metal remobilisation as a secondary source of pollution [7-10]. As a result of the absorption, coprecipitation and secondary mineralisation that are specific to heavy metal species, the concentrations in solution show a certain removing order downstream of the discharge point [11, 12], although hydrological seasons definitely affect the spatial variation, fate and transport of metals [13-15]. Under certain geochemical and hydrological circumstances, AMD can generate significant loads of contaminants that acidify streams and reservoirs [16]. Therefore, even at abandoned mining sites, in addition to monitoring, the continuous neutralisation of the effluents of the mine and the tailings is required to reduce the environmental risk that is posed by heavy metal migration [17].

The aim of the present study was to investigate the quality of the surface water of the stream sediments of the Toka bed stream, which are affected by an abandoned Pb-Zn mine and its tailing dump in North Hungary, with respect to potentially toxic elements in a summer dry season.

2. MATERIALS AND METHODS

2.1. Site Description and Sampling

In Gyöngyösoroszi, North Hungary, nearly 2.1 Mm³ of sulphide-bearing mining waste was abandoned in 1986. Starting in 1952, Pb and Zn were mined with a flotation technique, and the tailing dump was continuously charged

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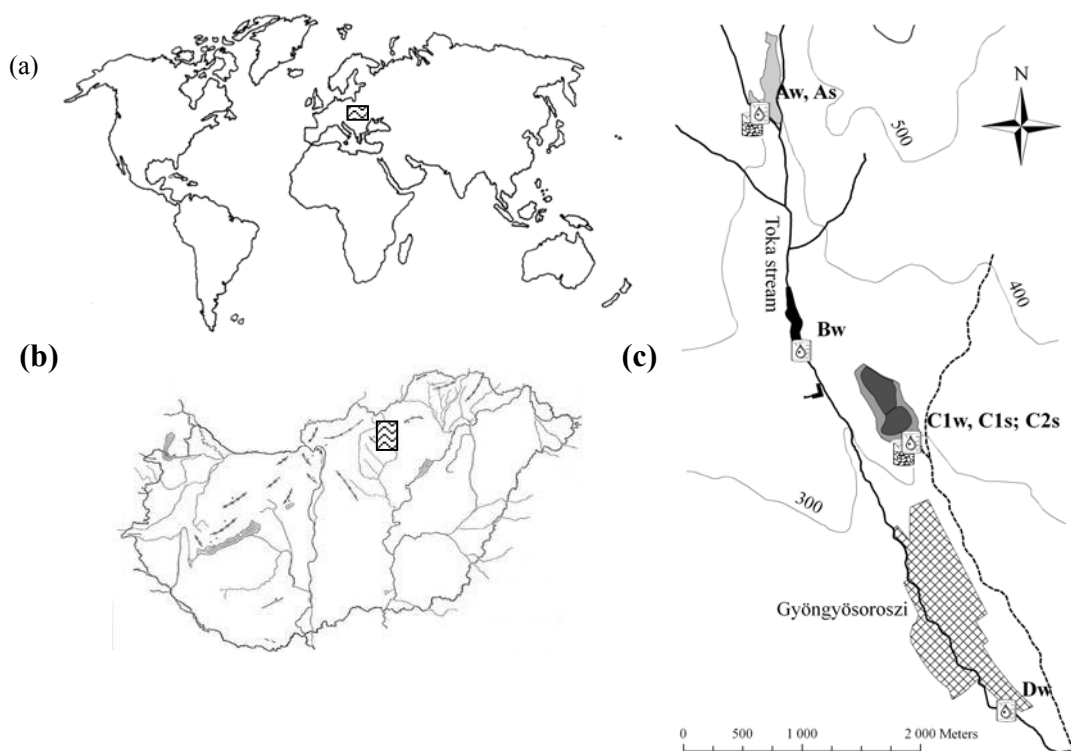


FIGURE 1 – Geographical location of (a) Hungary, (b) Mátra Mountain and (c) Watershed of the Toka Stream. Sampling points – *A*: neutralised acidic mine drainage, *B*: industrial reservoir, *C*₁: mine tailing discharge, *C*₂: mine tailing discharge drainage, which was dried out at the date of sampling and *D*: Toka stream below the Gyöngyösoroszi village (*S*: sediment; *W*: water sample)

with the mining waste. The site is now under rehabilitation, and it will be submitted to a new revegetation process by the end of 2011. There are two water discharges to the Toka stream: a discharge (*C*₁) from the tailing dump, where remediation has not yet been completed, and another discharge (*A*) from the AMD that was treated with $\text{Ca}(\text{OH})_2$ and settled (Fig. 1).

At the sampling points *A* and *C*₁, the water and sediment samples were taken (long. 47°51'53.02" N, lat. 19°52'23.69" E, and long. 47°50'25.39" N, lat. 19°53'18.95" E, respectively) in a dry season during September, 2009. In addition, dry sediment was obtained, in which the secondary mineralisation on the surface of the tailing discharge channel was assumed (*C*₂; long. 47°50'24.70" N, lat. 19°53'19.91" E). Additional water samples were procured downstream from the Toka; one (*B*) was obtained from the tube that transports water from Toka to the flotation processing and another (*D*) was obtained from below the bridge downstream of the village (long. 47°50'49.85" N, lat. 19°52'34.63" E, and long. 47°49'10.90" N, lat. 19°53'56.87" E, respectively).

*C*_{1s} is the sediment that was obtained from the drainage of the mine tailing where possible natural neutralisation processes by original buffering agents may have occurred during the last three decades, while *C*_{2s} represents the sediment that was formed when the water drainage from the tailing dried out, and its total element con-

tent appeared in solid phases. Therefore, *C*_{1s} primarily represents small particles of primary minerals and chemical forms that are unstable in solution of less than pH 5.90, which precipitate and are transported further in the solid phase, while in *C*_{2s}, all of the elemental content that was released from the mine tailing should be found in its precipitated form. Because *A*_s is the sediment that resulted from the artificial neutralisation of the AMD with $\text{Ca}(\text{OH})_2$, which was added in this sample, primarily hydroxides and sulphates were expected as the precipitates.

2.2. Sample treatment and analyses

The sediment samples were first air-dried and then sieved using a standard sieve with a 2-mm diameter (Fritsch, Germany). The mineralogical composition of the sediment was determined using a Philips X-Pert MPD X-ray diffractometer. The crystalline phases that were obtained using a computer program (X Pert High score 2002, Philips) were selected by comparing the *d*-values from the JCPDF cards that were listed in the Powder diffraction file [18]. A semi-quantitative mineralogical analysis was performed as described by Boldrin et al. [19]. The elemental concentrations in the sediments (*f* < 2 mm) were determined in aqua regia extracts at the ACTLABS commercial laboratory, Ontario, Canada, using inductively coupled plasma mass spectroscopy (ICP-MS) and the program "Ultrace 2". The solution was diluted and ana-

lysed using a Perkin Elmer SCIEX ELAN 6100 ICP-MS instrument for 44 elements. For the discussion, the elements that were typically present at the Pb-Zn mining sites were selected; any potentially toxic elements with very low concentrations, e.g., Ag, Sn and Hg, were omitted.

Water samples were taken manually, and they were deposited directly into pre-cleaned 250-mL PFA bottles. In the laboratory, they were acidified by the addition of super-pure concentrated HNO₃ (0.5 mL in a 250-mL sample) and were additionally digested by UV irradiation (24 h, 150 W low-pressure Hg-lamp) to destroy any organic matter. The water samples were analysed using high resolution inductively coupled plasma mass spectroscopy (HR ICP-MS). For ICP-MS, the detection limit for all of the elements was below 1 µg L⁻¹. The measurements were repeated three times for each sample. Before the ICP-MS analysis was performed, the samples were filtered (0.45 µm polycarbonate). Element2 HR ICP-MS (Thermo Finnigan, Bremen, Germany) was used for the determination of 23 trace elements. The samples for the analyses were prepared in pre-cleaned polyethylene tubes by adding 100 µL of concentrated HNO₃ and 50 µL of indium (115) internal standard (0.1 mg/L) into 5 mL of a sample aliquot. The concentrations of the elements were determined by means of external calibration plots. No special setup of the instrument operating conditions was needed [20]. The pH of the water samples was measured in the laboratory by Orion PerpHecT Meter, model 320 using a combined glass electrode.

3. RESULTS AND DISCUSSION

3.1. Sediment samples

Mineralogical composition: the mine tailing was previously assessed based on hyperspectral remote sensing data that were obtained under the Hysens Programme. According to the results, the contents include sulphides, such as pyrite, sphalerite, galena, buffering agents, such as calcite and illite, and iron-bearing minerals, such as siderite, jarosite and goethite [21]. In addition, the mineral composition of the mine tailing was analysed by XRD and SEM/EDX; the results have been provided by Kovács et al. [22].

The XRD analysis of all of the samples studied in the present work showed that the dominant mineral phase was quartz [SiO₂], which is a primary mineral. The minor mineral was calcite [CaCO₃], which was found only in the A_S sample at the neutralised mine drainage at an abundance of 10-30%, while anorthite [CaAl₂Si₂O₈] in the C_{2S} sample and muscovite [KAl₂Si₃O₁₀(OH)₂] in the A_S sample were found at an abundance of 5-10%. A significant difference was found in the trace minerals (<5%), such as in the C_{1S} sample, where pyrite [FeS], tetrahedrite [(Cu, Fe, Zn, Ag)₂₄(Sb, As)₈S₂₆], sanidine [KAlSi₃O₈], muscovite, and illite [(K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂(H₂O)]] were detected; in the C_{2S} sample, [Al₃(SO₄)₂(OH)₅·9H₂O] was pre-

sent. In the A_S sample, butlerite [Fe(SO₄)(OH)·2H₂O] and illite could be identified. The mineralogical composition of the samples is detailed in Table 1.

By comparing the assumed mineralogical composition of the mine tailing and the measured composition of the sediment, among the tracers, no secondary Pb- and Zn-bearing minerals or other potentially toxic elements could be identified with XRD. In addition, ferric hydrate, [Fe₄O₃(OH)₆] or jarosite, [KFe₃(OH)₆(SO₄)₂], could not be identified as secondary minerals of pyrite, and gypsum, [CaSO₄·2H₂O], which is a commonly occurring mineral where acidic mine drainage is neutralised with added Ca(OH)₂, was absent as well. Therefore, it can be assumed that the significant retention of solid phases that bore potentially toxic elements occurred in both the sediment that resulted from the artificial neutralisation of the acid mine drainage and the mine tailing, in which natural geochemical processes, such as zonal acidification, neutralisation and the redistribution of particles, were confirmed.

The results for the trace minerals, however, can only be considered tentative due to the limitation of the XRD method.

TABLE 1 – Minerals in the sediment samples detected by XRD

Mineral	C _{1S}	C _{2S}	A _S
Quartz	+	+	+
Calcite			+
Anorthite		+	
Muscovite	+	+	+
Pyrite	+		
Tetrahedrite	+		
Sanidine	+		
Illite	+		+
Butlerite			+
Talc	+		
Tridymite	+		
Tetradymite		+	
Sophiite	+		
Gupeite		+	+
Halite		+	
Sylvite			+
Sodium tecto-alumotrisilicate			+
Al ₃ (SO ₄) ₂ (OH) ₅ ·9H ₂ O		+	
Zirconia			+
Lavendulan			+
Tricopper(I) tetrarselenoantimonate		+	

+: presence of the mineral

Total element concentrations: concentrations of the selected elements and the maximum admissible values (MAD) for geological media in Hungary are presented in Table 2. The highest concentration of Fe that was found in the C_{1S} sample cannot be explained with the trace minerals that were found in that location because neither hematite nor goethite was found. Therefore, it can be assumed that Fe is in the form an amorphous iron hydroxide. The existence of tetrahedrite in the C_{1S} sample can be supported by the elevated concentrations of Zn, Ag, Sb, As, Cu and S that were observed. The highest concentration of Al that was found in the C_{2S} sample can justify the

formation of the white secondary aluminium phase, such as $\text{Al}_3(\text{SO}_4)_2(\text{OH})_5 \cdot 9\text{H}_2\text{O}$. In a weathering study of pyrite, Darmody et al. [23] reported that the white coatings that were formed at $\text{pH} > 5$ were Al compounds. The highest concentration of Ca that was found in the A_S sample supports the identification of calcite by XRD. The presence of butlerite can be explained as weathering product of pyrite, while Tl that was found in the investigated sediments was also detected in a pyrite slag depositing area by Yang et al. [24].

TABLE 2 - Concentrations of major and selected trace elements in sediments and the relevant maximum admissible values for geological media

Element	$C1_S$	$C2_S$	A_S	MAD*
Fe (%)	4.42	3.37	2.07	-
Al (%)	2.7	4.08	1.4	-
Ca (%)	0.75	1.78	3.24	-
Mg (%)	0.47	0.59	0.37	-
S (%)	1.019	0.362	0.221	-
K (%)	0.22	0.25	0.15	-
Mn (mg kg^{-1})	599	876	1800	-
Ni (mg kg^{-1})	8.4	15.1	10.9	40
Cu (mg kg^{-1})	220	44.5	10.8	75
Zn (mg kg^{-1})	670	218	1200	200
As (mg kg^{-1})	240	64.9	22.3	15
Cd (mg kg^{-1})	2.2	0.9	8.6	1
Pb (mg kg^{-1})	939	85.9	30.3	100
Ag (mg kg^{-1})	1.68	0.172	0.063	-
Sn (mg kg^{-1})	8.15	1.9	0.76	-
Tl (mg kg^{-1})	2.63	1.54	0.67	-
Cr (mg kg^{-1})	25.2	36.2	17.9	75
Hg (mg kg^{-1})	1.760	1.040	0.137	0.5

$C1_S$: tailing discharge sediment; $C2_S$: dried tailing discharge sediment; A_S : treated AMD sediment; * MAD – maximum admissible value established by the Decree of the Hungarian Ministry of Environment and Water, Ministry of Health, and Ministry of Agricultural and Rural Development No. 6/2009 (14.04.2009), Appendix 1

Despite the neutralisation and sedimentation of the acidic mine drainage, the concentrations of Zn, Cd, and As that were detected in A_S were still above the levels that could potentially cause environmental risk, and these elements were further transported in a small particle solid phase in the Toka Stream even though the trace mineral hosting could not be identified with XRD.

When considering $C1_S$ and $C2_S$, the difference in the element concentrations is an indicator of the stability of the potential hosting solid phases. The higher element concentrations in $C1_S$, which particularly included Fe, Cu, Zn, As, Cd, and Pb, indicate that these elements are the least stable mineral forms in solution under the pH and chemical composition of the drainage. However, for $C2_S$, in which the dried sediment had a higher element concentration, which included Al, Mn, and Ni, the difference indicates that the element content was released and transported primarily in solution in the surrounding environment of the Toka Stream valley.

When compared to the MAD values for geological media (Table 2), the $C1_S$ sample shows that several toxic elements, including Cu, Zn, As, Cd, Pb, and Hg, occur in elevated concentrations, and they can potentially cause

toxic effects under variable environmental conditions, e.g., pH change or microbiological transformation, which could lead to dissolution if they were transported.

3.2. Surface waters

Element concentrations and pH of water: the pH values, element concentrations and the relevant environmental quality standards for the surface water are given in Table 3.

The release from the acidic mine drainage that was neutralised with $\text{Ca}(\text{OH})_2$ is represented by A_W , in which the Mn and Al concentrations can be considered to be high; however, the concentration of Fe was slightly elevated according to the Hungarian Standard 12749:1993 (which, however was not valid in 2010). According to the relevant environmental quality standards that were provided in Directive 2008/105/EC, the Cd concentration just reached the maximum allowable concentration given for waters with hardness of $\geq 200 \text{ mg CaCO}_3 \text{ L}^{-1}$. According to the Water Quality Classification for the Danube River Basin [25], the concentrations of Cu, Pb, Ni and Cr were below the target values, while As was approximately 2.5, Cd was approximately 15, and Zn was approximately 30 times higher than the corresponding values. Based on the data that were cited by Fügedi [26], in 2004, the effluent of the mine that lacked neutralisation contained $13,371 \mu\text{g L}^{-1}$ Zn, while the treatment resulted in $456 \mu\text{g L}^{-1}$; this is more than three times higher than the actually measured value. The concentration of Cd in the treated effluent was reported to be $2.1 \mu\text{g L}^{-1}$ in 1994, while in 2004, it was found to be below the detection limit; however, ICP-MS technique identified its presence at approximately $1.5 \mu\text{g L}^{-1}$. The concentration was found to be $1.24 \mu\text{g L}^{-1}$ in 1994, and it has been reported to be currently below the detection limit, although ICP-MS identified its presence in low concentrations, but the concentrations were higher than in 1994. The concentrations of Cu and Pb were already found to be low for both the untreated and treated effluents in 1994.

The B_W sample represents the water quality of the Toka Stream downstream from the mine. The concentrations for most of the elements were lower than for the A_W sample, the elevations in Ni and Zn concentrations were also not considerable, and pH was close to a natural value. For the D_W sample, among the measured elements, only the dissolved Pb and As concentrations were slightly higher when they were compared to the B_W sample. However, at the sampling time, potentially toxic element concentrations in D_W sample did not reflect the direct additional effect of the mine tailing. The $C1_W$ sample represents the output of the mine tailing entering the Toka Stream through a channel, which seasonally dries out (represented by the $C2_S$ sample). Here, excluding Al, all of the element concentrations were very much higher than for the A_W sample, though the pH was 5.90 due to the natural geochemical neutralisation processes in the abandoned mine tailing. Fe concentration was 22, Mn was 18, Ni was 112, Cu was

TABLE 3 - Concentrations ± standard deviations of elements in $\mu\text{g L}^{-1}$ determined in water (detection limit for all elements is below $1 \mu\text{g L}^{-1}$), pH and the relevant environmental quality standards

Elements	A_w		B_w		$C1_w$		D_w		EQS*		Target Value for Danube River Basin**
	ICP-MS		ICP-MS		ICP-MS		ICP-MS		AA-EQS Inland surface waters	MAC-EQS Inland surface waters	
Fe	465 ± 23		398 ± 8		10175 ± 257		37 ± 1		NG	NG	NG
Al	400 ± 26		109 ± 3		355 ± 4		5 ± 2		NG	NG	NG
Mn	750 ± 23		595 ± 22		13412 ± 317		74 ± 11		NG	NG	NG
Ni	0.29 ± 0.05		0.63 ± 0.02		32.6 ± 0.9		0.82 ± 0.03		20	NA	1
Cu	0.30 ± 0.02		0.37 ± 0.04		21.7 ± 0.2		1.2 ± 0.1		NG	NG	2
Zn	138 ± 7		221 ± 9		2612 ± 193		143 ± 2		NG	NG	5
As	2.3 ± 0.2		1.4 ± 0.1		2.69 ± 0.09		2.0 ± 0.1		NG	NG	1
Cd	1.46 ± 0.07		1.44 ± 0.03		9.4 ± 0.5		0.61 ± 0.03		≤0.08 (class 1) 0.08 (class 2) 0.09 (class 3) 0.15 (class 4) 0.25 (class 5)	≤0.45 (class 1) 0.45 (class 2) 0.6 (class 3) 0.9 (class 4) 1.5 (class 5)	0.1
Pb	0.41 ± 0.01		0.29 ± 0.01		2.1 ± 0.1		1.83 ± 0.05		7.2	NA	1
Tl	2.4 ± 0.1		1.60 ± 0.03		1.56 ± 0.09		0.88 ± 0.03		NG	NG	NG
Cr	0.026 ± 0.004		0.094 ± 0.004		0.06 ± 0.01		0.024 ± 0.004		NG	NG	2
pH	4.0		6.1		5.9		7.4		NG	NG	6.5-8.5

A_w : treated AMD; B_w : industrial reservoir; $C1_w$: tailing discharge; D_w : Toka Stream at Gyöngyösoroszi village. * EQS: Environmental quality standards for inorganic micropollutants according to the Directive 2008/105/EC, AA: annual average, MAC: maximum allowable concentration; for Cd, EQS values vary depending of water hardness specified in five class categories (Class 1: $<40 \text{ mg CaCO}_3 \text{ L}^{-1}$, Class 2: $40 \text{ to } <50 \text{ mg CaCO}_3 \text{ L}^{-1}$, Class 3: $50 \text{ to } <100 \text{ mg CaCO}_3 \text{ L}^{-1}$, Class 4: $100 \text{ to } <200 \text{ mg CaCO}_3 \text{ L}^{-1}$, and Class 5: $\geq 200 \text{ mg CaCO}_3 \text{ L}^{-1}$; ** Target values for Danube River Basin according to the Trans National Monitoring Network (TNMN) Yearbook 2001, published by the International Commission for the Protection of the Danube River (ICPDR); NA: not applicable; NG: not given

72, Zn was 19, and Cd was 6.5 times higher, approximately than the corresponding values for the neutralised AMD. Thus, in rainy seasons, the mine tailing having very high element concentrations for most of the measured elements compared to B_w and D_w , definitely has negative effect on the water quality of the Toka stream. In this way, dissolved Zn and Cd concentrations are expected to be even higher than at the neutralised AMD discharge point.

Considering Tl, although it is not controlled by any EU or national surface water quality standards, in the A_w sample, it was found to be ten times higher than the data that were suggested as a maximum in the FOREGS database for Hungary ($0.22 \mu\text{g L}^{-1}$) [27], and it was more than three times higher than the maximum that was suggested by the Canadian Water Quality Guidelines ($0.8 \mu\text{g L}^{-1}$ for fresh water) [28].

3.3. Relations between sediment and water composition

Considering the relations between the element content of the water and the sediment samples, the locations A and $C1$ can be compared. For the neutralised acidic mine drainage and the abandoned mine drainage, the equilibria that were assumed between the solid and water phases that based on the low flux for the former case and no flux at all in the latter case resulted in different ratios. In the former (A), all of the elements were concentrated in the sediment, while in the latter ($C1$), only Fe, Al, Cu, As, and Pb were concentrated in the sediment, whereas Mn,

Ni, Zn, and Tl still remained in the solution in considerable amounts. High concentrations of toxic elements Cu, As and Pb in the sediment suggest their adsorption on amorphous iron hydroxide [29].

Concentrations of toxic elements Mn, Ni, Cu, Zn, Cd and Pb in water of treated effluent are significantly lower than in the mine tailing effluent, suggesting their efficient removal from the water. Some of them, such as Mn, Zn and Cd are possibly incorporated in calcite structure, detected by XRD in sample A . Mn behaves similarly to Zn and Cd. These metals are strongly sorbed under neutral pH conditions, although in acidic conditions are readily desorbed and are stable in solution.

Altogether, the results for the dry season revealed that most of the investigated elements remained within the area of the mine, which suggests their significant removal from solution by neutralisation. However, the mine tailing is a considerable source of the potentially toxic elements, since its effluent enters the Toka stream in rainy seasons, and its element concentrations are very high both in solution and sediment. However, in rainy seasons, water flow rate of the Toka stream and that of the AMD also increases contributing to dilution, while sediment transport may take place, as well. Thus the overall effects of the AMD and the mine tailing to the water quality of the Toka stream should be approached in a more complex way, including geo-hydrological aspects. As seasonal water quality variations were found for rivers affected by acid mine

drainage at other, similar sites [30], further studies will aim to monitor changes in the rainy seasons to investigate the complex effect of different water loads on both the dissolution and desorption from the contaminant sources and the dilution by the surface water.

4. CONCLUSIONS

The discharges of abandoned Pb-Zn mining sites, such as Gyöngyösoroszi in Hungary, of both acidic mine drainages that are neutralised and mine tailings still require continuous monitoring because under acidic to near neutral pH values, most of the dissolved potentially toxic elements are present in elevated concentrations; downstream of the mine discharge, these may still cause inadequate water quality. For the Toka Stream, Mn, Zn, Fe and Cd were especially found in elevated concentrations at a location that was close to the discharge. At the same time, the abandoned mine tailing was found to be secondary contamination source, e.g., the discharge of the tailing at Gyöngyösoroszi was found to contain high Fe, Mn, Cd, Zn and Al concentrations and elevated Ni and Cu concentrations; however, the outflow rate is generally low, especially in the dry seasons.

Altogether, for the potentially toxic elements, the water quality of the Toka Stream on the date of the sampling was not significantly affected by the mining site, with the exception of the Zn and Cd concentrations.

As a secondary potential source of toxic elements, the sediment of the discharge at the neutralised mine drainage primarily contained amorphous iron hydroxide; however, despite the neutralisation, the concentrations of Zn and Cd were still above levels that continuously cause environmental risk through the precipitation-dissolution equilibria between the solid and water phases. In addition, further Zn, Cd, As, Pb, Cu, and Hg loads may occur by the dissolution from the sediment at the abandoned mine tailing.

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REFERENCES

- [1] García, C., Ballester, A., González, Blázquez, M.L. and Acosta, M. (1996). Chemical and microbiological transformations in a pyritic tailing pond. *Minerals Engineering*, 9 (11), 1127-1142.
- [2] Hayes, K.F., and Traina, S.J. (1998). Metal ion speciation and its significance in ecosystem health. In: Huang, P.M, Adriano, D.C., Logan, T.J., and Checkai, R.T. (Eds.), *Soil chemistry and ecosystem health*. SSSA Special Publication 52, Madison, USA, 45-84.
- [3] Lacal, J., Silva, M.P., García, R., Sevilla, M.T., Procopio, J.R., and Hernández, L. (2003). Study of fractionation and potential mobility of metal in sludge from pyrite mining and affected river sediments: changes in mobility over time and use of artificial ageing as a tool in environmental impact assessment. *Environmental Pollution*, 124, 291-305.
- [4] Salomons, W. (1995). Environmental impact of metals derived from mining activities: Processes, predictions, prevention. *Journal of Geochemical Exploration*, 52, 5-23.
- [5] Fowler, T.A., and Crundwell, F.K. (1999). Leaching of zinc sulfide by *Thiobacillus ferrooxidans*: Bacterial oxidation of the sulfur product layer increases the rate of zinc sulfide dissolution at high concentrations of ferrous ions. *American Society for Microbiology*, 65 (2), 5258-5292.
- [6] Puura, E. and Neretnieks, I. (2000). Atmospheric oxidation of the pyritic waste rock in Maardu, Estonia, 2: An assessment of aluminosilicate buffering potential. *Environmental Geology*, 39 (6), 560-566.
- [7] Pagnanelli, F., Moscardini, E., Giuliano, V. and Toro, L. (2004). Sequential extraction of heavy metals in river sediments of an abandoned pyrite mining area: pollution detection and affinity series. *Environmental Pollution*, 132, 189-201.
- [8] Cappuyns, V., Swennen, R., Vandamme, A. and Niclaes, M. (2006). Environmental impact of the former Pb-Zn mining and smelting in East Belgium. *Journal of Geochemical Exploration*, 88, 6-9.
- [9] Giuliano, V., Pagnanelli, F., Bornoroni, L., Toro, L. and Abbuzzese, C. (2007). Toxic elements at a disused mine district: Particle size distribution and total concentration in stream sediments and mine tailings. *Journal of Hazardous Materials*, 148, 409-418.
- [10] Nikolaidis, C., Zafiriadis, I., Mathioudakis, V. and Constantinidis, T. (2010). Heavy metal pollution associated with an abandoned lead-zinc in the Kirki region, NE Greece. *Bulletin of Environmental Contamination and Toxicology*, 85 (3), 307-312.
- [11] Lee, J.S. and Chon, H.T. (2006). Hydrogeochemical characteristics of acid mine drainage in the vicinity of an abandoned mine, Daduk Creek, Korea. *Journal of Geochemical Exploration*, 88, 37-40.
- [12] Palumbo-Roe, B., Klinck, B., Banks, V. and Quigley, S. (2009). Prediction of long-term performance of abandoned lead zinc mine tailings in a Welsh catchment. *Journal of Geochemical Exploration*, 100, 169-181.
- [13] Butler, B.A., Ranville, J.F. and Ross, P.E. (2009). Spatial variations in the fate and transport of metals in a mining-influenced stream, North Fork Clear Creek, Colorado. *Science of the Total Environment*, 407, 6223-6234.
- [14] Sarmiento, A.M., Nieto, J.M., Olias, M. and Cánovas, C.R. (2009). Hydrochemical characteristics and seasonal influence on the pollution by acid mine drainage in the Odiel River Basin (SW Spain). *Applied Geochemistry*, 24, 697-714.

- [15] Pulford, I.D., MacKenzie, A.B., Donatello, S. and Hastings, L. (2009). Source term characterisation using concentration trends and geochemical associations of Pb and Zn in river sediments in the vicinity of a disused mine site: Implications for contaminant metal dispersion processes. *Environmental Pollution*, 157, 1649-1656.
- [16] Galván, L., Ollas, M., Fernandez de Villarán, R., Domingo Santos, J.M., Nieto, J.M., Sarmiento, A.M. and Cánovas, C.R. (2009). Application of the SWAT model to an AMD-affected river (Meca River, SW Spain). Estimation of transported pollutant load. *Journal of Hydrology*, 377, 445-454.
- [17] Wu, X., Huapin, W., Nansheng, D. and Feng, W. (2003). Feasibility study on heavy metal removal from mine water by using geological material. *Fresenius Environmental Bulletin* 12 (11), 1400-1406.
- [18] Powder Diffraction File (1997). International Center for Diffraction Data, Newtown Square, PA, USA.
- [19] Boldrin, A., Juračić, M., Mengazzo Vitturi, L., Rabitti, S., and Rampazzo, G. (1992). Sedimentation of river-borne material in a shallow shelf sea: Adiga River, Adriatic Sea. *Marine Geology*, 103, 473-485.
- [20] Fiket Ž., Roje V., Mikac N. and Kniewald G. (2007). Determination of arsenic and other trace elements in bottled waters by high resolution inductively coupled plasma mass spectrometry. *Croatica Chemica Acta*, 80, 91-100.
- [21] Kardeván, P., Vekerdy, Z., Róth, L., Sommer, S., Kemper, T., Jordán, Gy., Tamás, J., Pechmann, I., Kovács, E., Hargitai, H. and László, F. (2003). Outline of scientific aims and data processing status of the first Hungarian hyperspectral data acquisition flight campaign, HYSENS 2002 Hungary. In: Habermeyer, M., & Mülle, A. and Holzwarth, S. (Ed.) *Proc. 3rd EarSel Workshop on Imaging Spectroscopy*. Herrsching, Germany, 324-332.
- [22] Kovács, E., Dubbin, W.E. and Tamás, J. (2006). Influence of hydrology on heavy metal speciation in a Pb-Zn mine tailing. *Environmental Pollution*, 141(2), 310-320.
- [23] Darmody R.C., Thorn C.E. and Dixon, J.C. (2007). Pyrite – enhanced chemical weathering in Karkevagge, Swedish Lapland. *Geological Society of America Bulletin*, 119, 1477-1485.
- [24] Yang, C., Chen, Y., Peng, P., Li, C., Chang, X. and Xie, C. (2005). Distribution of natural and anthropogenic thallium in the soils in an industrial pyrite slag disposing area. *Science of The Total Environment*, 341, 159-172.
- [25] International Commission for the Protection of the Danube River (2001). *Water Quality in the Danube River Basin*, TNMN Yearbook 2001, Resch Druck, Vienna
- [26] Fügedi U. (2007). *Geochemical investigation of the environmental contamination in Gyöngyösorsósi*. PhD thesis (In Hungarian). University of Miskolc, Hungary, 1-111.
- [27] Salminen, R., Batista, M.J., Bidovec, M., Demetriades, A., De Vivo, B., De Vos, W., Duris, M., Gilucis, A., Gregorauskiene, V., Halamic, J., Heitzmann, P., Lima, A., Jordan, G., Klaver, G., Klein, P., Lis, J., Locutura, J., Marsina, K., Mazreku, A., O'Connor, P.J., Olsson, S.Å., Ottesen, R.-T., Petersell, V., Plant, J.A., Reeder, S., Salpeteur, I., Sandström, H., Siewers, U., Steenfelt, A. and Tarvainen, T. (2005). *Geochemical Atlas of Europe. Part 1: Background Information, Methodology and Maps*. Espoo, Geological Survey of Finland.
- [28] Canadian Council of Ministers of the Environment (2007). *Canadian Environmental Quality Guidelines – Canadian Water Quality Guidelines for the Protection of Aquatic Life*.
- [29] Johnson A.C. and Thornton, I. (1987). Hydrological and chemical factors controlling the concentrations of Fe, Cu, Zn and As in a river system contaminated by acid mine drainage. *Water Research*, 21 (3), 359-365.
- [30] Ollas, M., Nieto, J.M., Sarmiento, A.M., Cerón, J.C. and Cánovas C.R. (2004). Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River (South West Spain). *Science of the Total Environment*, 333, 267-281.

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