# The effect of iron leaching on Arieş River ecosystem (Romania)

Andreea BODOCZI FLOREA

"Babes-Bolyai" University, Faculty of Biology and Geology, Experimental Biology Departament, 1 M. Kogalniceanu Street, 400084 Cluj-Napoca, Romania; Phone: +40 746228774; Fax: +40 264316494; E-mail: andy13\_florea@yahoo.com

Received: 19. April 2011 / Accepted: 05. October 2011 / Available online: 11. October 2011

**Abstract.** The effect of iron leaching was investigated on Arieş River ecosystem. Ten samples of water and ten of sediment from Arieş River were studied for their physicochemical, mineralogical and microbiological properties during the four seasons of the year 2008. The overall study showed high variations of the iron content in water samples more than the permissible limit recommended by Arieş Water Law No. 107/1996. A direct correlation between the inhibition of microbial development and the pollution degree of the sediment specific to each sampling point was observed. In its upper reaches, the river system is characterized by high contents of SO<sub>4</sub><sup>2</sup> as a direct result of acid mine effluents and the oxidation of sulphide minerals on mine dumps as well as inflows from settling ponds. Although continuous dilution by natural branch waters and natural water- rock interaction reduces the pollution to some extend, the total level of SO4<sup>2-</sup> remains above European averages. As compared to the values registered in unpolluted water, the Cu and Zn contents of River Arieş are 100 times higher than those admitted by law.

Keywords: iron bacteria, Arieş River, pollution, sediment, bacterial leaching.

## Introduction

Due to its high abundance within the earth's crust, iron is ubiquitous in all freshwater environments and often reaches significantly higher concentrations in water and sediments than other trace metals (Livingstone 1963). Mining of Fe enriched ores, intensified forestry, peat production, and agricultural draining have increased the load of iron in many river ecosystems (Dahl 1963, Brown 1977, Boult et al. 1994). More recently, intensified draining of peatlands, forests and arable lands, as well as dredging of iron enriched river sediments, has increased the leaching of iron in many river ecosystems (Ahtiainen 1992, Palko 1994, Vuori 1993).

The formation of some sedimentary iron deposits has been directly attributed to microbial activity (Ewers 1983, Widdel et al. 1993). In spite of its importance very little is known about the microbial ecology associated with the mobilization of iron in nature (Amils et al. 2002). There is increasing evidence that iron may play a crucial impact on the structure and function of a river ecosystem (Vuori 1995).

Iron enters into the vegetal tissues constitution under the form of organic compounds. Under the fermentative processes fulfilled by some microorganisms, the organic compounds are mineralized and oxidised to ferrous state, to  $Fe^{2+}$ , that can be reutilised by plants. In this way, it is fulfilled a complete iron cycle in the nature (Amils et al. 2002).

The oxidation of Fe(II) is accelerated by trace metals, phosphate, fluoride and particles, including autocatalysis by fresh Fe oxides. Microorganisms greatly enhance the Fe(II) oxidation in acid streams (Davison & DeVitre 1992). The role of the iron on the rhizosphere is important, due to the small existent quantity this element stays at the base of a competition between plants and microorganisms, and between different microbial species, competition that creates some strategies of rapid absorption, that implies local acidification, chelation and reductive processes (Robin et al. 2008). In aerobic conditions and neutral pH, the ferrous iron is rapidly oxidized in compounds that at the level of the sediments are transformed into pyrite (Rickard 1969). In most river waters, iron is predominantly transported in the particulate fraction (Burman 1983, Johnson & Thornton 1987, Davison & DeVitre 1992). The oxidized Fe particles in river water are removed by settling on the riverbed where they may be periodically resuspended, depending on their size and velocity of the current (Vuori 1995). In reducing sediment layers some of the Fe(III) oxy-hydroxides are reduced to Fe(II) (Vuori 1995). One part of this reduced Fe(II) diffuses upwards and is re-oxidized, while the other part is removed by the formation of authigenic minerals such as siderite, vivianite or iron sulphide (Davison & DeVitre 1992).

A high content of iron in the surface waters is indicative of pollution with industrial waste waters or with mining spills. Iron concentrations above 0.3mg/l change the organoleptic properties, prevent the use of these waters for technological purposes, and cause technical difficulties in using water for household needs by forming precipitates (Forray & Hallbauer 2000). Iron-hydroxide precipitates may drastically alter the physical characteristics of rivers receiving iron-rich runoff from acid sulphate soils disturbed by mining activities (McKnight et al. 1992, Boult et al. 1994).

When the water reaches a certain level of acidity, a naturally occurring type of bacteria called *Thiobacillus ferrooxidans* may kick in, accelerating the oxidation and acidification processes, leaching even more trace metals from the wastes (Xavier 1990). The environmental changes have a strong influence on the river dynamics, leading to river instability, and thus to changes in the erosion, transport and accumulation processes, in the sediments dynamic, heavy metal transport and geographical distribution throughout the river basin (Macklin 1996). Heavy metals accumulate in the sediments through complex physical and chemical adsorption mechanisms depending on the nature of the sediment matrix and the properties of the adsorbed compounds (Maher & Aislabie 1992, Ankley et al.1992, Leivouri 1998, Marin et al. 2010).

Previous researches have shown that problems with Fe load from mine field prevail decades after the abandonment of the mines (Boult et al. 1994, Gower et al. 1994). The hydrographic basin of Arieş River is situated in the north-

western part of Romania, in the middle of Apuseni Mountains. The Arieş River basin has an S form, a length of 131 km and an average width of 17.5 km (Ujvari, 1972). The study of Aries River quality is a major current issue, regarding human health, as well as the flora and fauna. Pollution sources of the Aries River are various, among them being the mining activity, the atmosphere pollution, house holding activity, as well as the anthropic influence. Another source of pollution is represented by waste dumps and settling ponds, which are usually placed near the Arieş River. Because of their position, the waste dumps are percolated by rainwater and the resulting water enters the phreatic and/or the surface water. During periods of heavy rain, the river level rises sufficiently to reach the base of waste dumps and thus, large amounts of barren gangue can also be transported into the river system contaminating the water. Further, the stability of the settling ponds can be affected, endangering the downstream areas (Forray & Hallbauer 2000).

The aim of our study was to realize a better understanding of the mechanisms by which the pollution of Arieş River affects the microbial population and activity in the river sediments. The present paper completes the enzymological research carried out on the same sediments (Bodoczi & Drăgan-Bularda 2008) and with a similar purpose Arieş.

### Materials and methods

Microbiological analyses were carried out on water and sediments sampled from the Arieş River over the year 2008. The water and sediment samples were taken from the upstream and downstream of five major sampling sites in the following order: Abrud, Baia de Arieş, Sălciua, Turda and Luncani (Fig. 1). Sampling points were established taking into consideration the river's characteristics, the influence exerted by its tributaries and the pollution sources. Water and sediment samples were taken seasonally, according with SR ISO 5667-6/97 and SR ISO 2852/94. Water samples were collected aseptically in 250 ml glass bottles. Sediment samples were taken from the riverbed at 50 cm from the bank following the removal of the first 5-10 cm of sediments. The water and sediment samples were placed in 4°C cooling boxes and immediately transported to the laboratory; no more than 9 hours elapsed between sampling and microbiological analysis.

The physico chemical analysis consisted in determination of some important parameters as: pH, sulphate  $(SO_4)^2$ , and the presence of trace metals (iron, copper, lead, zinc) in the water samples. Water samples were filtrated through a 0.45 µm filter. pH was determined in the field at the time of sample collection using a calibrated portable pH meter. Sulphate, iron and lead concentrations in water samples were analyzed spectrophotometrically using standard methods. Zn concentration was detected by colorimetric method according to STAS 8314-69 and the total copper using the iodometric method according to STAS 3224-69. In iodometric determination of copper, iodides are oxidized into iodine in the presence of copper (II) ions which are reduced to cuprous ions.

Mineralogical composition of the sediment samples was established microscopically with chromatic objectives 4x (red), 10x (yellow) and 40x (blue) and a 10x ocular thus obtaining a 40, a 100, respectively, a 400 times magnification.

Assessment of iron reducing bacteria was performed through MTM (multiple tubes method) according to STAS 3001-91 (Cuşa 1996, Drăgan-Bularda 2000) on Optov culture media. The most probable number of bacteria was calculated according to the statistical table of Alexander (1965). After incubation at 25°C under aerobic conditions for 14-21 days, in each test tube were added 2-3 drops of  $\alpha$ ,  $\alpha$  – dipiridil reagent.

There were considered positive those test tubes in which a pink colour appeared in 30 seconds, indicating the presence of  $Fe^{2+}$  resulted from  $Fe^{3+}$ .

The statistical correlation between bacteria implied in the iron cycle in Arieş River and some physico chemical parameters was established based on the application of two statistical tests: the ANOVA test of variances and the correlation coefficient test (r).



Figure 1. Map of Aries River showing the sampling points (Bodoczi 2009)

## **Results and Discussion**

The evaluation of water and sediment quality of Arieş River at the sampling sites was made based on the results of physicochemical, mineralogical and microbiological analyses with the goal of elaborating an original method for monitoring their quality. The presence or absence of an organism in an aquatic media is in close relationship with the biotic and abiotic factors of that environment (Zarnea 1994). On the other hand, the quality of freshwaters from source to outlet is increasingly affected by human activities, thus the conditions of existence for most of the aquatic organisms may be modified. Under these new conditions, an alteration of the initially established ecological relations between the community members can be observed, as compared to the situations encountered in other, similar, less affected ecosystems which we used as reference.

The concentrations of the measured chemical parameters from water samples are shown in Table 1. Heavy metals salts found in the water and in the sediments represent a very serious form of pollution for surface waters due to their toxicity and stability. They can induce disorders of the biological balance, with negative consequences over the various uses of water. Table 1 shows that the concentration values of heavy metals are lower in the upstream sampling points as compared with those registered in the downstream of the river. It can be affirmed that these elevated values are a consequence of the pollutants` accumulation as a result of mining activities.

Arieş catchments have the highest metal concentration from Apuseni Mountain. There are about 20 ore deposits, the most important ones being in exploitation at Roşia Montana and Roşia Poieni. Sediments are relatively more contaminated than surface waters in the Arieş River, particularly with Cu and Zn, whose concentrations increase downstream of the mining-affected tributaries, suggesting that the mines upstream act as a source of metals to channel sediments in Arieş River. Data collected from Arieş River have indicated that the degree of pollution is dependent upon the nature of mine waste, the hydrological link between mines and local rivers, and upon the local physicochemical environment (Forray& Halbauer 2000).

The sedimentary formations from Arieş River are diverse. In Abrud upstream they are represented by sandstones, laminated conglomerates and shales. Lithologically one can notice a predominance of conglomerates, macroconglomerates, sandstones, clays and limestones in flysch facies (Ianovici et al. 1976, Chira 2000).

Baia de Arieş has sedimentary formations represented by igneous bodies consisting of andesites, and by a predominance of quartz, kaolinite, mica, feldspar, gypsum and alunite. The magmatic products are accompanied by mineralized polymetallic Au, Ag and Cu which contribute significantly to the increase of the local and regional geochemical background, due to the large area of distribution and the alteration phenomena accompanying them (Ghergari et al. 1991).

At Sălciua sampling sites from lithological point of view the low terrace deposits are constituted of from clayey sands, sands with gravels and boulders and totally subordinated salty sands (Ianovici et al. 1976, Chira 2000).

Sampling points	Physicochemical parameters	Annual mean upstream	Annual mean downstream		
	pH	7.3	7.2		
	Sulphates (SO <sub>4</sub> ) mg/l	163.1	314.7		
Abrud upstream and down-	Iron mg/l	0.26	0.39		
stream	Copper mg/1	0.237	0.084		
	Lead mg/1	0.001	0.001		
	Zinc mg/1	0.643	0.835		
	pН	6.8	6.6		
	Iron mg/1	0.073	0.25		
Baia de Arieş upstream and	Sulphates (SO <sub>4</sub> ) mg/l	73.45	90.3		
downstream	Copper mg/1	0.008	0.018		
	Lead mg/1	-	0.001		
	Zinc mg/1	0.111	0.197		
	pH	8.2	7.8		
	Iron mg/1	36.4	0.23		
Sălciua upstream and down-	Sulphates (SO <sub>4</sub> ) mg/l	8.6	67.46		
stream	Copper mg/1	0.006	0.003		
	Lead mg/l	-	0.001		
	Zinc mg/1	-	0.043		
	pH	8	7.6		
	Iron mg/1	0.35	0.40		
Turda upstream and down-	Sulphates (SO4) mg/l	97.4	103.5		
stream	Copper mg/1	0.010	0.019		
	Lead mg/l	0.003	0.005		
	Zinc mg/l	0.042	0.055		
	pН	8.0	7.3		
	Iron mg/1	0.21	0.53		
Luncani upstream and	Sulphates (SO4) mg/l	103.05	132.45		
downstream	Copper mg/1	0.006	0.069		
	Lead mg/1	0.00	0.00		
	Zinc mg/l	0.043	0.086		

Table 1. The values of some physicochemical parameters registered in the Arieş River water over the year 2008.

The inferior basin of Arieş River (Turda and Luncani sections), as result of the selective erosion of the contact between the resistant formations of Mesozoic limestones and ophiolites and the Neogene sedimentary formations, was carved by the Arieş, whose valley was progressively enlarging. It consists of Sarmatian and quaternary sediments (sands, clays, gravels, volcanic tuffs) represented as terraces and meadows (Diaconu 1971, Popescu-Argeşel 1977, Ghergari et. al. 1991; Chira 2000). Due to their high content of highly soluble salts, they exert a strong influence on the chemistry of Arieş River in these sections.

The mineralogical composition of the studied sediment samples is presented in Table 2, and it can be observed that the diameters of mineral particles are mainly between 2  $\mu$ m and 0.4 mm. Also, it has been observed that in all sediment samples the quartz is predominant and it was detected in high percentage. Hornblende and iron oxide and hydroxide are also present in all analyzed samples. At Turda and Luncani sampling sites there have been detected traces of opaque minerals.

Iron-reducing bacteria lead to iron reduction in the presence of organic substances (glucose) and at low redox potential in the medium (Ailiesei et al. 1999). Iron has an important role in the metabolism of animal and plants, but in high quantities it may determine an unbalance in the function of an ecosystem and may affect the existing organisms.

The numerical evolution of iron reducing bacteria in Arieş River is represented in Fig. 2. In the analyzed water samples, iron-reducing bacteria had densities between 10<sup>2</sup> and 10<sup>4</sup> cells/ml water. It can be observed a high numerical fluctuation of these bacteria from one sampling point to another (Fig. 2A). A high number of these bacteria were registered in Abrud and Baia de Arieş downstream sampling sites. This fact could be explained by the pollution of Arieş River as a consequence of confluence with the effluents of Abrud and Valea Sesei both containing mining spills derived from the mining tailings from the area: SM Cuprimin SA Abrud, respectively, SM Roşia Poieni.

Roşia Poieni represents Romania's largest cupriferous ore deposit and the second in Europe, possessing over 1 billiard tones of ore with a concentration of 0.36% Cu and 1.8% S. Roşia Poieni holds 64.5% of the national reserve of copper. Waste waters resulted here have a red characteristic colour induced by the high concentration of ferric iron maintained in solution due to the acidity of these waters. Also, a high number of iron reducing bacteria was registered in Turda downstream in the summer.

According to the literature (Corches et al. 2007, Lucaciu et al. 2010) the idea of bacterial leaching from mining dumps was adopted, that has as result the development of Thiobacillus ferrooxidans bacterial strains, water pH reduction and the enrichment of waters in Cu and Fe and other heavy metals (Cd, Zn, Pb, Mn) which finally get in the Arieş River leading to water degradation with negative effects over the water catchment's systems and the fresh water supplies from downstream of the river. Simultaneously, the water degradation may entail the possibility of aquatic flora and fauna destruction in those areas. Comparing the results obtained with those found in literature (Amils et al. 2002, Forray & Hallbauer 2000), a strong correlation between the activities aimed at reducing iron and sulphur contents in ecosystems that are characterised through high concentrations of heavy metals (Fe. Cu, Zn, Cd), can be observed.

The numerical evolutions of iron-reducing bacteria in the sediment samples are represented in Fig. 2B. Also, a numerical fluctuation of the iron-reducing bacteria (IRB) has been observed according to the sampling period. The ironreducing bacteria were registered in lower densities in water samples than in the sediment ones (Fig. 2B), or they were even undetectable in some sampling sites, for example in Sălciua downstream in the winter. A progressive increase of

Sampling point	Principal mineral elements	Percentage (%)	Particles diameter	Predominant particle size
	Quartz	70%	2-80 μm	2-10 μm
A 1 J	Orto-pyroxenes	8%		
Abrud	Iron oxides and hydroxides	20%		
	Feldspar	2%		
	Quartz	58%	0.01-0.4 mm	0.05-0.1 mm
Baia de Arieș	Hornblende, peroxides	30%		
	Iron oxides and hydroxides	2%		
	Biotite	10%		
	Quartz	72%	0.01-0.3 mm	0.01-0.1 mm
	Hornblende, peroxides	23%		
Luncani	Iron oxides and hydroxides	3%		
	Biotite	2%		
	Feldspar and opaque mineral trace	1%		
	Quartz	65%	0.01-0.3 mm	0.05-0.1 mm
	Hornblende	30%		
Sălciua	Biotite	2%		
	Opaque minerals	1%		
	Trace of iron oxides and hydroxides and chlorite	2%		
	Quartz	87%	0.01-0.27 mm	0.08-0.2 mm
Turda	Hornblende, peroxides	9%		
Turda	Iron oxides and hydroxides	3%		
	Biotite and opaque minerals trace	1%		

Table 2. The mineralogical composition of Arieş River sediments.



Figure 2. Numerical evolution of iron-reducing bacteria in Arieş water (A) and sediment samples (B) over 2008.
(1 – Abrud upstream; 2 – Abrud downstream; 3 – Baia de Arieş upstream; 4 – Baia de Arieş downstream;
5 – Sălciua upstream; 6 – Sălciua downstream; 7 – Turda upstream; 8 – Turda downstream;
9 – Luncani upstream; 10 – Luncani downstream).

the number of bacteria can be observed from spring to summer, with maximum numerical density registered in the autumn in Baia de Arieş sampling points.

At the sediment levels the IRB registered different numerical densities according to the sampling seasons and sites. Best represented from the numerical point of view of iron-reducing bacteria was Baia de Arieş upstream, and the least represented was the Sălciua downstream sampling point.

The maximum value for the sediment samples was registered in autumn in Baia de Arieş upstream (24.292 bacteria/gram dry sediment- g.d.s.), and the minimum in Sălciua downstream (83 bacteria/g.d.s) in the winter. The numerical increases are correlated with the high quantities of iron and organic substances found in the water of the river in the upstream sampling sites.

According to the seasonal quantitative variation (%) of the iron-reducing bacteria it can be seen that the number of these bacteria increase progressively, from spring to summer in the water and in the sediment samples as well. These bacteria were more abundant in warm seasons with maximum numerical densities registered in the autumn. Comparing our results with those regarding Mureş River (Muntean et al. 2005) and Crişul Alb River (Filimon & Drăgan-Bularda 2004), it can be observed that in our study had been achieved

highest values especially at the level of the sediment samples. Nevertheless, the registered values from our study are very close to those recorded in the case of the sediments sampled from lakes (Curticăpean & Drăgan-Bularda 2005).

Based on the results obtained, we may state that the circumstances of bacterial leaching phenomena in the upstream of Arieş River basin, as result of anthropic factors of risk, require monitoring (according to Law No. 645/2002 and 85/2003) and implementation of some prevention and intervention measures over the danger of pathogenesis induced by the bacteria-substrate interactions, which represent the main cause of water acidification and dumps instability (according to Law No. 466/2001). Also, it is needed an evaluation of the impact on the environment and prevention of some ecological disasters, according to Law 195/2005.

Apuseni Mountains represent a rich area in ore reserves, particularly pyrite. Because of the chemical or biochemical alteration of pyrite and other minerals, it was observed that from these deposits and abandoned mines come highly acidic "mining waste waters" and intense mineralization which overflowed in Arieş River determine the massive pollution of the water.

Even though sulphur metabolism has a great importance in aquatic ecosystems, iron seems to be the key element in these habitats (Pârvu 1999). Iron is not only an important substrate for bacterial communities that induce the iron oxidation processes, but it may also function as electron acceptor in anaerobic respiration, in the anoxic parts of the river.

The obtained correlation results (Table 3 and 4) show that the high iron concentration in the water of Arieş River has a strong influence on the bacteria implied in the iron cycle in these habitats. Thus, a positive and significant correlation from statistically point of view has been registered between the number of IRB and the iron concentration in Baia de Arieş upstream sampling point. Also, the number of IRB is positively correlated with other physicochemical parameters as: temperature, pH, CCO-MN, ammonia concentration (p<0.05) in Abrud and Turda upstream sampling points (p<0.01) and with nitrites in Abrud and Luncani upstream

 Table 3. The coefficients of correlation between the number of IRB and some physicochemical parameters from Arieş River water over the year 2008.

 (1-Abrud upstream; 2-Abrud downstream; 3-Baia de Arieş upstream; 4-Baia de Arieş downstream;

 5-Sălciua upstream; 6-Sălciua downstream; 7-Turda upstream; 8-Turda downstream; 9-Luncani upstream; 10-Luncani downstream;

Samplir sites	ng T (°C)	) pH	Dissol <sup>.</sup> oxyg (mg/	$\begin{array}{c} \text{ved} \\ \text{en} \\ \text{O}_2/1 \\ \end{array} $	ng CCO-M (mg/l)	In Ammonia ) (mg N/l)	Nitrates (mg N/l)
1	0.8999	0.2564	-0.8504	-0.8475	0.2961	0.9699*	-0.2515
2	0.6368	0.7167	-0.5415	-0.2803	0.5469	0.7131	-0.2935
3	0.7578	0.7617	0.264	0.5243	-0.4373	-0.1049	0.3575
4	0.7744	0.4031	0.5821	0.7197	0.6754	0.5652	-0.8608
5	0.5881	0.8326	-0.3679	-0.3206	0.8428	0.8398	0.6767
6	0.7463	0.00692	-0.0302	0.6072	0.0255	0.9736*	0.7283
7	0.6803	0.4524	0.00097	0.0967	0.3862	0.9159	-0.3529
8	0.8722	0.4378	0.5848	0.2272	0.3556	-0.3069	-0.2433
9	0.02039	0.358	0.5185	-0.0127	-0.7581	-0.1634	-0.3241
10	0.7633	-0.434	0.3984	0.8917	0.7852	0.946	0.6415
_	Sampling	Nitrites	Total Fe	Sulphates	Cu (mg/l)	Pb (mg/l)	Zn

Sampling	Nitrites	Total Fe	Sulphates	Cu	Pb	Zn
sites	(mg N/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)
1	0.9806*	0.8756	-0.6992	0.3865	-0.928	0.8699
2	0.6414	0.5656	-0.0245	-0.5684	-0.6016	-0.2406
3	-0.3083	0.9901**	0.6329	0.0796		-0.8224
4	0.9182	-0.3688	0.2357	0.2295	-0.6421	0.5972
5	0.1619	0.0317	-0.4037	-	0.3373	
6	0.8124	-0.3674	-0.6228	-0.6097	-0.6097	-0.5053
7	-0.335	-0.694	0.9716*	0.8149	-0.7886	-0.7269
8	-0.7462	-0.4625	0.7074	-0.5088	-0.5521	-0.09749
9	0.9801*	-0.7558	0.8137	-0.0245	-0.7713	-0.3401
10	0.7008	-0.2369	0.5413	0.9378	-0.9018	0.05012

\*p<0.05; \*\*p<0.01

 Tabel 4.
 The coefficients of correlation between the number of IRB and some physicochemical parameters from Arieş River sediments over the year 2008.

 (1-Abrud upstream; 2-Abrud downstream; 3-Baia de Arieş upstream; 4-Baia de Arieş downstream;

 5-Sălciua upstream; 6-Sălciua downstream; 7-Turda upstream; 8-Turda downstream; 9-Luncani upstream; 10-Luncani downstream).

Samplin sites	g T°C	рН	Disso oxyg (mg	lved gen ;/1)	COD O2	) (mg /1)	CCO- (mg,	Mn /1)	Ammo (mg N	nia /1)	Nitrates (mg N/l)
1	0.6421	0.04353	-0.7439		-0.837	'5	0.3956		0.901		-0.6198
2	0.7378	0.7886	-0.4777		-0.136	1	0.6641		0.7758		-0.2401
3	0.722	0.739	0.2209		0.4911	L	-0.4858		-0.1145		0.3779
4	0.8454	0.4761	0.6758		0.8119	9	0.7611		0.6746		-0.7828
5	0.7035	0.8137	-0.3614		-0.463	3	0.8846		0.9132		0.6954
6	0.7728	0.7328	-0.4535		-0.544	.9	0.9376		0.9469		0.6167
7	0.7285	0.5147	0.07359		0.1688	3	0.4517		0.9423		-0.4159
8	0.6007	-0.2988	-0.6077		-0.316	5	-0.7864		-0.04635		-0.2396
9	-0.1835	0.02729	0.2048		-0.005	0	-0.5595		0.01366		-0.3828
10	0.6155	-0.3758	0.3271		0.7952	7	0.7908		0.9905**		0.7823
	Sampling	Nitrites	Total Fe	Sulpha	ites	Cu	1	P	5	Zr	
	sites	(mg N/l)	(mg/l)	(mg/	1)	(mg	/1)	(mg	/1)	(mg	/1)
	1	0.8115	0.5804	-0.6205	,	-0.0068	7	-0.7112	2	0.6289	
	2	0.7365	0.6757	0.119		0.6272		-0.6421	l	-0.0976	
	3	-0.3556	0.9825*	0.6385		0.1015		-		-0.793	
	4	0.948	-0.4096	0.3179		0.3217		-0.6602	2	0.7034	
	5	0.3138	-0.00582	-0.431		-		0.4596		-	
	6	0.3989	-0.1291	-0.3413		-		0.4587		-	
	7	-0.4027	-0.7392	0.9831*		0.7722		-0.7928	3	-0.7043	
	8	-0.164	-0.7983	0.5414		-0.4364		-0.261		0.0643	
	9	0.9174	-0.8916	0.8944		-0.0856	3	-0.5182	2	-0.5908	
	10	0.7286	-0.08677	0.4392		0.8783		-0.7949	)	-0.0459	2

\*p<0.05; \*\*p<0.01

sampling points (p<0.05). A direct correlation between the inhibition of microbial development and the pollution degree of the sediment specific to each sampling point was observed in the mountainous zone due to mining industry and on the inferior course due to urban wastes as in the case of other tested ecophysiological bacteria (Bodoczi & Carpa 2010). Negative correlations have been established in the case of the concentrations of dissolved oxygen, COD (mgO<sub>2</sub>/l) and nitrites.

### Conclusions

Iron-reducing bacteria have been present in each analyzed water and sediment sample, excepting those from Sălciua downstream sampling point where these bacteria have not been detected in winter. The registered bacterial densities show numerical fluctuations according to the sampling sites and the sampling seasons. Their numbers were by the order of hundreds in the water samples and by the order of thousands in the sediments.

The higher values registered in spring may be due to the increased temperature of water during this period and to the organic substance accumulation during the vegetation period. The maximum values were recorded in autumn due to the accumulation of organic substances by vegetal origin. The lowest values were registered in Sălciua upstream, in winter, for the water and sediment samples as well.

According to the horizontal numerical variation of the IRB it can be observed that the highest numerical densities were registered at the levels of the two tails of the river that may be explained through the correlation of these bacteria with the high concentrations of Fe ions in these areas. The high values of IRB on downstream of the river may be due to the accumulation of organic substances brought here by Racilor and Racosei effluents, both rich in waste waters resulted from households and industrial wastes. The number of IRB is positively correlated with some physicochemical parameters such as: temperature, pH of the water, CCO-Mn (mg/l), ammonia concentration (p<0.05) in Abrud and Turda upstream, and (p<0.01) and nitrites in Abrud and Luncani upstream sampling points (p<0.05). Negative correlation has been established with the dissolved oxygen content, the biochemical oxygen demand and the nitrites. A direct correlation between the inhibition of microbial development and the pollution degree of sediments specific to each sampling point was observed.

#### References

- Ahtiainen, M. (1992): The effects of forest clear-cutting and scarification on the water quality of small brooks. Hydrobiologia 243-244(1): 465-473.
- Ailiesei, O., Nimiţian, E., Jâpa, F., Dunca, S. (1999): Aspects of the microbiological iron cycle in the Bicaz Dam Lake. Scientific Annals of "Al. I. Cuza" University of Iaşi 44(II): 163-175.
- Ankley, G.T., Cook, P.M., Carlson, A.R., Call, D.J., Swenson, J.A., Corcoran, H.F., Hoke, R.A. (1992): Bioaccumulation of PCBs from sediments by oligochaetes and fishes: Comparison of laboratory and field studies. Canadian Journal of Fisheries and Aquatic Sciences 49(10): 2080-2085.
- Alexander, M. (1965): Most-probable-number method for microbial populations. pp. 1467-1472. In: Black, C.A., Evans, D.D., White, J.L., Ensminger, L.E., Clark,

- Amils, R., González-Toril, E., Fernández-Remolar, D., Gómez, F., Rodríguez, N., Durán, C. (2002): Interaction of the sulfur and iron cycles in the Tinto River ecosystem. Reviews in Environmental Science and Biotechnology 1(4): 299–309.
- Bodoczi, A. (2009): Anthropic influence impact on microbial population and enzymatic activity of the River Arieş water and sediments. PhD Thesis Babes-Bolyai University Cluj-Napoca, pp. 48.
- Bodoczi, A., Drăgan-Bularda, M. (2008): The enzymatic activity from the sediments of the Aries river from upstream to downstream. Studia Universitatis Babeş-Bolyai Cluj-Napoca 53(2): 129-138.
- Bodoczi, A., Carpa, R. (2010): The quantitative variation of some ecophysiological group of bacteria from Arieş River sediments affected by pollution. Carpathian Journal of Earth and Environmental Sciences 5(2): 145-152.
- Boult, S., Collins, D.N., White, K.N., Curtis, C.D. (1994): Metal transport in a stream polluted by acid mine drainage - The Afon Goch, Anglesey, UK. Environmental Pollution 84(3): 279-184.
- Brown, B.E. (1977): Effects of mine drainage on the River Hayle, Cornwall. A). Factors affecting concentrations of copper, zinc and iron in water, sediments and dominant invertebrate fauna. Hydrobiologia 52(2-3): 221-233.
- Burman, J.O. (1983): Element transports in suspended and dissolved phases in the Kalix River. In: Hallberg, R.O. (ed.), Environmental biogeochemistry: Proceedings of the 5th International Symposium on Environmental Biogeochemistry (ISEB) arranged in Stockholm 1-5 June, 1981. Ecological Bulletins 35: 99-113.
- Chira, C. (2000): Nannoplancton calcaros şi moluşte miocene din Transilvania, România. Editura Carpatica, Cluj-Napoca, p.183. [in Romanian]
- Corcheş, M., Borza, I., Corcheş, I., Iordache, M., (2007): Possibilities of ecological rehabilitation of the areas affected by copper exploitation activity from Roşia Poieni. Research Journal of Agricultural Science 39(2): 143-148.
- Curticăpean, M., Drăgan-Bularda, M. (2005): The quantitative distribution of some ecological groups of bacteria from the Tarniţa dam reservoir-Cluj county. Studia Universitatis Babeş-Bolyai, Biologia 50(2): 147-163.
- Cuşa, V., (1996): Instrucțiuni metodologice pentru analiza microbiologică a sedimentelor din ecosistemele acvatice. Institutul de Cercetări şi Ingineria Mediului, Bucureşti 4: 14-20. [in Romanian]
- Dahl, J. (1963): Transformations of iron and sulphur compounds in soil and its relation to Danish inland fisheries. Transaction of American Fisheries Society 92: 260-264.
- Davison, W., DeVitre, R. (1992): Iron particles in freshwater. pp. 315-355. In: Buffle, J., Leeuwen van, H.P. (eds.), Environmental particles Vol I., Environmental analytical and physical chemistry series, I ed.
- Diaconu, C. (1971): Râurile României. Monografie hidrologică. Serviciul de studii documentare şi publicații tehnice ale Institutului de Meteorologie şi Hidrologie, Bucureşti, pp. 124-127. [in Romanian]
- Drăgan-Bularda, M. (2000): Microbiologie generală, Lucrări practice. Cluj-Napoca. [in Romanian]
- Ewers, W.E. (1983): Chemical factors in the deposition and diagenesis of banded iron-formation. pp. 491-512. In: Trendall, A.F., Morris, R.C. (eds.), Iron-Formation: Facts and Problems. Elsevier Science Publishers B.V., Amsterdam, The Netherlands.
- Filimon, M.N, Drăgan-Bularda, M. (2004): The activity of iron reducing bacteria in the sediments of the Crişul Alb river. Proceeding of VI<sup>th</sup> International Sympozium "Young People and Multidisciplinary Research", 23-24 September 2004, Timişoara, Romania, p. 378-383.
- Forray, F.L., Hallbauer, D.K. (2000): A study of the pollution of the Aries River (Romania) using capillary electrophoresis as analytical technique. Environmental Geology 39(12): 1372-1884.
- Ghergari, L., Mészáros, N., Hosu, A., Filipescu, S., Chira, C. (1991): The gypsiferous formation at Cheia (Cluj County). Studia Universitatis "Babes-Bolyai", Geologia 36(1): 13-28.
- Gower, A.M., Myers, G., Kent, M., Foulkes, M.E. (1994): Relationships between macroinvertebrate communities and environmental variables in metalcontaminated streams in south-west England. Freshwater Biology 32(1): 199-221.
- Ianovici, V., Borcoş, M., Bleahu, M., Patrulius, D., Lupu, M., Dimitrescu, R., Savu, H. (1976): Geologia Munților Apuseni. Editura Academiei Republicii Socialiste România, Bucureşti, p. 631. [in Romanian]
- Johnson, C.A., 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.
- Leivouri, M. (1998): Heavy metal contamination in surface sediment in the Gulf of Finland and comparison with the Gulf of Bothnia. Chemosphere 36(1): 43– 59.
- Livingstone, D.A. (1963): Chemical composition of rivers and lakes. In: Fleischer, M. (ed.), Data of Geochemistry, 6<sup>th</sup> ed., U.S. Geological Survey Professional Paper 440-G. p.64.

- Lucaciu, A., Moţoc, C., Jelea, M., Jelea, S.G. (2010) Survey of heavy metal deposition in Romania: Transylvania plateau and western Carpathian Mountains. Scientific Bulletin University Politechnica of Bucharest, Series A 72(2):171-178.
- Macklin, M.G. (1996): Fluxes and storage of sediment-associated heavy metals in floodplain systems: assessment and river basin management issues at a time of rapid environmental change. pp. 441-460. In: Anderson, M.G., Walling, D.E., Bates, P.D. (eds.), Floodplain Processes. John Wiley & Sons Ltd., Chichester (UK).
- Maher, W.A., Aislabie, J. (1992): Polycyclic aromatic hydrocarbons in nearshore marine sediments of Australia. Science of the Total Environment 112(2-3): 143-164.
- Marin, C., Tudorache, A., Moldovan, O.A., Povară, I., Rajka, G. (2010): Assessing the contents of arsenic and of some heavy metals in surface flows and in the hyporheic zone of the Arieş stream catchment area, Romania. Carpathian Journal of Earth and Environmental Sciences 5(1): 13-24.
- McKnight, D.M., Bencala, K.E., Zellweger, G.W., Aiken, G.R., Feder, G.L., Thorn, K.A. (1992): Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. Environmental Science and Technology 26(7): 1388-1396.
- Muntean, V., Ştef, L.C., Drăgan-Bularda, M. (2005): Cercetări microbiologice asupra unor sedimente de pe cursul mijlociu al râului Mureş. Studia.Universitatis Babeş-Bolyai, Biologia 50(2): 175-181. [in Romanian]
- Palko, J. (1994): Acid sulphate soils and their agricultural and environmental problems in Finland. PhD Thesis. Acta Universitatis Ouluensis, Series C, Technica 75, University of Oulu, Finland. pp.58.
- Pârvu, C. (1999): Ecologie generală. Editura Tehnica, București, p.387-395. [in Romanian]
- Popescu-Argeșel, I. (1977): Munții Trascăului. Studiu geomorfologic. Editura Academiei Republicii Socialiste România, București, p. 147-153. [in Romanian]
- Rickard, D.T. (1969). The microbiological formation of iron sulphides. Stockholm Contributions to Geology 20: 49-66.
- Robin, A., Vansuyt, G., Hinsinger, P., Meyer, J.M., Briat, J.F., Lemanceau, P. (2008): Iron dynamics in the rhizosphere: consequences for plant health and nutrition. Advances in Agronomy 99: 183-225.

- Ujvary, I. (1972): Geografia apelor României. Editura Științifică, București. p. 171-183. [in Romanian]
- Vuori, K.M. (1993): Influence of water quality and feeding habits on the wholebody metal concentrations in lotic tricopteran larvae. Limnologica 23: 301-308.
- Vuori, K.M. (1995): Direct and indirect effects of iron on rivers ecosystems. Annals Zoology Fennici 32: 317-329.
- Widdel, F., Schnell, S., Heising, S., Ehrenreich, A., Assmus, B., Schink, B. (1993): Ferrous iron oxidation by anoxygenic phototrophic bacteria. Nature 362: 834-836.
- Xavier, A.G. (1990): Environmental-biochemical aspects of heavy metals in acid mine water. Mine Water and the Environment 9(1-4): 43-55.
- Zarnea, G. (1994). Tratat de microbiologie generală. Vol. V. Editura Academiei Române, București.
- \*\*\*Water Law No. 107/1996, amended and completed.
- \*\*\*SR ISO 5667-6/97. Calitatea apei. Prelevare. Partea 6: Ghidul pentru prelevarea probelor din râuri şi cursuri de apă. Fondul Național de Standarde. [in Romanian]
- \*\*\*SR ISO 2852/94. Apă potabilă. Prelevarea, conservarea, transportul, păstrarea și identificarea probelor.
- \*\*\*STAS 8314-69. Calitatea apei. Determinarea zincului.
- \*\*\*Mining Law No. 85/2003 amended by Law No. 237/2004 and updated by Law No. 284/2005.
- \*\*\*Law No. 645/2002 for the approval of Government Emergency Ordinance No. 34/2002 on prevention, reduction and integrated control of pollution.
- \*\*\*Law No. 466/2001 for the approval of Government Emergency Ordinance No. 244/2000 on the safety of dams.
- \*\*\*Law of the medium protection nr. 137/1995, republicated, with modifications (Government Emergency Ordinance No. 195/2005 regarding environmental protection, amended by Law No. 265/2006).