



CHEMICAL WATER QUALITY CHANGES ALONG A STREAM AT AN ABANDONED Pb-Zn MINING SITE

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In the present study, chemical water quality changes downstream a pool-riffle type stream located at a former Pb-Zn mining site are discussed. The watershed of the Toka stream (Mátra mountain, Hungary) being under rehabilitation is still continuously affected by a neutralised acidic mine drainage, and temporarily, by an abandoned mine tailing. Upstream the AMD confluence which gives the major part of the water flux in dry season, indeed, the stream is of high water quality, while, directly after that, the electric conductivity is app. quintupled, and the pH as well as the trace element concentrations increase, as expected. However, within the range of 10 kilometres, Fe, Zn and Pb concentrations are all remarkably decreased in relation to the distance from the contamination source, and they almost reach the actual background levels. The electric conductivity does not show significant change along the investigated section of the stream, which would indicate dilution. At the same time, presence of amorphous Fe(OH)₃ in the sediment is obvious, based on the pH-Eh relations and geochemical analysis, thus the adsorption processes have considerable role in the decrease of trace element concentrations in solution.

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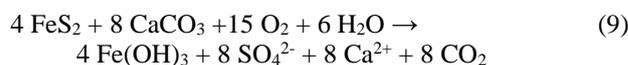
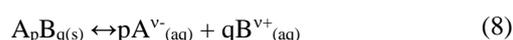
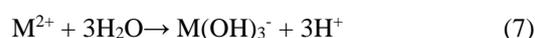
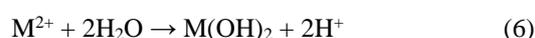
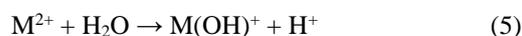
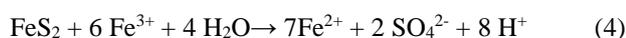
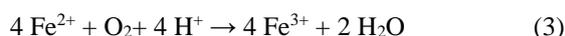
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Considering the mines and their drainages, sediments in the affected surface water pose risk of heavy metal remobilisation as a secondary source of pollution.¹⁻⁵ As a result of increase in pH (Eq. 9), the adsorption, precipitation and co-precipitation specific to heavy metal species take place, and the concentrations in solution show a certain removing order downstream of the discharge point⁶⁻⁸, although hydrological seasons definitely affect the spatial variation, fate and transport of metals.⁸⁻¹¹

Introduction

At the sulphide-bearing mining sites, potentially toxic elements take part in complex biogeochemical interactions. They have many chemical forms that can readily be transformed into one another, under the dynamically changing environmental conditions. In order to assess the contaminant transport it is inevitable to know the controlling (bio)-chemical and physical mechanisms, such as weathering (Eq. 1-4), secondary mineralization, hydrolysis (Eq. 5-7), precipitation, dissolution (Eq. 8), complexation, and co-precipitation, adsorption, desorption, which all dependent on the species present, their concentrations, and can hardly be measured and monitored simultaneously resulting from the complexity of the system.



The aim of the present study was to investigate the change in surface water quality and the main governing chemical and physical mechanisms downstream of the Toka stream (Mátra mountain, Hungary) which is affected by an abandoned Pb-Zn mine and its tailing dump, with respect to potentially toxic elements.

Experimental

Site Description and Sampling

According to the Watershed Management Action Plan (WMAP) in Hungary, Toka stream belongs to the class of the silicate-based mountainous small watersheds with gravel stream bed. In the watershed, a Pb-Zn mine and an ore processing plant were operated from 1952 to 1986, however, neutralized acid mine drainage is still led to the stream. There are two discharges, a continuous one from the AMD treated with Ca(OH)₂ and settled, and a temporary one from a tailing dump of 2.1 Mm³, where remediation has not yet been completed. The site has already been investigated from several aspects.⁵ Change in surface water quality downstream and the effects of the neutralized AMD discharge were investigated along 10 km, from the source of the Toka to the town Gyöngyös. Site and the sampling points are given in Fig. 1.

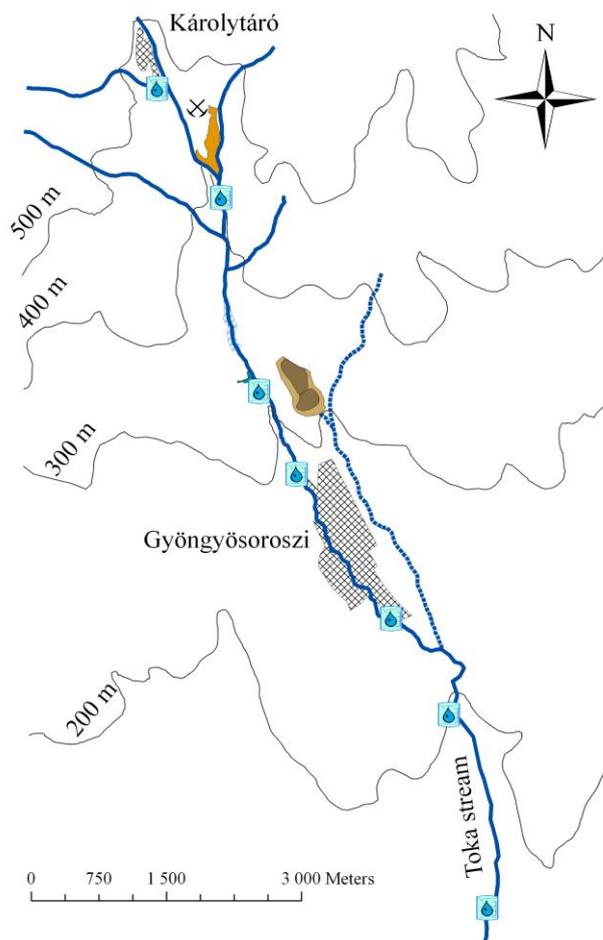


Figure 1. Abandoned Pb-Zn mining site and the sampling points

Sample treatment and analyses

Water samples were taken at 7 different sites along 10 km long transect of the Toka. Sampling was carried in April, 2011, during a dry period. Estimated flow of the river was ca. 0.15 m³/s upstream, while after the confluence ~ 80% of the water originated from the treated AMD.

Samples for metal analysis were taken by 60 mL pre-cleaned plastic syringe. At each site, before taking final sample, syringe was rinsed at least 5 times by ambient water. Syringe is placed against water flow to avoid contamination of water. For dissolved trace elements, water was filtered by 0.45 µm capsule filters (Sartorius) mounted on syringe into the pre-cleaned (washed with 10% HNO₃ then thoroughly MilliQ water rinsed) HDPE bottles. First few milliliters of filtered sample were discarded to avoid possible contamination from the filter. Blank test of capsule filters and syringes were performed in laboratory and no contamination was found for any element. Samples for metals analysis (total-unfiltered and dissolved-filtered) were acidified in laboratory by addition of concentrated nitric acid (Fluka, *TraceSelect*) - 100 µL on cca 60 mL of water.

Physico-chemical parameters (temperature, pH, dissolved oxygen, conductivity and redox potential) were measured *in-situ* (in the river main body and in each source) by HACH HQ40d portable multi-parameter instrument and associated probes. High Resolution Inductively Coupled Plasma Mass

Spectrometer (HR ICP-MS, *Element 2*, Thermo Finnigan, Bremen, Germany) was used for the determination of dissolved element concentrations. 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. Quality control (QC) of HR ICP-MS measurements was checked by the determination of elements concentration in "River Water Reference Material for Trace Metals" (SLRS-4, National Research Council Canada). For most elements, a good agreement with the certified data was obtained.

Results and Discussion

General surface water quality

The Water quality along the Toka stream is affected by the neutralized acidic mine discharge as a point of source of heavy metals. Based on previous measurements, despite neutralization, the concentrations of Zn and Cd of the treated AMD itself were found above the environmental permissible levels, though Zn concentration was reported one third of the that in the untreated AMD. Pb concentration was found low for both the untreated and treated effluents.^{5,6}

The dissolved element concentrations, measured in filtered samples, and the relevant environmental quality standards for surface water are given in *Table 1*. In the sampling campaign, and for the whole length of the stream, dissolved Pb concentration was significantly below both the standard for annual average provided in Directive 2008/105/EC, and the target value given in the Water Quality Classification for the Danube River Basin¹², as expected. Average Zn concentration was rather high along the whole stream, though it was higher by one order of magnitude compared to the target value even at the source of the stream which might be considered as background since no other source upstream was identified. Same was reported by others for similar sites.¹³ *Note:* relevant regulation on surface water quality does not give limit value for Zn.

Table 1 Concentrations ± standard deviations of elements in µg L⁻¹ determined in water (detection limit for all elements is below 10 ng L⁻¹), pH and the relevant environmental quality standards

Element	Concentration ranges along the stream	EQS*		Target Value for Danube River Basin**
		AA-EQS Inland surface waters	MAC-EQS Inland surface waters	
Fe	73.8 ± 43.6	NG	NG	NG
Mn	1123 ± 829	NG	NG	NG
Zn	264.5 ± 190.2	NG	NG	5
Pb	0.120 ± 0.044	7.2	NA	1
pH	7-8.5	NG	NG	6.5-8.5

* EQS: Environmental quality standards for inorganic micropollutants according to the Directive 2008/105/EC, AA: annual average, MAC: maximum allowable concentration; ** 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

Downstream water quality changes

Based on the analytical results, treated AMD has higher pH than the Toka upstream, and even further increase of 1 pH was measured along the stream (Fig. 2). It may result from the basic mineralogical composition of the watershed, the riverbed itself and gradual removal (degassing) of CO₂ from the water. Redox potential decreased significantly at the confluence (Fig. 3), however, reaching ~340 mV within 1-1.5 km and remained constant thereafter.

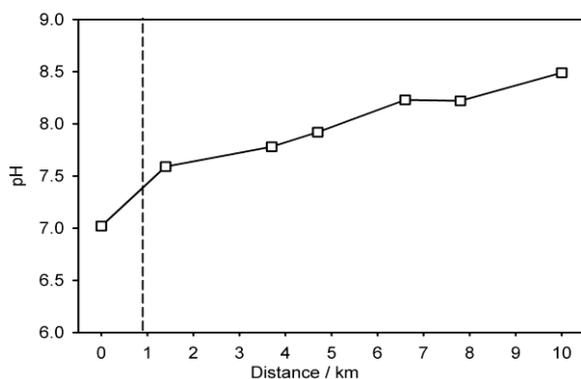


Figure 2. pH profile of the Toka stream, dry season

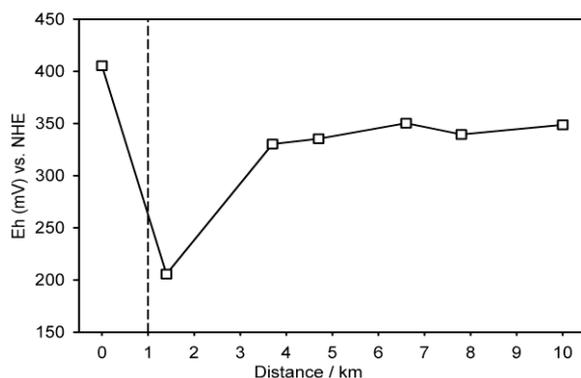


Figure 3. Eh profile of the Toka stream, dry season

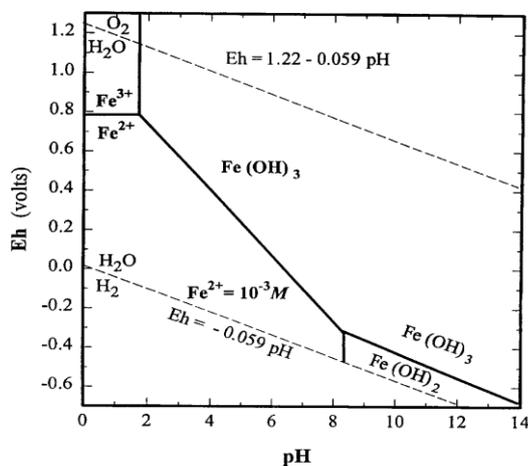


Figure 4. Pourbaix diagram for iron

In the function of pH and Eh relations, metal species can be dynamically transformed into one another. Considering the basic Pourbaix diagram for iron, and taking the measured pH and Eh into consideration, Fe(OH)₃ is expected to form instantaneously at the confluence, thus local conversion of dissolved Fe²⁺ to Fe(OH)₃ precipitate may have considerable role in co-precipitation mechanisms (Fig. 4). Nevertheless, surface water is a highly complex system from chemical point of view, thus presence of carbonate and sulphate ions that are common in treated AMD, cannot be ignored, when heavy metal precipitates are investigated.

Total Fe concentration in water, governing total Pb and Zn concentrations, decreases gradually, indicating settling resulting from flow rates decreasing temporarily at several locations downstream (Fig. 5).

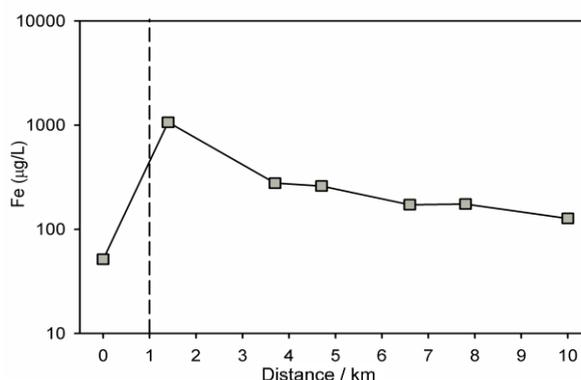


Figure 5. Total Fe concentrations in both solution and colloidal form

Considering the heavy metal concentrations in water, though total Pb concentration is low even in the treated AMD, it decreases further by 5 times downstream (Fig. 6). Among its species, thermodynamically Pb(OH)₂ is stable above pH 6.5 within the Eh range of the Toka, and dissolved Pb takes part in a further equilibrium, since it is strongly associated with amorphous iron-hydroxide, which results in low, almost constant dissolved Pb concentrations measured along the stream.

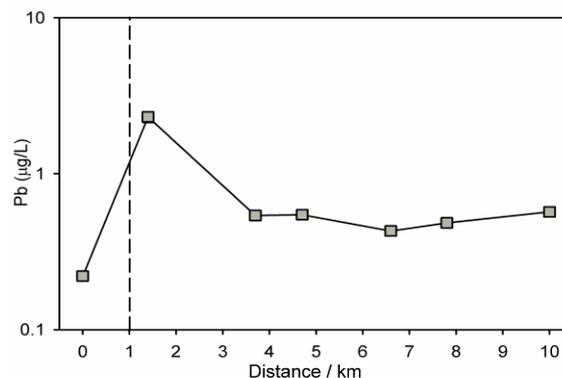


Figure 6. Total Pb concentrations in both solution and colloidal form

Zinc concentration profile is similar to that of Pb (Fig. 7), however, Zn prefers dissolved ionic form up to pH 8.5, while Zn(OH)₂ is stable in range of pH 8.5-11.5, which explains elevated concentrations along the whole stream¹⁴. Though, co-precipitation and adsorption on the newly

formed amorphous iron-hydroxide colloidal particles cannot be ignored¹⁵. Based on the above experiments, Zn elimination from the AMD requires an additional process to neutralization, such as the application of a passive treatment system¹⁶.

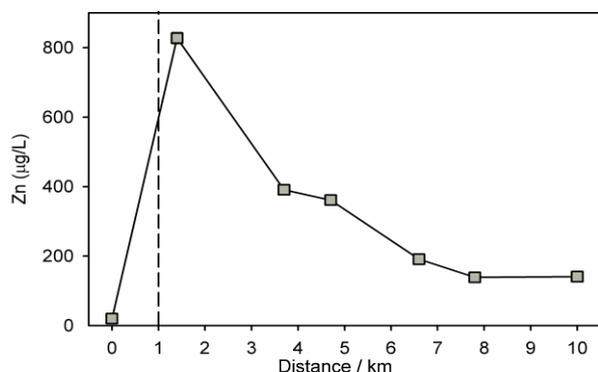


Figure 7. Total Zn concentrations in both solution and colloidal form

Original electric conductivity of the Toka is $200 \mu\text{S cm}^{-1}$, which corresponds to the WMAP classification ($<300 \mu\text{S cm}^{-1}$) while it is app. quintupled at the AMD confluence, as expected (Fig. 8). Basically, neutralization agents determine the magnitude of ion concentrations which control conductivity; Fe, Mn and Al concentrations were 465 ± 23 , 750 ± 23 and $400 \pm 26 \mu\text{g L}^{-1}$, respectively, measured previously in dry season in the neutralized AMD, in average.⁵ However, major ion concentrations do not show decrease in relation to the distance from the ions' source, which confirms that the gradual decrease in total Fe, Pb and Zn concentrations does not result from dilution, but settling of colloidal adsorbed and co-precipitated species.

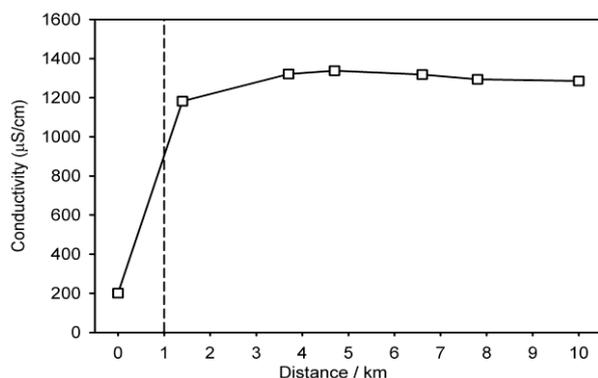


Figure 8. Conductivity profile of Toka stream, dry season

Conclusions

Though, according to WMAP, the watershed of the Toka stream is relatively small, slope of the bed is $\sim 3\%$, and the flow rate as well as the stream water discharge can change extremely; rate of the minimum and maximum for the latter one can be up to 1/1,000. Thus, solid particles settled continuously from the confluence at the neutralized AMD along the stream bed can be resuspended resulting in increase in the total heavy metal concentrations¹³ measurable in unfiltered water samples, however, dissolved

concentrations are not expected to increase in case of stable pH and Eh conditions.

At the same time, while Pb and similar elements such as Cu and As are primarily in solid phase under neutral – basic conditions, Zn and similar ones e.g. Cd still have high dissolved concentration. Thus AMD treatment by neutralization cannot result in reaching the target limits¹² for these elements in such surface waters like Toka stream. Though, it definitely and obviously changes pH that could affect dramatically the ecological systems and the environment, in the acidic range.

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