

## ENVIRONMENTAL IMPACT OF MINING ACTIVITY ON THE TURȚ CREEK, EASTERN CARPATHIANS, ROMANIA

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**Abstract:** Our research goal was to investigate geological and biological effects of acid mine drainage. For this purpose we have used different types of analytical methods, such as electric conductivity and pH measurements, optical microscopy (on thin sections, TS), X-Ray Powder Diffraction (XRD), electron microprobe analysis (EPMA) and Mössbauer Spectroscopy (MSP) and inductively coupled plasma optical emission spectroscopy (ICP-OES) for solved, fine-grained and coarser solid components of the rivulet water. The biological investigations consisted of ecotoxicological algal tests and biodiversity studies. The geological methods evidenced the presence of poorly crystallized Fe-phase(es), like akageneite, ferrihydrite and schwertmannite, with heavy metal content (Cu and Zn). Our work provides the first description of such geological materials from the study area. The acid mine drainage contaminates the creek excessively by high amounts of solved metals (e.g.: Cd, Zn, Cu, Pb and  $\text{SO}_4^{2-}$ ), while the low pH of the water causes extensive leaching of silicate minerals of the bottom rock and soil, resulting in a very high solved concentration of elements such as Al and Si, unusual in natural waters. The results of the phytotoxicological tests are in good agreement with the geochemical data, and reveal several inhibitory effects of the mine water leakage on the development of aquatic microalgae. The high concentrations of Al, Cd, Pb, As, Cr and Zn inhibit the growth, the metabolism, the nitrate up-take and are responsible for oxidative stress.

**Keywords:** environmental pollution, heavy metals, acid mine drainage (AMD), ecotoxicology, Turț Creek (Oaş Mountains).

### 1. INTRODUCTION

Acid mine drainage (AMD) generated by the oxidation of pyrite and other sulphides reacts with country rock, resulting in the leaching of many elements (Sullivan et al., 1988; Bigham et al., 1990; Bigham et al., 1992). It mainly occurs in areas of active and abandoned coal and metal-ore mining areas and represents a long-term pollution problem. High concentration of Fe, Mn, many other heavy metals and  $\text{SO}_4$  typically dominate the drainage seep as well as the receiving streams (Singh et al., 1999; Dold & Fontboté, 2002; Balistrieri et al., 2007;

Majzlan et al., 2007; Andráš et al., 2009; Horaicu et al., 2010; Stumbea, 2010). Oxidation of Fe sulphides and the production of AMD is a complex biogeochemical process involving several redox reactions and microbial and eukaryotic catalysis (Nordstrom, 1982; Brake et al., 2001; Brake et al., 2002; Andráš et al., 2008).

Whilst metal mining activity in Romanian river systems has been happening since at least the Roman period (Lang, 1979; Cioflică et al., 2002), little material was published until very recently on the systematic evaluation of the effects of this activity on local rivers (Brewer et al., 2002, 2003; Bird et al., 2003a; Fodorpataki, 2003; Forray, 2002; Macklin et

al., 2003). This is particularly the case in the Turț River – Turț Creek drainage basin (Fig. 1), which is affected not only by the base and precious metal mining but also represents the Satu Mare county's largest by acid mine drainage polluted area.

The objectives of this study are first, to investigate the geochemical characteristics of acid mine drainage generated from the abandoned Pb-Zn mine, and second, to characterize the *in situ* biological effects of the AMD on the microhabitats in the Turț creek and third, to predict the phytotoxicity of the AMD under laboratory conditions by using polluted and unpolluted water samples from the stream.

## 2. SITE DESCRIPTION

The Oaș Mountains are the north-western part of the volcanic chain of the inner part of the Romanian East Carpathians. They consist of Neogene volcanic and sedimentary rocks located in the north-western part of the Oaș Basin, an Eastern extreme of the Pannonian Basin. Epithermal lead and zinc ore formation was connected to the Neogene volcanic activity in the area. Although the first silver mines in the zone had been established in the 17<sup>th</sup> century (Szellemy, 1896), the exploitation on industrial scale started in the valley of the Turț Creek near Turț only in 1973.

Turț belongs to the Maramureș region, which is the main centre for mining and metallurgy of lead, zinc, copper, gold and silver in Romania, and in the same time, one of the environmental „hot spots” of the country due to the significant pollution with heavy metals (Rauta et al., 1995; Sárkány-Kiss & Sîrbu, 1999; Cordos et al., 2003). In 1996, 1997 and 1999 as a result of some technological problems, the Turț mine seriously polluted the byflowing creek (Sárkány-Kiss & Sîrbu, 1999), and, through that rivulet, also the river Tur (the latter one is under environmental protection). Unfortunately the creek was polluted again in the summer of 2005. We sampled the area in the July-September period of 2005 (Fig. 1). The present study is the first investigation on the sediments and on the phytotoxicity of water in the Turț Creek area.

The epithermal Pb and Zn mineralization is related to Upper-Sarmatian to Lower-Pannonian pyroxene- microdiorites and -andesites and hyalodacites. The main mineral paragenesis contains elements which are important from environmental point of view as well, such as: Pb, Zn, Cu, Au, Ag, Hg, Sb and As; and is represented by: pyrite, sphalerite, galena, chalcopyrite,

marcasite, tetrahedrite, quartz and calcite (Manilici et al., 1970; Jude, 1986).

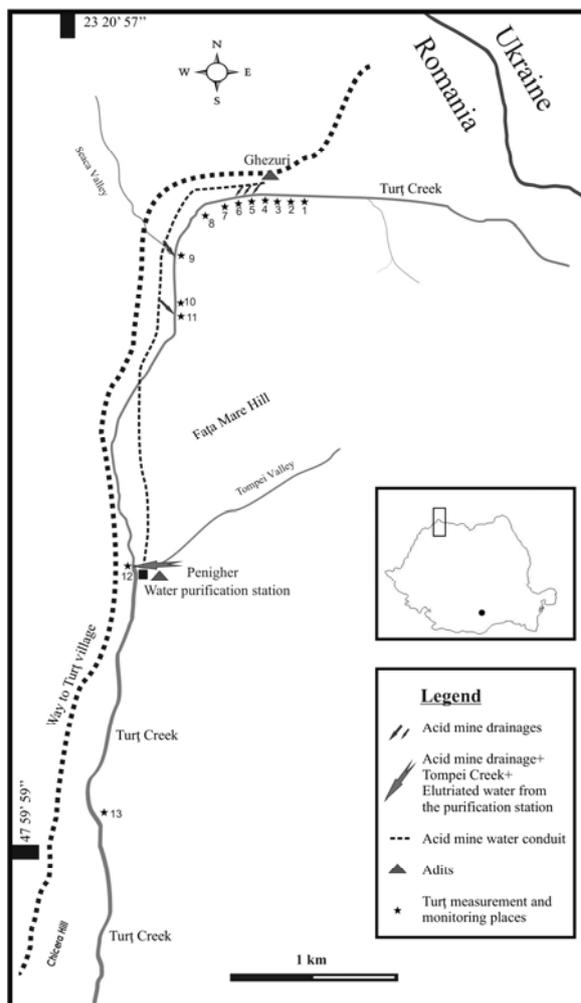


Figure 1. The image represents the Turț creek and the inflowing acid mine drainages, with the measurement and monitoring places. The inset shows the studied section on the map of Romania.

The Turț creek springs near the Ukrainian-Romanian border, and following from north to southwest its flowing direction the bed is formed by: andesitic tuffs, andesitic agglomerates, after these Pliocene and Holocene sediments, and at the foot of the Fața Mare-hill andesitic tuffs could be found as stream borders. Close to this location the Turț creek meets with the Turț-Băi stream, and with the Tompei Creek. The latter is one of the greatest arms of the creek, which in the same time flows through the former mining point, the Penigher adit, by washing away a relevant part of the dumped mine spoil. At the Penigher adit the Turț stream-flux is approximately  $0.3 \text{ m s}^{-1}$  with a  $3 \text{ m}^3 \text{ s}^{-1}$  out-put. From its spring to the inflow with the Tur River the Turț creek does not flow through natural ore outcrops.

By crossing Holocene sediments and the Turț village the creek flows to the Tur River, the latter one is under environmental protection. Due to the snow

melting the highest stream-flux is during the winter season. The contamination at the Penigher water purification centre is relevant, but the main problem is caused by the acid mine water conduit system, which is sinuating along the creek. The distance between the creek and the conduit is generally varying from 0 to 30 meters. The upper part of the mine acid water conduit is made of concrete. The yellowish-brown, iron-rich solution is often overflowing, and through the leakages it flows directly to the creek without any previous treatment. This way the pollution reaches the environmental protected Tur River, which belongs to the Tisza water basin; the latter was polluted several times during the last decade. The tailings dam failures that occurred in January and March 2000 in the upper Tisza basin, Maramureş County, northwest Romania are the most well known. They resulted in the release of 200,000 m<sup>3</sup> of cyanide contaminated water and 40,000 tonnes of tailings into tributaries of the Tisza River (Bird et al., 2003a, 2003b; Macklin et al., 2003; Osán et al., 2004). It is hard to estimate the volume of the polluted water reaching the Tisza, from the Tur creek, but it could be very relevant, since it has unwished environmental fingerprints on the stream and on the Tur River as well.

The purification station could neutralise 5.5 l\*s<sup>-1</sup> acid mine water, but due to the technical problems does not assure one hundred percent efficiency, generally achieving far less, and being almost off function in the winter season. One of the article's purposes is to highlight the environmental problems that are present at the Oaş mining region.

### 3. Methods

The sample collection has been carried out in February and July-September 2005. The pH, electric conductivity (EC) and temperature (t) had been measured at the site. Dissolved oxygen and temperature Consort C534 1.0 type tool (with 0.2% accuracy) has been employed for the pH. A WTW LF-56 type conductometer, with a 0 – 20,000 µS cm<sup>-1</sup> scale and an accuracy of ± 1% was used for the electric conductivity. The electrodes of the pH-meter have been kept more than 12 hours in distilled water before starting each serial measurement (Wilde & Radtke, 1998).

Several water samples (with polluted and unpolluted creek water) were used for biological studies: algal ecotoxicology test with *Scenedesmus opoliensis*, Richter (Felföldy, 1980), algal biodiversity studies (Fodorpataki, 2003;

Stauber et al., 2005). The photon-flux density was measured with a SKP 200 Hansatech Quantum Sensor SKP 216 type device.

The X-ray powder diffraction measurements were carried out on the brownish pebble encrustation and the unconsolidated sediments at the University of Eötvös Loránd with an automatic Bragg-Brentano-Diffractometer (Siemens D500) equipped with a secondary graphite monochromator. Samples were measured from 3 to 75° 2θ (step size 0.02°, measuring time 3 seconds per step) with Cu Kα radiation (λCuKα = 1.54178 Å, 41 kV, 20 mA).

For the quantitative geochemical analyses as a first step an AMRAY X 1830 I/T6 type electron microscope (20 keV and 1–2 nA energy voltage), together with an EDAX PV 9800 type energy dispersive roentgen-spectrometer were used in the University of Eötvös Loránd. The yellowish-brown unconsolidated sediment was studied by Mössbauer type spectroscopy, at the Nuclear-chemistry Department of the above mentioned institute. The inductively coupled plasma emission spectroscopy was used to study the water chemistry of the polluted Tur creek, by measuring the concentration of the following parameters: 23 element and 13 ion, total alkalinity (mmol\*l<sup>-1</sup>), silicic acid (H<sub>2</sub>SiO<sub>3</sub>), total water-hardness (mg CaO l<sup>-1</sup>), carbonate hardness (mg CaO l<sup>-1</sup>) and total dissolved solids. The inductively coupled plasma optical emission spectroscopy (ICP-AES) was carried out by a Jobin Yvon ULTIMA 2C type, mono – and polychromatic state-of-the-art apparatus, in the Hungarian Geological Institute by following the MSZ 13-177:1992 (Collective determination of total trace element contents in solid pollutants with plasma emission spectrophotometry, ICP-AES) and MSZ 21470-50:1998 (Environment protection. Testing of soils. Determination of total and soluble toxic element, heavy metal and chromium VI content) Hungarian standards.

### 4. Results and discussion

#### 4.1.1 Electric conductivity (EC) and pH

The inflowing acid mine drainages change the creek's chemistry from alkaline to acidic, down to almost pH 3 (Fig. 2). Due to the high ion concentrations the EC increases along with the decreasing pH (Fig. 3). In September 2005 due to the AMDs we measured 8 times the electric conductivity of the normal value (cc. 240 µS cm<sup>-1</sup>).

In the same time the pH decreased below 5 (in July down to 2.5); at this value all fish species were vanished due to the lethal conditions (Jambor et al., 2000; Wilhelm, 2000).

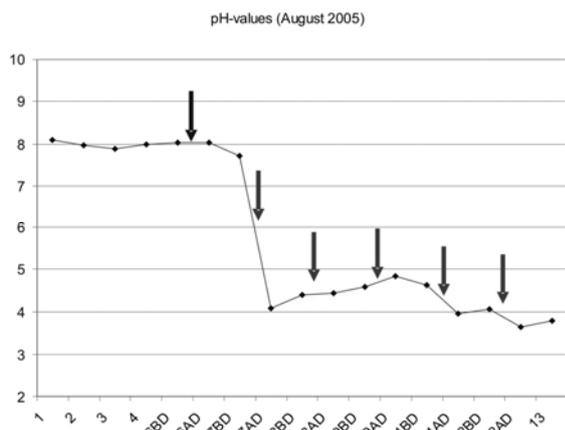


Figure 2. Represents the pH values in the Turf Creek in August 2005. The measurement points are numbered from 1 to 13; “BD” – measurement upstream the inflowing AMD; “AD” – measurement downstream the inflowing AMD; the first arrow represents inflowing oil-water mixture from the Ghezuri-adit’s engine-house, all others are inflowing AMDs.

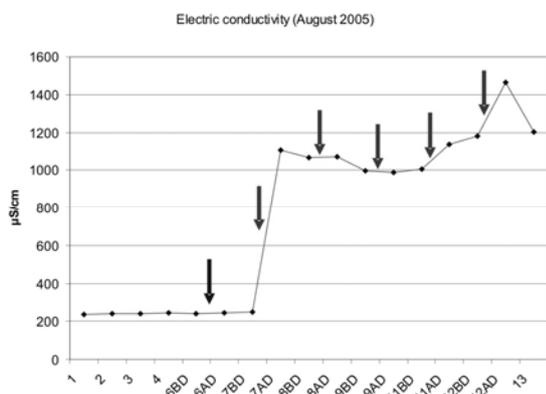


Figure 3. Represents the EC values (in  $\mu\text{S m}^{-1}$ ) in the Turf Creek in August 2005. The measurement points are numbered from 1 to 13; “BD” – measurement upstream the inflowing AMD; “AD” – measurement downstream the inflowing AMD; first arrow represents inflowing oil-water mixture from the Ghezuri-adit’s engine-house, all others are inflowing AMDs.

#### 4.1.2 Thin sections

In the isotropic yellowish-brown matrix small (cc.  $10 \mu\text{m}$ ) angular quartz and goethite crystals were only separable in few cases. Near the

above mentioned phases the main Fe-O-OH-SO<sub>4</sub> matrix is entrapping the other minerals, such as the micas and calcite. The presence of the carbonate could be explained by the applied water treatment. At the Penigher purification station the main water pH increasing method is the dosing of the hydrated lime. However this should be handled very carefully, in the light of the studies of Evangelou & Zhang (1995). They have reported increased oxidation rates of pyrite by addition of HCO<sub>3</sub><sup>-</sup> due to the formation of pyrite surface Fe(II)-CO<sub>3</sub> complexes. This means that this relative frequently applied limestone treatment for mine waste management must be discussed critically, because if it is able to neutralize the acid produced, it can also increase the kinetic of pyrite oxidation (Dold, 2005).

#### 4.1.3 X-Ray Powder Diffraction

The pebble encrustation is composed of poorly crystallised, more or less consolidated phases (Fig. 4) Based on the creek-water physical parameters the encrustation wide peaks at 2.51 and 3.37 Å could refer to schwertmannite (Bigham et al., 1990; Fukushi et al., 2004; Loan et al., 2004; Hochella et al., 2005).

#### 4.1.4 Scanning electron microscopy combined with EDX

Besides a small amount of detrital phases (sphalerite, galena, goethite, quartz, muscovite, ilmenite, barite and pyrite) the bulk of the yellow encrustation consists of a poorly crystallised (grainsize <  $0.1 \mu\text{m}$ ) matrix containing elements Fe>>S>Al>Si>P>Cu>Zn>K. From these elements the Fe is the dominant, the Al, Si, P and K are in a very small concentration, sometimes below the detectable limit. In the creek’s environment the S is most likely sulphate than sulphide.

The presence of heavy metals, such as: Zn and Cu in this specific carrier mineral matrix is very obvious due to the sphalerite and chalcopyrite mineralization, and to the „sponge – effect” of the Fe-O-OH-sulphate mineral(s).

#### 4.1.5 Mössbauer Spectroscopy

Mössbauer type spectroscopy was applied to determine the main phase(es) of the pebbles encrustation.

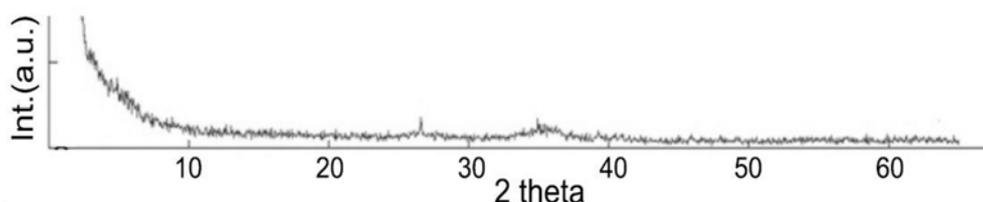


Figure 4. The diffractogram of the pebble encrustations represents poorly crystallised phases (quartz and schwertmannite?). The abbreviation stays for the intensity which is in arbitrary units.

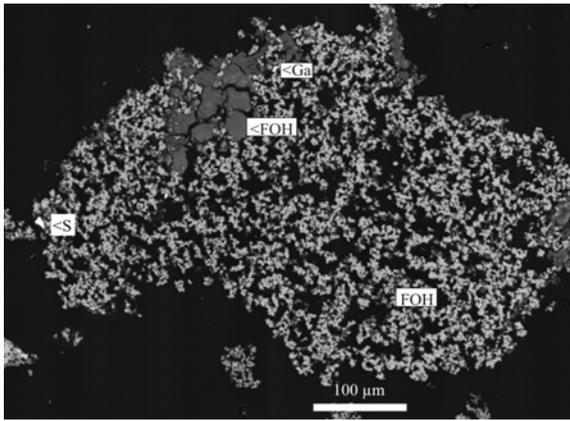


Figure 5. The image represents the backscattered electron image of the pebbles encrustation (S – sphalerite; Ga – galena; FOH – iron-oxide-hydroxide-sulphate).

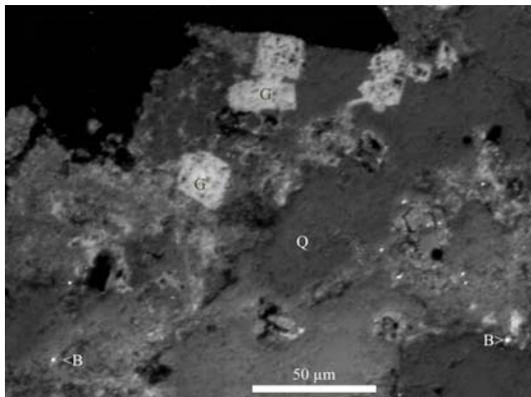


Figure 6. The image represents the backscattered electron image of pebbles encrustation (Q – quartz; G – goethite; B – barite).

The measurement was carried out under room temperature and results were coupled with doublets. A good chi-square distribution value ( $\chi^2 = 1.3365$ ) can be obtained by fitting two doublets with the same line-widthness. The quadrupole-splitting was determined by using linear correlation equation (1) where “ $\Delta$ ” represents the frequency, “ $\delta$ ” is the isomer-shifting and “ $b$ ” and “ $m$ ” are the variables.

$$\delta = b + m\Delta \quad (1) \text{ equation}$$

In fact we analysed the probability of an isochronous change of the isomer-shifting and quadrupole splitting. However this resulted in a high chi-square distribution and in the same time in a high quadrupole. At the end we can conclude the recent yellow-brownish encrustation showed  $\text{Fe}^{3+}$  in two very similar octahedral coordinations. Based on isomer shifting (0.35104) and quadrupole splitting (0.61844) values best fitting phases are ferrihydrite ( $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ) and/or akaganeite ( $\beta\text{-FeOOH}$ ) (McCammon, 1995).

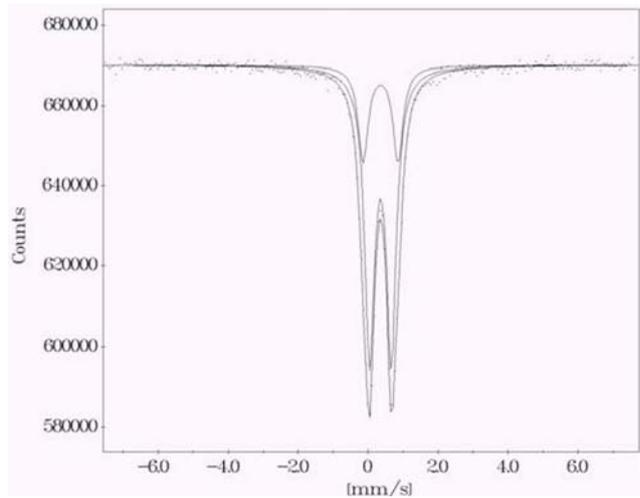


Figure 7. The Mössbauer spectra of the pebbles encrustation's contains of ferrihydrite and/or akaganeite.

The Mössbauer spectroscopy did not confirm the presence of the iron-oxide-hydroxide-sulphate. However Loan et al. (2004) show that (a maghemite like) 2-line ferrihydrite could be a main structural component in schwertmannite. From the crystallisation point of view the schwertmannite could be a transition phase between the 2- and 6-line ferrihydrite.

When the acid mine water (rich in ferric iron), reaches the Turț creek it will be fully oxidized, hydrolyzed and may precipitate to ferrihydrite, schwertmannite, goethite, or jarosite depending on pH-Eh conditions, and availability of key elements such as sulfur and potassium (Nordstrom et al., 1979; Bigham et al., 1996). From the forming minerals: jarosite, schwertmannite and ferrihydrite are meta-stable with respect to goethite (Bigham et al., 1996). The hydrolysis and precipitation of iron hydroxides (and to a lesser degree, jarosite) will produce most of the acid in this process (Dold, 2005). The formation of the well-crystalline ferric sulfate minerals may require prolonged time; elevated temperatures; high concentration of  $\text{Fe}^{3+}$ ,  $\text{SO}_4$ , and  $\text{H}^+$ ; or the presence of additional ions, such as Na and K for jarosite (Majzlan & Myneni, 2005).

#### 4.1.6 Inductively coupled plasma optical emission spectroscopy (ICP-AES)

##### 4.1.6.1 Water chemistry in the Turț creek

In August and September 2005 we sampled the Turț creek on four measurement points: 1 – at the Turț-spring; 2 – before the main drainage at the 11<sup>th</sup> measurement point; 3 – after the main drainage at the 11<sup>th</sup> measurement point; 4 – from the creek after the purification station; and in one case from the main inflowing acid mine drainage (11B). All the samples were strained through 450 nm filters, than measured for the dissolved (<450 nm) and solid material ( $\geq 450$  nm). Due to the inflowing acid mine drainages in both

months the total dissolved solids significantly increased. Before the main inflowing acid mine drainage point (11B) other acid waters were affecting the creek from the mine water conduit, because of this the increasing cation – and in few cases anion – values show good correlation with

the water electric conductivity and the pH parameters. At the last sampling point (just after the water purification station) the total dissolved solids value increases with over than six times the original unpolluted spring water (Fig. 8).

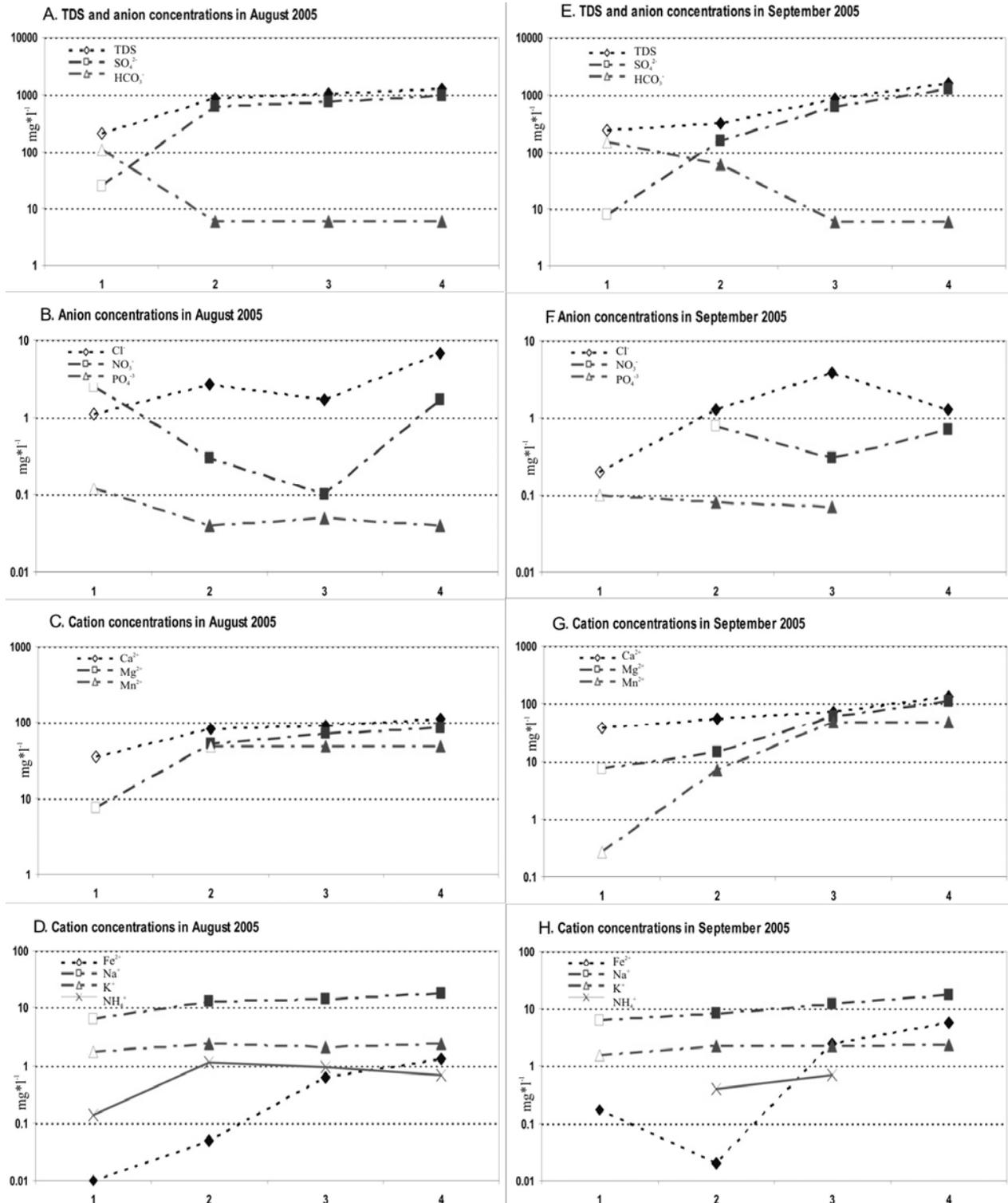


Figure 8. The charts represent the water chemistry values on logarithmic scales in the creek in August (A–D) 2005 and September (E–H) 2005 (in mg·l<sup>-1</sup>): 1 – Turç-spring; 2 – upstream the main drainage; 3 – downstream the main drainage; 4 – Turç creek downstream the purification station.

The alkali earth metals show good correlation, both increase simultaneously (Ca and Mg correlation factor is 0.99). But in other cases the correlation is negative, as the Mg and Mn: -0.99; Ca and Mn: -0.983. The increase of Ca<sup>2+</sup> downstream the water purification station is caused by the treatment method with hydrated lime. Meanwhile the alkali metals values correlate very well the potassium and ammonium ions are in less extent. The latter has an increasing concentration, which is connected with the bacterial activity, organic material metabolism (Ainsworth & Goulter, 1998; Takabatake et al., 2004). The pH curve has been reflected by the increasing free SO<sub>4</sub> which actually refers to the „free vitriol“ concentration.

The HCO<sub>3</sub> quantity is decreasing in negative correlation (R = -0.93). The Cl, NO<sub>3</sub>, NO<sub>2</sub> and PO<sub>4</sub> anions as the cations show increasing trends (Fig. 8). Although the NO<sub>2</sub> concentration does not exceed 0.1 mg\*l<sup>-1</sup>, the ammonium value shows ascending trend. In September 2005 before the 11<sup>th</sup> measurement point the inflowing acid mine drainages were ceased, because of this the pH increased and most of the elements mobilised. This is why the element concentration slope – between the Turț-spring and the main AMD – is higher in August and is lower in September,

Regarding the physiological relevance the water samples' metal cation content is very important. The heavy metal concentration exceeds with several decimals the unpolluted spring level

and the maximum admissible values – MAC, based on the STAS 4706/88 Romanian National Standard (Table 1). In September compared with August the values decrease with one decimal (e.g.: Zn, Cu, Ni, Al, Pb, Cd and Li) upstream the 11<sup>th</sup> measurement point, but were still higher than the MAC.

In August 2005 the Turț spring Zn quantity exceeds the MAC (STAS 4706/88 Romanian National Standard) which refers to the Pb-Zn ore mineralization and represents the background value for the zinc. As the summary of data shows, for heavy metals and anions concentration (Table 1) in the creek the Cu, Pb, Zn, Cd and SO<sub>4</sub><sup>2-</sup> exceeded the maximum admissible values (MAC, 4706/88 Romanian National Standard) in most cases, for the Zn more than 4.6 million times and for the Cd 145 times in September downstream the purification station.

#### 4.1.6.2 Encrustation analysis and adsorption

The applied ICP-OES analyses enabled the better understanding of the adsorption of the heavy metals on the recent pebble encrustations.

Due to the pyrite-sphalerite-galena ore mineralization already at the Turț spring (1.VTP.AU and 1.VTP.SE measurement points) the concentration of Fe, Zn and Pb exceed the soil average concentrations (SAC) as well (Mason, 1966). The background levels are increased, in the case of iron from 43.1 to 43 g\*kg<sup>-1</sup> (35 000 mg\*kg<sup>-1</sup> SAC); for zinc from 417 to 598 mg\*kg<sup>-1</sup> (127 mg\*kg<sup>-1</sup> SAC); and for the lead from 137 to 180 mg\*kg<sup>-1</sup> (16 mg\*kg<sup>-1</sup> SAC) – (Table 2a and 2b).

Table 1 Contains the summary of heavy metal and anion concentration in the Turț creek. Measurement points: 1. - 1.VTP.AU - Turț spring in August; 2. - 11.BE.VTP.AU - Turț Creek upstream the main drainage in August; 3. - 11.B.VTP.AU - Main inflowing AMD in August; 4. - 11.BU.VTP.AU - Turț Creek downstream the main drainage in August; 5. - 12.BU.VTP.AU - Turț Creek downstream the purification station in August; 6. - 1.VTP.SE - Turț spring in September; 7. - 11.BE.VTP.SE - Turț Creek upstream the main drainage in September; 8. - 11.B.VTP.SE Main inflowing AMD in September; 9. - 11.BU.VTP.SE - Turț Creek downstream the main drainage in September; 10. - 12.BU.VTP.SE Turț Creek downstream the purification station in September. Maximum admissible concentration – MAC† STAS 4706/88 Romanian National Standard, - Surface waters; Romanian Standards Association, Bucharest.

Measurement point/ Element concentrations (mg*l <sup>-1</sup> )	Cu	Pb	Zn	Cd	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	HCO <sub>3</sub> <sup>-</sup>
MAC† (in mg*l <sup>-1</sup> )	0.050	0.050	0.030	0.003	250	200	-
1. - 1.VTP.AU	0.003	<0.003	0.031	<0.0002	1.1	24.9	105.53
2. - 11.BE.VTP.AU	1 885	0.175	67 170	0.189	2.7	611	6.10
3. - 11.B.VTP.AU	27 430	0.0558	879 000	2 650	58	8 190	12.20
4. - 11.BU.VTP.AU	2 258	0.432	86 340	0.269	1.7	760	6.10
5. - 12.BU.VTP.AU	2 782	0.385	105 600	0.327	6.7	953	6.10
6. - 1.VTP.SE	<0.001	<0.003	0.0121	0.0003	0.2	8.10	149.45
7. - 11.BE.VTP.SE	0.015	<0.003	7 990	0.0255	1.3	155	62.22
8. - 11.B.VTP.SE	41 880	0.048	903 600	2 770	56.2	7 960	6.10
9. - 11.BU.VTP.SE	3 024	0.111	69 550	0.221	3.9	612	6.10
10. - 12.BU.VTP.SE	5 515	0.169	140 640	0.435	1.3	1 239	6.10

Table 2a Contains the heavy metal concentration of precipitated residues. Measurement points: 1. 1.VTP.AU - Turç spring in August; 2. - 11.BE.VTP.AU - Turç Creek upstream the main drainage in August; 3. - 11.B.VTP.AU - Main inflowing AMD in August; 4. - 11.BU.VTP.AU - Turç Creek downstream the main drainage in August; 5. - 12.BU.VTP.AU - Turç Creek downstream the purification station in August; 6. - 1.VTP.SE - Turç spring in September; 7. - 11.BE.VTP.SE - Turç Creek upstream the main drainage in September; 8. - 11.B.VTP.SE Main inflowing AMD in September; 9. - 11.BU.VTP.SE - Turç Creek downstream the main drainage in September; 10. - 12.BU.VTP.SE Turç Creek downstream the purification station in September.

Measurement point/ Element in mg*kg <sup>-1</sup>	Cr	Zn	Co	Ni	Ba	Mn	Cu	Sr
1. - 1.VTP.AU	22.3	417	21.7	47	331	1720	125	38.5
2. - 11.BE.VTP.AU	26.4	3250	12.1	36.7	174	381	266	58.5
3. - 11.B.VTP.AU	57.9	14930	4.07	33.4	55.9	1560	550	23.5
4. - 11.BU.VTP.AU	54.8	7275	24.9	79.6	178	3410	5045	81.1
5. - 12.BU.VTP.AU	13.4	3725	12	15.4	42.8	6970	1205	78.4
6. - 1.VTP.SE	17.8	598	14.2	18.5	77.5	7340	1740	167
7. - 11.BE.VTP.SE	103	55520	6.53	30.6	889	3320	1830	41.8
8. - 11.B.VTP.SE	107	16670	6.27	21.5	88.6	2870	1450	43.1
9. -11.BU.VTP.SE	45.8	6680	3.25	16.3	228	1730	1055	19.7
10.- 12.BU.VTP.SE	93.2	16500	11.6	41.5	98	7060	1510	67.6

Table 2b Contains the heavy metal concentration of precipitated residue. Measurement points: 1. 1.VTP.AU - Turç spring in August; 2. - 11.BE.VTP.AU - Turç Creek upstream the main drainage in August; 3. - 11.B.VTP.AU - Main inflowing AMD in August; 4. - 11.BU.VTP.AU - Turç Creek downstream the main drainage in August; 5. - 12.BU.VTP.AU - Turç Creek downstream the purification station in August; 6. - 1.VTP.SE - Turç spring in September; 7. - 11.BE.VTP.SE - Turç Creek upstream the main drainage in September; 8. - 11.B.VTP.SE Main inflowing AMD in September; 9. - 11.BU.VTP.SE - Turç Creek downstream the main drainage in September; 10. - 12.BU.VTP.SE Turç Creek downstream the purification station in September.

Measurement point/ Element in mg*kg <sup>-1</sup>	V	Mo	P	Pb	Cd	As	Ti	Li
1. - 1.VTP.AU	37.6	<0.2	730	180	3.7	7.23	17	30.9
2. - 11.BE.VTP.AU	17.9	0.2	612	1670	7.3	28.4	26	22.6
3. - 11.B.VTP.AU	17.7	<0.2	395	7460	31.5	68.1	<2	20.0
4. - 11.BU.VTP.AU	28.3	<0.2	718	2520	15.8	49.3	27	32.8
5. - 12.BU.VTP.AU	13.1	<0.2	536	792	8.0	30.1	21	16.5
6. - 1.VTP.SE	34.7	<0.2	671	137	<0.1	<0.6	20	88.9
7. - 11.BE.VTP.SE	32.2	<0.2	966	1110	77.1	43.5	92	36.1
8. - 11.B.VTP.SE	27.5	<0.2	559	10790	36.8	65.6	18	21.0
9. -11.BU.VTP.SE	31.6	<0.2	1015	4830	15.6	63.2	58	48.5
10.- 12.BU.VTP.SE	27.2	<0.2	824	1320	33.0	50.5	44	54.3

Due to the inflowing acid mine drainages the above mentioned elements concentration has changed significantly. The acid mine-waters decrease the pH of the creek and in the same time increase the quantity of the heavy metal loaded iron-oxide-hydroxide-sulphate precipitations. This process was confirmed by the electronmicroprobe analyses (e.g.: the presence of Cu and Zn) as well. Extremely high concentrations of Zn, Cu, Mn, Pb, Cd and As characterize the fine grained material transported by the stream water (> 450 nm).

In the main inflowing acid mine drainage (11.B.VTP) most of the major elements of the suspension (e.g.: Ca, Mg, Al, K and Na) are

transported in solution (Fig. 9), while others (Fe and S) adsorbe the heavy metals present in Tables 2a and 2b, and finally precipitate.

#### 4.2.1 Algal toxicology test

Because the algae life is dependent on the water-soluble inorganic chemicals, microalgal strains can be used in toxicological tests to study the influence of ions on developmental and metabolic processes (Felföldy, 1980; Kaputska, 1997; Nyholm & Peterson, 1997). Axenic cultures of the highly tolerant algal species *Scenedesmus opoliensis* P. Richter were used (Knauer et al., 1997; Fodorpataki & Papp, 2002; Awasthi & Rai, 2005).

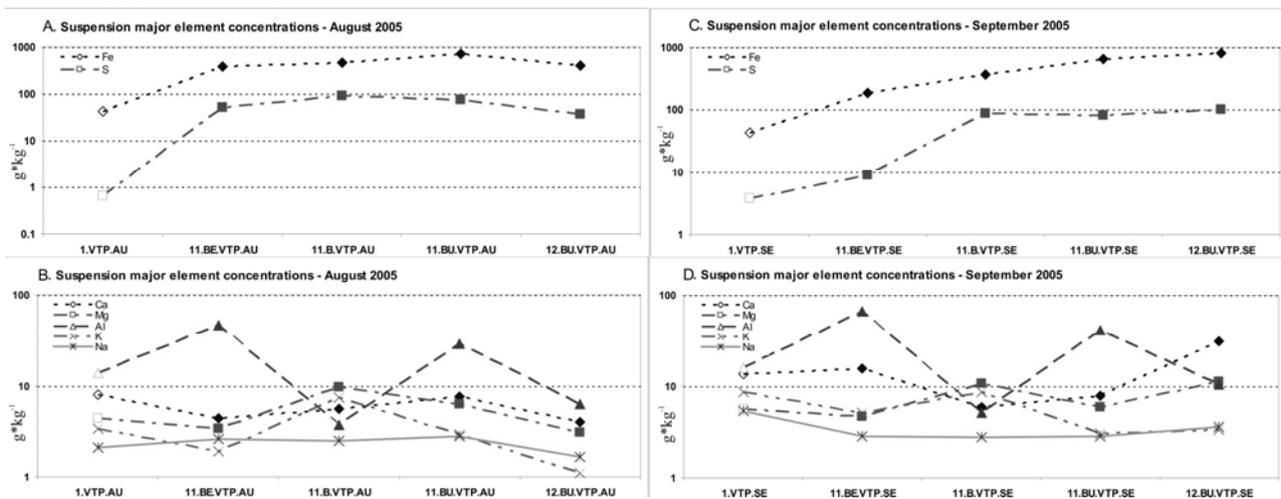


Figure 9. The charts represent the Turŭ creek suspension major element concentration values on logarithmic scales in the creek in August (A–B) 2005 and September (C–D) 2005 (in  $g \cdot kg^{-1}$ ).

This is a test organism with pronounced metabolic plasticity, suitable for detection of physiological changes induced by adverse environmental conditions. The used water samples were the following: 1 – Turŭ Creek spring (1.VTP.AU); 2 – inflowing main acid mine drainage (11.B.VTP.AU); 3 – upstream the main AMD (11.BE.VTP.AU); 4 – downstream the main AMD (11.BU.VTP.AU), and 5 – creek water downstream the purification station (12.BU.VTP.AU).

The density of algal cells in the cultures was determined periodically in order to study the effects of water pollution on the reproduction rate and on the morphology of the cells. Due to chemical pollution, a significant difference was detectable in the algal cultures treated with AMD

water samples, as compared with control cultures.

The heavy metals of the main inflowing AMD are toxic to the microalgae, causing a drastical decrease of the cell density in algal populations (Fig. 10). The high concentrations of Al, Cd, Pb, As, Cr and Zn inhibit growth, metabolic vitality and nitrate uptake of algae, as it was also found in similar studies (Awasthi & Rai, 2005; Yu et al., 2007), being also responsible for oxidative stress (Tripathi et al., 2006). All these conditions result in a significant inhibition of reproductive capacity of algae, and in a lowered primary production in aquatic habitats. While the cell cultures grown in spring water show a normal, healthy morphology trend, the test algae grown in the AMD waters exhibit different modifications detectable by microscopy.

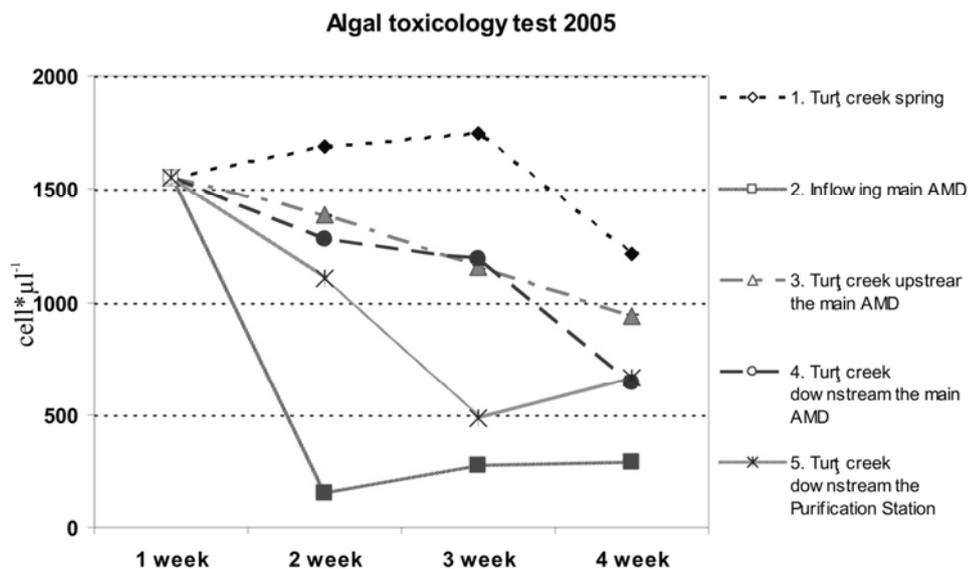


Figure 10. Influence of water samples from different sampling sites along the Turŭ creek on the dynamics of cell density in cultures of the test alga *Scenedesmus opoliensis*. 1 – Turŭ Creek spring; 2 – Inflowing main AMD; 3 – upstream the main AMD; 4 – downstream the main AMD; 5 – creek water downstream the purification station. In all cases the standard deviation from means is less than  $\pm 15\%$  ( $n = 15$ ).

Cell morphology in the algal cultures exposed to polluted water showed the negative effects induced by heavy metals: cells became spherical instead of fusiform, wearing reclinate spikes and exhibiting pale green, fragmented chloroplasts. After several days of exposure to the inflowing AMD, under the selective pressure of excessive amounts of heavy metals and decreased pH values, only the most resistant algal cells remained in cultures and managed to reproduce, resulting in new algal populations with a much lower cell density as compared with the control

#### 4.2.2 Phytoplankton and periphyton diversity

The phytoplankton at the Turç creek spring showed a clear difference to polluted creek area. At high polluted media all *Conjugatophyceae* disappeared face to increasing dominance of non-photosynthetic microorganisms (article in praep.).

The special niche formed by acid mine drainage represents the habitat of several species, we identified *Euglena mutabilis* Schmitz, an indicator microalgal species of acidic water (Brake et al., 2001 and 2002; Casiot et al., 2004; Forray, 2002) and high amount of total dissolved solids (in our case: pH 2.9 and TDS: 9772 mg\* $\Gamma^{-1}$ ), which formed green mats in the inflowing AMD (Fig. 11 and 12). Based on data represented in Fig. 12, several other microbiotic species may be found in this acidic niche, which is characterised by high concentration of dissolved elements, very low pH, and high electric conductivity.

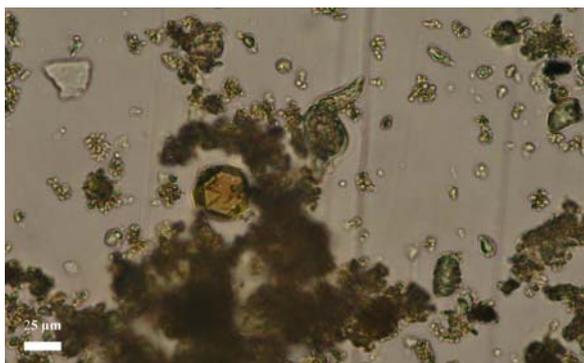


Figure 11. The image represents a pyrite crystal with iron-oxide-hydroxide-sulphate suspension and the acidophilic protista - *Euglena mutabilis*.

These extreme conditions that favor the growth of *Euglena mutabilis* would be lethal to most of other aquatic organisms (Allan, 1995). The most stable Fe species in AMD hosting *E. mutabilis* is  $\text{FeSO}_4^{\text{aq}}$ , suggesting that *E. mutabilis* prefers an environment where Fe is in the reduced state (Brake

et al., 2001). The Eh-pH conditions supporting *E. mutabilis* fall well within the Eh-pH range for S- and/or Fe-oxidizing bacteria. *Euglena mutabilis* does, however, prefer less oxidizing conditions than that which support *T. ferrooxidans* and *T. thiooxidans*, bacteria that also reside in AMD systems (Fig. 12). The presence of *E. mutabilis* has the potential to greatly influence water chemistry, particularly Fe concentrations, because of its capacity to sequester iron intracellularly and to precipitate it in an inorganic form, via  $\text{O}_2$  production (Brake et al., 2001).

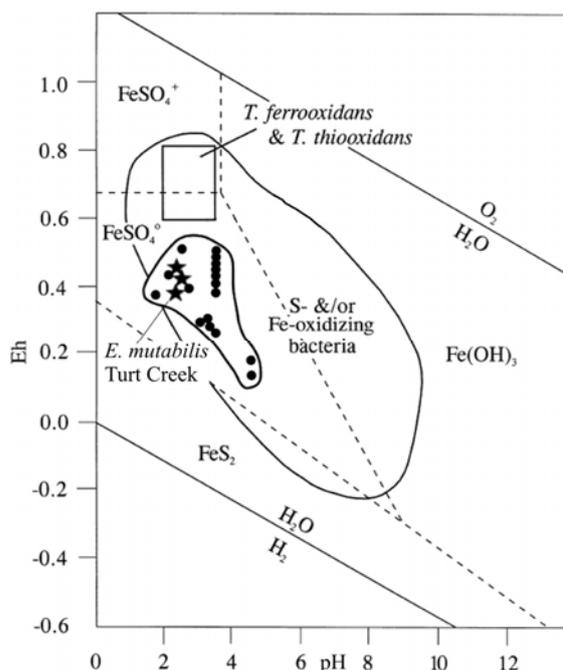


Figure 12. Variation Eh-pH diagram for the Fe-S-O<sub>2</sub>-H<sub>2</sub>O system at 25 C°.  $\Sigma\text{Fe}=10^{-1}$  m, and  $\Sigma\text{S}=10^{-1}$  m. Stability fields for Fe phases are shown as dashed lines. Superimposed on the Fe stability fields are the Eh and pH conditions supporting S- and/or Fe-oxidizing bacteria. *Euglena mutabilis* at Turç Valleys (marked with stars) and at Green Valley, Indiana, U.S.A. marked by dots and *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* (with modifications after Brake et al., 2001).

## 5. CONCLUSION

Based on the macroscopical and microscopical studies and the analytical tests the fine grained encrustation of pebbles consists of nanometer scale domains of ferrihydrite and/or akaganeite. Heavy metals are adsorbed on their surfaces enhancing pollution time and space expansion. The acid mine drainage brings into the creek excessively high amounts of solved metals (e.g.: Cd, Zn, Cu, Pb and  $\text{SO}_4^{2-}$ ), while the low pH of the water causes extensive leaching of silicate minerals of the bottom rock and soil, resulting in a very high solved concentration of elements like Al and Si, unusual in natural waters.

When the acid mine water (rich in ferric iron), reaches the Turč creek it is fully oxidized, hydrolyzed and may precipitate to ferrihydrite, schwertmannite, goethite, or jarosite depending on pH-Eh conditions, and availability of key elements such as sulfur and potassium (Nordstrom et al., 1979; Bigham et al., 1996). The forming minerals: jarosite, schwertmannite and ferrihydrite are metastable with respect to goethite (Bigham et al., 1996). The hydrolysis and precipitation of iron hydroxides (and to a lesser degree, jarosite) will produce most of the acid in this process.

The soluble salts of some of the above mentioned metals accumulate in aquatic microorganisms and cause an imbalance in the ecological equilibrium; the low pH, high electric conductivity, increased total dissolved solids conditions favour the appearance of acidophilic microorganisms, such as *Euglena mutabilis*. The toxic cations (as the: Al, Cd, Pb and Cu) inhibit the germination and the metabolism enzymes by connecting to the proteins S atoms. The special conditions form a specific toxic habitat for the majority of living beings, however several bacteria and protists live in this acid mine drainage niche, wherof research could be further continued.

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