

Characterization of the rivers system in the mining and industrial area of Baia Mare, Romania

E. Cordos¹, R. Rautiu³, C.Roman², M. Ponta¹, T. Frentiu¹, A.Sarkany¹, L. Fodorpataki¹, K.Macalik¹, C. McCormick⁴, D. Weiss⁴

¹University "Babes Bolyai" Cluj-Napoca, Romania; ² Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania; ³ IC Consultants Ltd, Imperial College, London, UK; ⁴ Imperial College, Department of Environmental Science and Technology, London, UK

Received; accepted

ABSTRACT

The status of the river system in the mining region of Baia Mare is examined, following the long term mining activity in the area and the cyanide spill accident that occured in January 2000. The cyanide spill released more than 100,000 cubic meters of liquid and suspended waste that contained cyanide and heavy metals. Most of it, estimated at 50 to 100 tons of CN, reached the local river catchment. More than 50 km of river, upstream and downstream the cyanide spill inflow were sampled for water, sediments and aquatic ecosystem. The heavy metal content in water is within the limits of Romanian standards in most of the sampling sites. No cyanide was found in the water. The sediments have a high content of heavy metals and cyanides with minimum and maximum values in mg/kg as following, Cu: 104 - 339, Pb: 59 - 465, Zn: 56 - 2060, Cd: 0.05 -14.14. CN: 0.33 - 15.86. These values demonstrate the potential toxicity of the sediments. The cyanide spill affected all components of the aquatic ecosystem. Some of the microalgae species with narrow tolerance to changes in water quality disappeared on Somes river. A recovery is taking place but with a smaller number of species and with cosmopolite species. The number of fish species decreased dramatically as compared with the period before the accident. The new fish individuals that were collected in the affected area are young and come from the upstream section of the rivers. It was demonstrated experimentally that many species of mollusks disappeared downstream the cyanide spill inflow mainly because their capacity to accumulate large amount of heavy metals was exceeded.

Keywords: Cyanides; Heavy metals; Baia Mare accident; Water pollution

1. INTRODUCTION

Baia Mare region is the Romanian main centre for mining and metallurgy of copper, lead, zinc, gold and silver and, in the same time, one of the environmental "hot spot" of the country due to significant pollution with heavy metals. (Cordos *et al.*, 1995; Frentiu *et al.*, 2000). It is situated in the north-west of Romania, covering an area of about 900 kilometers square, with a population of about 250,000. There is a long history of mining in the region but the pollution became an important issue in the recent decades following the development of large industrial facilities in the last 50 years. The main polluting sources are a number of mines situated in the nearby mountain region, two smelters specialized on cooper and lead production, two large flotation plants and a number of decantation ponds, some of them active.

^{*}Corresponding author e-mail: cordos@mail.dntcj.ro

In 1999 a new plant for processing solid wastes from earlier mining activity to recover precious metals was added to the existing industries. Aurul S.A. (presently Transgold) was a stock company jointly owned by Esmeralda Ltd. Australia and REMIN Baia-Mare that use cyanide leaching and the carbon-in-pulp process (CIP) to extract gold and silver from older gold tailings in an existing dam. In January 2000 a breach occurred in the walls of the decantation dam of Aurul Company that released into surroundings about 100.000 cubic meters of tailing waters containing cyanide and heavy metals. The amount of released cyanide, calculated as CN, was evaluated at 50 to 100 tons. After a short way on the ground, about 2.5 km, the flow of the spill reached the river system. The cyanide and heavy metals plume that was formed initially on the Lapus river traveled further on Somes river, in Romania and after crossing the border to Hungary got into the Tisa and continued its way to Danube. The cyanide plume was diluted on its way, especially after entering Danube, and, in what could be considered an analytical feat, CN was identified, 4 weeks after the spill, at the mouth of the Danube.

Considering the surface flooded by the spill and the total volume of the waste water it could be estimate that most of the released cyanide and heavy metals got into the river system. It was the damage produced to the rivers that attracted attention of the mass media that transformed the cyanide spill in one of the most meditated environmental event. An UNEP/OCHA mission was appointed to fully investigate the accident. Following the report of the UNEP/OCHA mission an earlier European Commission project dealing with a cyanide spill in Kyrgyzstan (May 20, 1998), was extended to the Romanian accident. The extended project "Investigation of the Risk of Cyanide in Gold Leaching on Health and Environment in Central Asia and Central Europe", IRCYL, has, among other objectives, the task to estimate the extent of contamination and the effect on the ecosystem.

The aim of this paper is to present an evaluation of the status of the rivers system following the long-term mining activity and the cyanide spill accident in 2000. The study required the estimation of heavy metals and cyanide in water and river sediment and the investigation of phytoplankton, zooplankton, benthic fauna, ichthyofauna and mollusks based on existing data before the accident and data collected within IRCYL project. Copper, Cd, Pb and Zn have been selected to be determined in water and river sediment as they are the main products of the mining and nonferrous metallurgical industry in the area and are more likely to be found in the tailings and in the waste water in a significant amount. Sediments represent concentrated reservoirs for these metals that serve as sinks for the introduced trace metals or can become environmental sources (J. Sastre, et al., 2002: J.N. Beck, and J. Sneddon, 2000). However, unlike for water and aquatic ecosystem there are no data, previous of the cyanide spill, for the sediments in the considered area. The present study is the first one made on the sediments in Baia Mare area.

2. SAMPLING AND METHODOLOGY

Water, sediment and biological samples were collected upstream (20 km) and downstream (30 km) the Somes and Lapus rivers confluence (Fig1). In order to obtain an overall picture of the different phases the heavy metals are in, samples from dissolved, suspended and particulate phases were collected. This involved taking filtered and unfiltered samples of the water for the dissolved and suspended phases and collecting sediment samples for the deposited particulate phases.

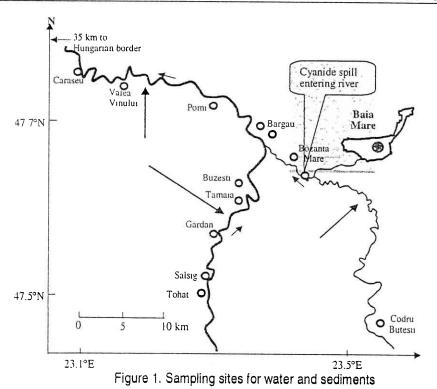
Sediments were collected from the surface of the river beds, in order to obtain samples from the same surface oxic layer and to ensure that all the sediment samples are under the same environmental conditions, avoiding sediments deeper down that have different redox conditions (oxygen depletes with depths and, as a result, the chemistry of the sediments change).

The number of and the sampling sites are presented in table 1.

The sampling site "Bozanta Mare" is located downstream from the dam. The station of Codru Butesii was selected as a control station because it is situated high up in the low population area of the mountains, free from any industrial or agricultural areas.

Table 1 Water and sediment samples

Area /site	Number of water samples for heavy metals determination	Number of water samples for anions determination	Number of sediment samples for heavy metals and cyanides determination	Observation
Somes / Tohat, Salsig, Gardan, Buzesti (upstream of the confluence with the Lapus river); Merisor, Bargau, Pomi, Valea Vinului, Caraseu (downstream the confluence with Lapus)	58	27	20	29 water samples for HM – filtered 29 water samples for HM – unfiltered (6 samples for each station)
Lapus / Bozanta Mare, Codru Butesii	16	6	4	8 water samples for HM – filtered 8 water samples for HM - unfiltered



Heavy metals.

Water. At each station, six water samples were collected in nitric acid (65%) clean 120 ml bottles. From the six samples three were filtered for dissolved metals by using a pre-washed 0.45 µm pore-diameter membrane filter and three were kept unfiltered.

Filtered sample After filtration, the filtrate was acidified to pH \leq 2 (with concentrated HNO₃ sample) and analyzed directly by ICP-AES.

Unfiltered sample were digested with HNO₃ and HCl. After cooling, the solution was filtered and analyzed by ICP-AES.

The measurements of the anions' concentration in water were carried out at the ROMANIAN WATERS Laboratory – Cluj-Napoca BRANCH EGA Maramures, according to the Romanian Standards 4706/88.

Sediments The samples were first dried at 105°C to constant weight. For the determination of heavy metals in sediment samples one has used an acidic digestion method with nitric acid and hydrogen peroxide, followed by the determination by AAS and/or ICP-AES.

Cyanide For the cyanide determination the samples were boiled with H₂SO₄ in a distillation flask. The HCN was collected by passing it through an alkaline trap. The cyanide content of the sample was then determined from the alkaline trap solution by a colorimetric method using pyridine-barbituric acid as reagent. A SFV-2 visible spectrophotometer (Centre for Analytical Instrumentation Co. -CAA, Cluj-Napoca, Romania), was used.

Phytoplankton To examine plankton populations, the river water samples were collected at midstream 0.5 m below the surface. As the water was well mixed vertically, subsurface sampling was considered adequate to get a representative sample. Different size categories of phytoplankton were separated by filtering through netting of the appropriate mesh size. For plankton a net with mesh openings of 80 µm was used. The containers were filled only partially in order to reduce inhibition of the metabolic activities of living plankton. The specimens were stored at ambient temperature and natural sunlight and were examined as soon as possible after collection (Greenberg et al., 1985, Fodorpataki et al., 2001)

Phytoplankton counting technique: As some phytoplankton was unicellular, while other was colonial, it was performed where possible, the count of individual cells as natural units using the standard Bürker's cytometer (counting error ±10% of the mean).

Determination of biomass (standing crop) of phytoplankton communities: Chlorophyll-a content determined using a spectrophotometric method was used as an algal biomass indicator. Assuming that chlorophyll-a constitutes on the average 1.5% of the dry weight of organic matter (ash-free weight) of algae, one can estimate the algal biomass by multiplying the chlorophyll-a content by a factor of 67 (Kelley, 1990, Fodorpataki and Papp, 2000).

Benthic fauna From each station 3 quantitative samples were collected from different types of substratum and water velocity, according to the heterogeneity of the habitats, using a bottom Surber sampler. The samples were preserved in 4% formaldehyde. The biological materials were sorted and the individuals belonging to the main groups of benthic macroinvertebrates were counted.

Ichthyofauna and Mollusks The fish capturing was made by electronarcotic method, using an electric generator set, and in some localities fishing nets had to be used. Mollusks were manually collected. The samples were refrigerated in the field. In laboratory, fish fillet and soft bodies (muscles and gills) of mollusks were separated, dried at 105° C to constant weight, ground and sieved. The 90 μm fractions were digested with a mixture of HNO3 65% and H_2O_2 30% using a high-pressure microwave system. In the resulting clear solutions the heavy metals were determined by ICP-AES.

Instrumentation. The AAS determinations were carried on a Perkin Elmer 3030B (Perkin Elmer, Uberlingen, Germany). For ICP-AES measurements a Spectroflame (Spectro Analytical Instruments, Kleeve, Germany) was used.

3. RESULTS AND DISCUSSIONS

3.1 Water

From the elements determined only the results for Cu, Pb, Zn, Cd are presented. These metals are the main products of the mining and nonferrous metallurgical industry of the area and are more likely to be found in the tailings and in the waste waters in a significant amount. They are the most suitable indicator of the pollution in the area, including that produced by the cyanide spill.

The summary of data for heavy metals and anions concentration in water are presented in table 2. The content of Cu, Pb, Zn, Cd in water, in the sampling points along the rivers is shown in Fig.2.

Table 2
Summary of data for heavy metals and anions concentration in water

MATERIAL PROPERTY OF THE PERSON AND PROPERTY OF THE PERSON AND PER	The second second							
	Cu	Pb	Zn	Cd	CN	Cl.	SO ₄ ²⁻	HCO ₃
Max. admissible concentrations (mg/l)*	0.05	0.05	0.03	0.003	0.01	250	200	-
Year 2001								-
Maximum concentration unfiltered sample (mg/l)	0.062	0.045	1.014	0.005	nd	106.8	96.4	199.1
Range unfiltered sample (mg/l)	0.005	0.015	1.009	0.004	•	99.4	58.2	57.3
Maximum concentration filtered sample (mg/l)	0.029	<0.03	0.882	0.004	•	¥		•
Range filtered sample (mg/l)	0.021	<0.03	0.877	0.001	•	(#		,
Year 1992**								
Maximum concentration (mg/l)	2.200	0.383	3.370	0.018	nd		: ₹2.	•
Range	2.182	0.366	3.324	0.017				

^{*}Romanian Standard 4706/88

As could be seen from Table 2 and Fig. 2, Cu and Cd exceeded the maximum admissible concentration (MAC) in few cases, while Zn exceeded in the majority of the collection sites.

For these elements there is also a maximum of concentration in the Bozanta Mare area. The source could be both the leakages from the close by decantation ponds and the river Sasar, an affluent of the Lapus river that crosses Baia Mare and is polluted with waste waters. Surprisingly enough, Pb was no detected or was present in concentrations less than MAC.

The cyanides concentration of the analyzed samples was below the detection limit of the used method.

An interesting case is that of the site taken as reference. Codru Butesii is a small village situated in the Lapus Gorges, far from the units with mining profile and close to its springs.

^{**}Hamar and Sárkány-Kiss, 1999

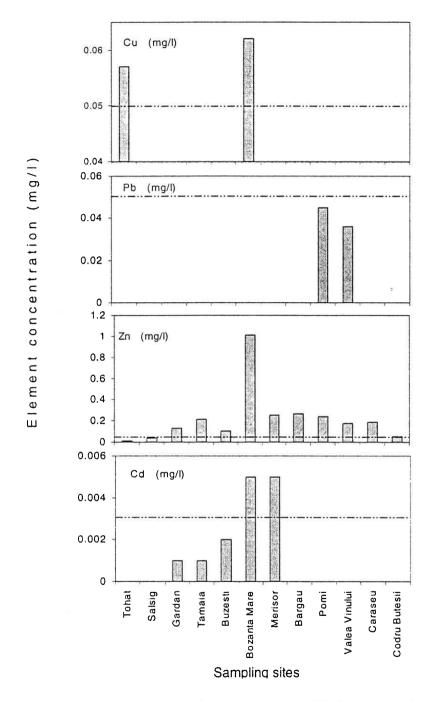


Figure 2. Element concentration in water; — -- Maximum admissible level

However, significant values of Fe and specially Zn concentration (higher than MAC) were recorded. It proves that the high Zn content of the Lapus river is due to the natural background. The chemistry of rivers is often greatly affected by the physical surroundings that characterize the water (Whiting & Olsen, 1997). The background geology dictates what minerals are present, but the physical layout and topography of the land can have an increased effect on the weathering and erosion rates of surrounding environment. This is the case of Codru Butesii station that is situated in a mountainous region that contributes to several small tributaries from the predominantly volcanic region into the Lapus and then into the Somes rivers.

Generally, the concentrations of the metals under study determined in the filtered water samples were lower (Table 2). This proves that the polluting elements are in a suspension form, being provided by the mining activity along the Lapus River. It should be pointed out that the determined concentrations characterize the water quality corresponding to the sampling date, because the pollution level is strongly influenced by the rivers' flow and the ambient temperature. Low discharge and a high temperature favor a high degree of pollution. So, it is important to recall that the samples were taken during summer period, which is the period of minimum velocity flow of the water. It is therefore expected that the majority of the suspended particulate matter, which is of major concern since it is the phase most associated with river transport of pollution (Abrameto et al 2000), (Szefer et al 1997), will be in the depositional side of the equilibrium between re-suspension and deposition.

The cyanide concentration of the analyzed samples was below the detection limit of the used method. The anions were within the normal limits with little variation along the sampled section of the rivers (Fig. 3).

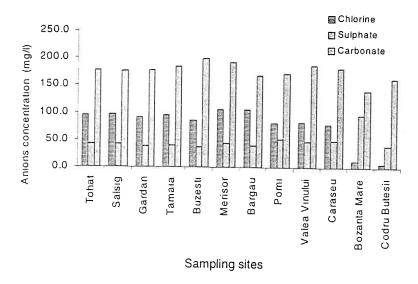


Figure 3. Anions concentration in water

Generally, the water quality does not present an alarming situation. There are zones of the rivers having critical values but they do not claim immediate measures. The water quality of the Lapus river is strongly influenced by the evacuation of the used waters insufficiently purified or unpurified, by the units processing non-ferrous ores.

The heavy metal content of the river water in the previous years is presented in the last rows of table 2 (Hamar and Sarkany Kiss, 1999). It could be seen that the actual situation is obviously improved, mainly because of the decreasing mining and industrial activity in the recent years. During 2001, accidents having an ecological impact have not been recorded in the area, and this also contributes to the fact that the water quality is in the range stipulated by the Romanian Standards.

3.2 Sediments

The content of heavy metals and cyanide in sediments are summarized in Table 3 and their distribution in sediments along the sampling sites is shown in Fig 4 and 5.

Table 3
Summary of data for heavy metals and cyanide concentration in sediments

	Cu	Pb	Zn	Cd	CN
Minimum concentration (mg/kg)	104	59	56	<0.05	0.33
Maximum concentration (mg/kg)	339	465	2060	14.14	15.86
Range (mg/kg)	235	406	2004	14.09	15.33

High values (in the order of hundreds of mg/kg) were recorded in every sampling site for Cu, Pb, Zn, and one order of magnitude for Cd. The highest values were recorded in the Bozanta Mare station. The cyanide presence in sediment could be explained by the cyanide spill, leakages of cyanide containing waters and tailings dust from decantation ponds situated next to the rivers. The excessive use of pesticides could be another source for cyanides in the sediments. The recorded values are dependent both on the natural background of the river and on the water quality (i.e. the pollution level). Also, the waters characteristics: flow, velocity and the turbulence determine the sediment quality and composition.

The possible toxic effect of the heavy metals present in the sediments is hard to evaluate since there are no Romanian Standards regarding the maximum admissible concentration for heavy metals or cyanides in sediment. The toxic potential could be estimated by assimilating the sediment with the soil and apply the Romanian standards (Romanian Ministry of the Forest, 1997) and/or by using the Canadian sediment quality guideline (Probable Effect Levels, PEL, Canadian Council of Ministers, 1999). For the elements from Fig. 4, the relation between the PEL limits and Romanian maximum admitted level for soil in residential and agricultural areas are given in table 4. As could be seen from the table 4, PELs for Cu and Pb are similar with Romanian intervention levels for soil and PELs for Zn and Cd with Romanian alert level for soil. In Fig. 4 and 5 the alert and intervention levels, according to the Romanian standards for soil are shown for all four elements. These limits are exceeded manifolds in most of the locations downstream Bozanta Mare that demonstrates the potential toxicity of the sediments.

Table 4.
Comparison between Canadian probable effect level and the accepted limits in soil, according to the Romanian standards

Element	Canadian probable	Romanian alert	Romanian intervention level		
	effect level (PEL)	level for soil			
	(mg/kg)	(mg/kg)	for soil, (mg/kg)		
Cu	197.0	100	200		
Pb	91.3	50	100		
Zn	315.0	300	600		
Cd	3.5	3	5		

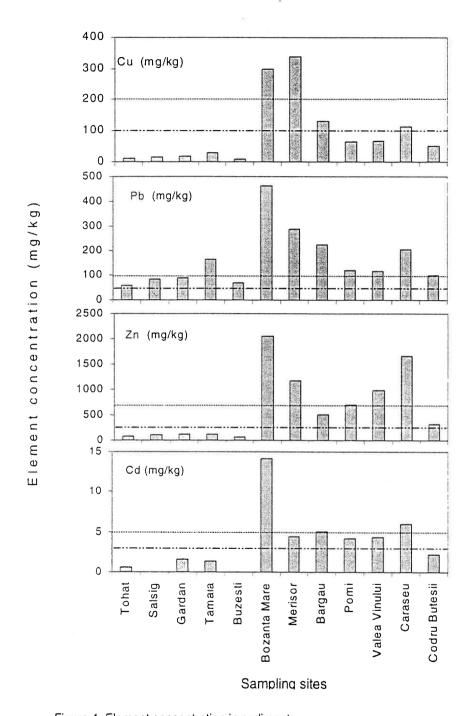


Figure 4. Element concentration in sediment.

— -- —Alert level for soil: - - - Intervention level for soil

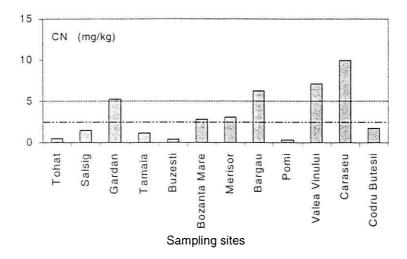


Figure 5. Cyanides concentration in sediment

— -- Alert level for soil: - - - Intervention level for soil

Analyzing the results for water and sediment in the Somes river, one ascertains higher values after the confluence with the Lapus river (it has "a great charge" of the polluting metals). The data from the Fig. 4 and 5 show a clear and distinct increase for all metals and cyanides corresponding to the stations after the dam but not in the expected ratio This may be due to the increased number of tributaries that flow into the Somes, and have a possible diluting effect for the sediment. The physical and chemical characteristics of these rivers that flow into the Somes further down may also aid chemical reactions that further reduce the concentrations of heavy metals and cyanides. This would be true if there was a dominant limestone area that increases the carbonate concentration of the area. The tributaries that flow into Somes and Lapus come from predominantly Igneous and Metamorphic regions, which are not expected to enhance buffering of the water. Also the rivers may, in some cases, increase the concentration by introducing different secondary sources of pollution, different from the dam. In this way one may explain the new increases in heavy metals and cyanides concentration downstream dam.

Data for sediments show a marked difference between Bozanta Mare on one side and the rest of the stations, on the other side

The pollution degree of the sediments is strongly influenced by the industrial activity and by the contribution of domestic waters into the Somes and Lapus rivers. Both natural and anthropogenic particles accumulate together, making it difficult to determine in the results which proportion of which, is present in the analyzed sediments. This is one of the problems and difficulties in monitoring sediments (Bakac, 1999). Unfortunately there are no background data available on heavy metal concentration in sediment for Romania.

3.3 Aquatic ecosystem

Phytoplankton Algal investigations on phytoplankton shown that in the period immediately after the cyanide spill accident in January 2000, the diversity of green microalgae decreased significantly in Somes river downstream of the Lapus inflow, leading to the disappearance of species with narrow tolerance, very sensitive to the abruptly change of water quality (Fig. 6) (UNEP/OCHA, 2000).

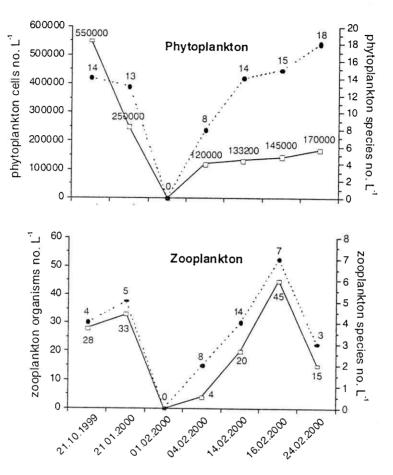


Figure 6. Evolution of phytoplankton (solid line: cells no.; dotted line: species no.) and zooplankton in Somes river downstream of the Lapus inflow (solid line: organisms number.; dotted line: species number.)

Species with larger tolerance persisted and, after a relatively short decline of population density, resistant ecotypes have been naturally selected and multiplied (Kullberg, 1995, Ray and Gaur, 2001). Thus, algae population recovered in spring 2000 although it suffered modification with regard to the number of species building the phytoplankton. Zone of Lapus River next to Bozanta Mare and that of Somes in line with Pomi site has been repopulated especially with cosmopolite species, like *Pediastrum boryanum*, *Scenedesmus intermedius*, *Scenedesmus quadricauda*, *Cyclotella meneghiniana*, *Pinnularia subcapitata*, *Synedra vauchariae*, *Ankistrodesmus gracile*.

Further studies revealed a continuous increase of biomass production of planktonic algae (standing crop) during the year 2001 (Fig. 7).

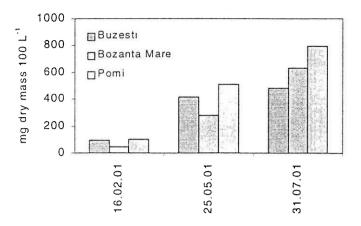


Figure 7. Biomass production of planktonik algae and cyanobacteria in water samples upstream (Buzesti) and downstream (Pomi) the confluence of Lapus with Somes (Bozanta Mare) after the cyanide spill accident

Benthic fauna In the benthic fauna collected in February 2000 from each sampling site (Fig. 1) prevailed Chironomida, followed by Oligochaeta. Other species like Ephemeroptera, Plecoptera, Trichoptera were poorly represented (Table 5). At the time, no benthic macroinvertebrate was identified, but traces of adults and crumbling larvae. Generally, the abundance of benthic species was significantly higher in Somes river upstream of the Lapus inflow than downstream, which meant that the rebuild of the affected fauna occurred slowly and partially. No benthic fauna was identified in Lapus near Bozanta Mare.

Table 5
Distribution of the systematic groups of benthic fauna and population density

Sampling site	Lapus	Tohat	Salsig	Gardani	Tamaia	Buzesti	Merisor	Bargau	Pomi	Valea Vinului	Caraseu
Systematic group	Individuals m ⁻²										
Oligochaeta	0	400	90	770	200	520	1170	70	10	140	0
Ephemeroptera	0	150	10	0	0	10	0	10	0	0	0
Plecoptera	0	70	0	0	0	10	0	0	0	0	0
Trichoptera	0	100	10	0	0	30	0	0	10	20	0
Chironomida	0	6110	1160	2340	260	740	290	230	370	1240	360
Others	0	90	70	80	60	0	60	10	0	0	80

Fish In August 2000 the fish population was investigated at 3 sampling sites: Tohat upstream Lapus, on the Lapus river at Bozinta Mare and in the Somes quite below the confluence with Lapus. A total of 675 individuals belonging to 14 species were collected compared to 62 species reported for the previous years in similar conditions (Banarescu et al., 1999). The number of species and individuals decreased obviously in the Somes river downstream Lapus. Thus, 443 individuals were collected at Tohat, belonging to 12 species, of which the most common were

Leuciscus cephalus, Barbus barbus, Rhodeus sericeus. In the Lapus river, in the vicinity of the pollution source, the 94 collected individuals belonged to only 6 species, while the 138 fishes collected in Somes downstream the confluence with Lapus represented only 11 species. It is obvious that the chemical pollution causes the disappearance of the most sensitive fish species and leads to a decreased number of individuals in the remaining populations. It could be also mentioned that the collected fishes were in majority young individuals, aged of 1-2 years.

As organisms with considerable mobility, fish collected from different sites presented a relatively uniform distribution of heavy metals and the determinations were considered to be not conclusive. The low content of metals in fish coming from the contaminated zone of Lapus river compared to that in plants and sediments have suggested that after the disappearance of intiofauna following the cyanide spill, the river repopulated naturally itself with fish coming from upstream the confluence.

Mollusks Unionidae mollusks are known as high rate accumulators of heavy metals, especially in gills. Their low mobility recommends them to monitor polluted water with such xenobiotics. An experiment was carried out with Unio crassus species, which is present in Somes river upstream of the Lapus river inflow, but misses downstream. In order to demonstrate that this species disappeared from the inferior course of Somes river due to heavy metals pollution (Sárkány-Kiss et al., 1999, Sárkány-Kiss, and Macalik, 1999), in October 2001 a number of 60 individuals were collected in an unpolluted zone of Somes. A number of 15 were considered as control group, and the rest were relocated to be exposed in a polluted zone. The determination of heavy metals in gills of the relocated mollusks revealed an accelerated accumulation of heavy metals, especially Cu, Mn and Pb, in the first 7 and 21 days, respectively, when the water temperature was around 8° C.

Thus, as compared to 14 (Cu); 1 (Pb) and 194 (Mn) $\mu g \, g^{-1}$ dry mass in the control group mollusk gills, the accumulation rates were 18.5; 19 and 94 after the first 7 days and 12.2; 27 and 74 after 14 days from translocation, respectively. Than, for the next 147 days, as the temperature of the water decreased towards 0°C, mollusks entered to hibernation and, consequently to catabolism, the accumulation rates decreased to 5.5; 13 and 42 for Cu, Pb and Mn (Fig. 8). It seems that the high capacity of freshwater mollusks to accumulate large amount of heavy metals was exceeded, as they have disappeared downstream the confluence with Lapus river.

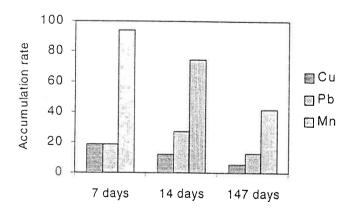


Figure 8. Accumulation rates of Cu, Pb and Mn in gills of molluscs translocated in polluted compared to control molluscs

4. CONCLUSIONS

The water quality of the river in the investigated area is within the range of Romanian standards. Critical values were found in a few sites but they do not require immediate measures. The polluting elements are in suspension forms and it proves that they are provided by the mining exploitation, especially the decantation ponds that are located next to the rivers. No cyanide was determined in the water.

The sediment situation is quite different. High values of heavy metals content, part of them as complex cyanides were recorded. The values are exceeding manifolds the critical limits for soil or Canadian PELs that demonstrates the potential toxicity of the sediments. The increased content of cyanides, downstream from Bozanta Mare could be partially attributed to the cyanide spill.

The aquatic ecosystem was affected by the cyanide spill. Some of the microalgae species with narrow tolerance to changes in water quality disappeared on Somes river, downstream the Lapus river inflow. The recovery started a few weeks after the accident but for a smaller number of species. Some of the river segments were repopulated with cosmopolite species. In the river segment affected by the spill only two species from the benthic fauna persisted, in a smaller number as compared with the upper part of the river. Less than a quarter of the species reported before the accident could be identified in the summer of 2000. The fish collected were only young individuals that could come from upstream of the confluence. An experiment involving mollusks from genre unionide demonstrates that these species dissappeared downstream the confluence with Lapus river since their capacity to accumulate large amount of heavy metals was exceeded.

REFERENCES

Abrameto, M., Gil, M.I., Freiji, R.H. and Marcovecchio, J., Fe, Mn, Ni and Cd geochemical partitioning in sediments from the Negro River, Argentina. International Conference on Heavy Metals in Environment 2000, Michigan.

Bakac, M., Factor Analysis applied to a Geochemical study of Suspended Sediments from the Gediz River. Western Turkey, 2000, **22(2)**, 93-111.

Bănărescu, M. P., Telcean, I., Nalbant, T., Harka, Á. and Ciobanu, M., The fish fauna of the River Someş/Szamos Basin, In: Sárkány-Kiss, A. and Hamar, J. (eds.): The Someş/Szamos River Valley, Tiscia Monograph Series, 1999, Szolnok/Szeged/Tg.Mureş, 249-268.

Beck J.N. and Sneddon J., Use of atomic absorption spectrometry for the determination of metals in sediments in south-west Louisiana, Microchem. J., 2000, 66, 73.

Canadian Council of Ministers of the Environmental, 1999.

Cordos E.A., Frentiu T, Rusu A.M. and Vatca Gh., Elemental Speciation of Pb, Zn and Cu in Sedimented Dust and Soil Using a Capacitively Coupled Atomic Emission Spectrometer as Detector. The Analyst, 1995, 20, 725.

Fodorpataki, L., Márton, A. L. and Csorba, T. L., Stress-physiological investigation of algal cell cultures in polluted media, Contrib. Bot., 2001, 36, 101-108.

Fodorpataki, L. and Papp, J., Studies concerning the physiology of microalgal communities isolated from natural habitats, Contrib. Bot., 2000, **35**, 121-130.

Frentiu T., Ponta M.,.Anghel S.D., Simon A, Cordos E.A., Cadmium determination in sedimented dust by atomic emission spectrometry with a new radiofrequency capacitively coupled plasma source. Analyt. Letters, 2000, **33 (2)**, 323 – 335.

·Greenberg, A.E., Rhodes-Trussell, R. and Clesceri, L.S., Standard Methods for the Examination of Water and Wastewater, 1985, Port City Press, Baltimore.

Hamar, J. and A. Sárkány-Kiss,. The upper Tisa valley. Preparatory proposal for Ramsar site designation and an ecological background. Hungarian, Romanian, Slovakian and Ukrainan cooperation. TISCIA monograph series. Tisza Klub and Liga Pro Europa, 1999, Szeged.

Kelley, J.G., Photosynthetic Ph Advise In Fresh Water Aquatic Plants, Trends and Cole Evol, 1990, 5 (10), 330-333

Romanian Ministry of the Forest, Waters and Environment, Order No. 756/1997, Monitorul Oficial, 1997, No 303 bis/06.11.1997.

Kullberg, R.G., Decreased diversity caused by differential inhibition among artificial phytoplankton communities in an undisturbed environment, Eur. J. Phycol., 1995, **30**, 267-272.

Ray L.C.and Gaur J.P., Algal adaptation to environmental stresses, 2001, SpringerVerlag, Heidelberg, 363-388.

Sárkány-Kiss, A. and Macalik, K., Bioaccumulation of certain toxic metals by fish and unionidae shells in River Someş/Szamos, In: Sárkány-Kiss, A. and Hamar, J. (eds.):The Someş/Szamos River Valley, Tiscia Monograph Series, 1999, Szolnok/Szeged/Tg.Mureş, 269-373.

Sárkány-Kiss, Sîrbu, I. and Bába, Α.. K., Freshwater mollusc species from the RiverSomes/Szamos related to their ecological conditions, In: Sárkány-Kiss, A. and Hamar, J. Somes/Szamos River Valley. Monograph Tiscia Series. 1999. Szolnok/Szeged/Tg.Mureş, 197-202.

Sastre J., Sahuquillo A., Vidal M., Rauret G., Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted digestion versus aqua regia and nitric acid extraction. Anal. Chim. Acta, 2002, 462, 59,

Szefer, P., Kusak, A. and Szefer, K., Evaluation of anthropogenic influx of metallic pollutants into Puck Bay, Southern Baltic. Applied Geochemistry, 1995, **13**, 293-304.

UNEP / OCHA, Report of the UNEP / OCHA Assessment Mission on the "Cyanide spill at Baia Mare Romania", 23 February - 6 March 2000. Geneva, March 2000.

Whiting, K.S. and Olsen, R.L., Identification of sources of metals in stream sediments using Electron Microprobe techniques. Tailings and Mine waste 1997 Conference, pp. 519-528, Balkema publishing.