HEAVY METAL DINAMIC SURVEY IN THE WATER OF CRIŞUL NEGRU RIVER NW ROMANIA

Fodor Alexandrina*, Petrehele Anda Ioana Graţiela, Stănăşel Oana Delia, Cărăban Alina Maria, Bereczki Eniko, Calapod Adriana Melania, Blidar Cristian Felix, Vancea-Petruş Adriana

**University of Oradea, Faculty of Environmental Protection, 26 Gen. Magheru St., 410048 Oradea, Romania, e-mail: afodor@uoradea.ro*

Abstract

The aim of the study is the survey of several heavy metals accumulation in the aquatic environment on along the Crişul Negru River course. The necessity of this study appeared due to the long tradition in mining activities in the area that could be a source of ecosystems contamination with heavy metals. The survey was undertaken during August 2008-July 2009 period. A total number of 140 water samples were taken. The analysed heavy metals were: the copper, cadmium, nickel, cobalt and zinc. These heavy metals were determinate using atomic absorption spectroscopy method. During the surveyed period it has been noticed a significant decrease in their concentrations among the sites, with the higher ones registered in the headwaters of the river, just in the vicinity of the mining area. The registered heavy metals concentrations were fluctuating as values in according to the season and the precipitations quantities. The heavy metals concentrations from the samples were also compare to samples taken in the same period from a control area considered not affected by mining pollution (Bulz on Crişul Repede River which flow in N-W Romania in the same County as Crişul Negru) revealing higher values. As a general classification of the water that flow through this sites due to Law no. 161/2006 reveal: third water quality class from the point of view of cadmium and cobalt. From the point of view of nickel, it can be noticed an increase of water quality from the first sampling site (third water quality class) on a downstream direction (for the rest of sampling sites, second class of water quality). From the point of view of copper and zinc, the river is still first class water quality.

Key words: heavy metals, atomic absorption, water

INTRODUCTION

Water pollution is affecting the phytoplankton and macrophytes in different ways, according to the nature of the contaminant. For example the chromates and copper salts are toxic to algae. Fish and plankton can die from all types of pollution but most fatal one is caused by lack of oxygen dissolved in water and toxic waste. Serious problems also raise the pollution of water with heavy metals, especially mercury, which reach a large degree in accumulation. The whole ecological consequences resulting from biosphere pollution with heavy metals is a warning sign to end the irresponsible behaviour of industrial activities on water quality. Heavy metals are elements with atomic mass between 63.546 and 200 m.a.u. Living organism require very small amounts (trace) of heavy metals (Co, Cu, Fe, Mn, Mo, Sr, Zn) whish are called essential heavy metals. The remaining heavy metals found in water are toxic for living animal and vegetal tissues, those called non-essential metals (for example: Cd, Cr, Hg, As) [1]. It is very important to investigate the pollution with heavy metals in the water samples because the essential and minor metals, when do occur in higher quantities than certain threshold values, do provide deteterious effects over the aquatic and vegetal species, such as: histological, morphological and ethological modifications, the decrease of growth rates, the necrosis of respiratory system, finally leading to potential lethal effects [2].

In the last years, several studies have focused over the accumulation rates of heavy metals in the soil, as a historical exposure mainly to the mining activities in the western and north-western areas of Romania [3-6], the same as for the surface waters and fish tissues [7-9]. Nevertheless, these studies lacked the additional habitats that do lie along the rivers, like the wetlands, back waters, oxbow lakes, or from the terrestrial habitats, like meadows, heath lands, riparian forests etc. The surface runoff, by washing the soil, does carry a significant volume of heavy metals in the catchments situated immediately downstream the affected area with unknown final effects over the aquatic ecosystems [8,10].

This study aims the survey of heavy metals dynamic in the water of the Crişul Negru River, Romania. The topic is a very important one, considering the fact that the Băi□a area is heavily impacted (although to an unknown extent) by the mining activities. The importance of this study is even bigger if one considers the trans boundary effects and the relevance for the neighbouring country, the Hungary, in what concerns the water quality in the locality of Ant (site 4), situated at the frontier (Figure 1).

Fig. 1. Map of the Crişul Negru River, Bihor County, Romania [8]

Monitoring was performed during the period: August 2008 - July 2009. Heavy metals that are the subject of this study are: Cu, Cd, Ni, Co, Zn.

MATERIAL AND METHOD

Sampling Procedures

The samples were taken from five sites, four of them along an upstream-downstream transect along the Crişul Negru River, and another one in the locality of Bulz, on a neighbouring river, Crişul Repede, chosen as a control, reference site. The GPS coordinates of sampling sites are provided below in table 1.

Table 1

GPS Coordinates of sampling sites

	Crişul Negru River				Crişul Repede *control*
	Staţia 1 Baita Plai	Staţia 2 Fanate	Staţia 3 Borz	Staţia 4 Ant	Staţia 5 Bulz
Latitudine	46°28'55" N	46°30'16" N	46°40'22" N	46°39'45" N	46°56'49" N
Longitudine	22°36'12" E	22°32'16" E	22°11'32" E	21°28'8" E	22°40'28" E
Altitudine (m)	483.7	355.6	210.7	98.5	366.8

Sampling Schedule

The sampling frequency comprised three campaigns of two days/each month. In December and August 2008 were organised only two sampling campaigns, due logistical issues. The sampling comprised 140 surface water samples.

Collecting water samples

The water sampling procedures followed the SR ISO 5667 – 6 standard (Guide for sampling the rivers), throughout the submergence of a vial in the river and then transferring the content in a plastic tube of 1 l capacity. The transport, preservation and storage were done according to the SR ISO 5667-3 standard; therefore, the water samples were fixed by acidulation and transferred in freezers.

Heavy metal analysis

The investigated metals were analysed by using the atomically absorption spectrophotometer, following the SR ISO 11047 standard, in the laboratory of the Environment Protection Agency, Bihor County. The spectrophotometer was of Varian 220 type. Before starting the analysis, the machine was standardised and the standard curves established. The buffer solutions comprised certificated materials routinely used for this kind of procedures. The obtained values were compared with the thresholds presented in table 2.

RESULTS AND DISSCUSIONS

The obtained results were compared to the admitted limits for the heavy metal concentration stipulated by law 161/2006 (table 2) and then the water from Crişul Negru River were classified in the surface water ecological class.

Table 2.

The upper admitted thresholds for heavy metals concentration according to the law 161/2006 concerning the classification of surface waters quality in ecological classes.

Nr. Crt	Metal	Measure units	Quality class Due to Law no. 161/2006 Regarding the surface water quality classification for the ecologic state evaluation					Standard analytical method
			I	II	III	IV	V	
1.	(Cu^{2+})	μg/l	0.02	0.03	0.05	0.1	>0.1	SR ISO 8288:2001
2.	(Cd^{2+})	mg/l	0.5	1	2	5	>5	SR ISO 8288:2002
3.	(Ni^{2+})	mg/l	0.01	0.02	0.05	0.1	>0.1	SR ISO 8288:2001
4.	(Co^{2+})	mg/l	0.01	0.02	0.05	0.1	>0.1	SR ISO 8288:2001
5.	(Zn^{2+})	mg/l	0.1	0.2	0,50	1,0	>1,0	SR ISO 8288:2001

Statistical analyses were performed using Excel for Windows. The estimated parameters were: **T** (scattering comparison) and **F** (averages comparison) to compare the heavy metals concentrations measured from the samples taken in the studied areas with those from the reference one.

The **T** criterion calculus formula is:

$$T = \frac{|\overline{X}_1 - \overline{X}_2|}{\sqrt{\frac{S_1^2}{n_1} + \frac{S_2^2}{n_2}}}$$

The **F** criterion calculus formula is: $\mathbf{F} = S_1^2 / S_2^2$ for $k_1 = k_2 = n - 1 = 9$, liberty degrees (n is the number of experimental determinations) and the probability P = 95 %.

The data obtained in the statistic interpretation show in the tables 3 and 4.

Table 3.

Metal content in samples of water taken from the studied and reference sites in August-December 2008 period

		T TEST	AVERAGE	Difference %	Min	Max	Std deviation
Cu mg/l	Băița	1,9241E-10	0,0156	79,99999	0,012	0,019	0,002028
	F□națe	0,116125064	0,022733	162,3077	0,011	0,14	0,032486
	Borz	8,1305E-07	0,012867	48,46154	0,01	0,015	0,001767
	Ant	0,001726957	0,011467	32,30769	0,008	0,016	0,002475
	Bulz		0,008667		0,006	0,012	0,001877
Cd mg/l	Băița	5,8032E-10	0,003067	359,9998	0,002	0,004	0,000704
	F□națe	1,07071E-07	0,002333	249,9998	0,002	0,003	0,000488
	Borz	5,59813E-05	0,0018	169,9999	0,001	0,003	0,000561
	Ant	0,003381804	0,001467	119,9999	0,001	0,003	0,00064
	Bulz		0,000667		0	0,002	0,000724
Ni mg/l	Băița	5,63882E-09	0,033267	556,5789	0,02	0,056	0,009098
	F□națe	7,63666E-07	0,026467	422,3684	0,014	0,051	0,010035
	Borz	5,43632E-05	0,022133	336,8421	0,012	0,05	0,011643
	Ant	8,79519E-07	0,0122	140,7895	0,005	0,016	0,00357
	Bulz		0,005067		0,002	0,009	0,001668
Co mg/l	Băița	0,891547422	0,030533	-5,95483	0,012	0,064	0,013721
	F□națe	0,974310702	0,018103	-44,2416	0,006	0,09	0,018103
	Borz	0,589602155	0,0402	23,8193	0,017	0,064	0,015176
	Ant	0,745390536	0,037133	14,37371	0,015	0,078	0,016252
	Bulz		0,032467		0,005	0,2	0,052275
Zn mg/l	Băița	0,013063969	0,022333	520,3704	0,011	0,111	0,025221
	F□națe	0,00756905	0,021133	487,037	0,004	0,066	0,021467
	Borz	0,058844248	0,0122	238,8889	0	0,06	0,015447
	Ant	0,042100385	0,0098	172,2222	0,003	0,04	0,009526
	Bulz		0,0036		0	0,02	0,005816

Table 4.

Metal content in samples of water taken from the studied and reference sites in 2008 March-July period

Metal	Studied Area	T Test	Avarage	Difference %	Min	Max	Standard Deviation
Cu mg/l	Băița	1,95276E-05	0,014286	227,8688	0,005	0,02	0,004827
	F□nate	0,000864844	0,012214	180,3279	0,003	0,02	0,00578
	Borz	0,46853608	0,006143	40,9836	0	0,015	0,007399
	Ant	0,504138319	0,006	37,70491	0	0,017	0,00739
	Bulz		0,004357		0	0,011	0,005242
Cd mg/l	Băița	0,848843709	0,002143	-9,09092	0	0,007	0,002349
	F□nate	0,722976939	0,001929	-18,1818	0	0,008	0,002868
	Borz	0,957227635	0,002429	3,030279	0	0,009	0,003546
	Ant	0,909767966	0,002214	-6,0606	0	0,008	0,003167
	Bulz		0,002357		0	0,009	0,003433
Ni mg/l	Băița	0,000656412	0,0235	376,8116	0	0,056	0,015639
	F□nate	0,055082652	0,024714	401,4493	0	0,096	0,034969
	Borz	0,002449701	0,022286	352,1739	0	0,05	0,017251
	Ant	0,6851563	0,005857	18,84059	0	0,018	0,007273
	Bulz		0,004929		0	0,012	0,004305
Co mg/l	Băița	0,277427432	0,012929	-50,6812	0	0,037	0,011932
	F□nate	0,985956478	0,0265	1,089917	0	0,111	0,042603
	Borz	0,268397509	0,045357	73,02452	0	0,108	0,046966
	Ant	0,379972171	0,040643	55,04087	0	0,103	0,043015
	Bulz		0,026214		0	0,106	0,042467
Zn mg/l	Băița	7,68358E-07	0,015264		0,011	0,0302	0,006484
	F□nate	0,003890457	0,020986		0,004	0,066	0,022414
	Borz		0		0	0	0
	Ant		0		0	0	0
	Bulz		0		0	0	0

The difference between the heavy metal concentration in the samples taken from the studied sites and the reference site are showed in the figure 2 and 3 as percentage values.

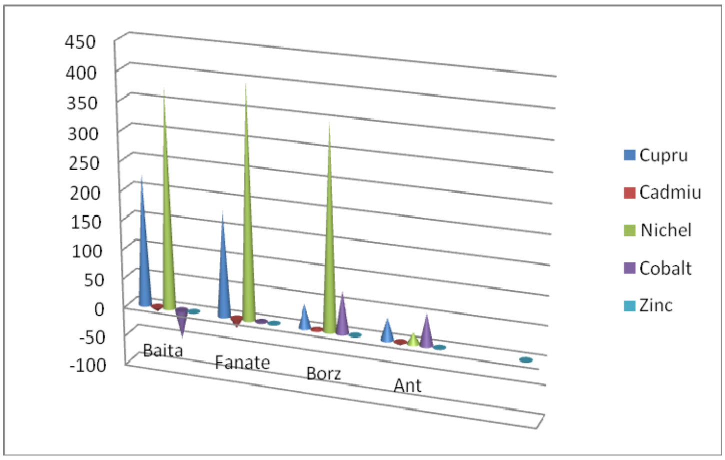

Fig. 2. Difference between studied station and reference station (Bulz) In August-Decembrer 2008 period

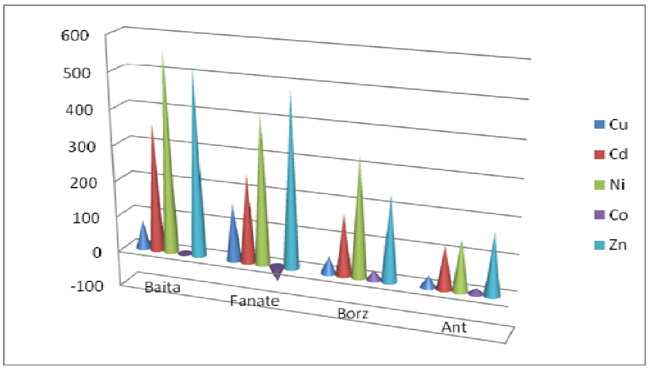

Fig. 3. Difference between studied station and reference station (Bulz)
in March-July 2009 period

CONCLUSIONS

Overall, as a general tendency, the sites can be classified, using the Law 161/2006 as follows:

- First class of water quality for zinc and copper;
- Third class at Site 1 and second class for the rest of sites situated along the main stem of Cri□ul Negru River from the point of view of nickel;
- Third class of water quality for cobalt for all the sites, and only temporarily (summer of 2008) decreasing towards second class in certain sites;
- Third class of water quality for cadmium, and for the first three sites, at the beginning of the survey and for the spring of 2009, even to the forth class of water quality;

Therefore, for an overall easiness in handling the quality of information for the general public, one can establish as a general classification of this sites as being of third water quality class from the point of view of cadmium and cobalt. From the point of view of nickel, it can be noticed an increase of water quality from the first sampling site (third water quality class) on a downstream direction (for the rest of sampling sites, second class of water quality). From the point of view of copper and zinc, the river is still first class water quality.

On a longitudinal basis, the heavy metals revealed a significantly decrease in their concentration along the upstream-downstream direction, due probably on the first instance to dilution.

It can be observed a clear pattern of decreasing in concentration as the sampling sites are further away from the mining sites, suggesting a strong point source of pollution in the headwaters from the mines and diffuse due the surface runoff during heavy rains, and possibly due the groundwater infiltrations into the river.

The dynamic of elements over years was always higher in 2009 than in 2008, probably due the increase of leaching from the mines, or surface runoff during heavy rains. Nevertheless, their concentration was significantly higher in the sampling stations only for copper, the remaining showing certain variability amid sites, but not enough to increase it in a significant manner. This could suggest that only the pollution with copper definitively increased in 2009 as compared to the previous year.

The control site, although initially considered pristine, proved not being as clean as initially thought, although providing the smallest concentrations or in the worst case (the one of cadmium) not higher than in the polluted river.

The difference in the heavy metals content in the water from the studied area and those obtained from the samples taken from the reference area are significant (figure 2 and 3) but the values are nor exceeding the legal admitted limits.

Usually, the first two sites, Băița and Fânațe, situated in the vicinity of the mining area and several tailing ponds displayed the higher concentrations in terms of the chemical species taken into consideration in the present study [8].

Acknowledgments. The authors acknowledges the support of the Environmental Protection Agency Bihor (PHARE CBC Project RO-2006/018 - 446.01.01.01.10).

REFERENCES

1. Kennish M. J, 1992, USA, CRC Press., pp. 494.

2. Authman M. M. N., 2008, Global Veterinaria, 2(3), pp. 104-109.

3. Damian F., Damian G. 2006, Geochemical characterization of some old mine waste dumps from Baia Mare area and their influence on the natural vegetation, Carpth. J. of Earth and Environmental Sciences, 1(2), pp. 63–72.

4. Damian F., Damian G., Lăcătuşu R., Iepure G., 2008, Heavy metals concentration of the soils around Zlatna and Copșa Mică smelters Romania, Carpth. J. of Earth and Environmental Sciences, 3(2), pp. 65-82.

5. Damian F., Damian, G., Lăcătuşu, R., Iepure, G., 2008, Carpathian Journal of Earth and Environmental Sciences, 3, nr.2, pp. 65.

6. Diaconescu C., Urdes L., Hangan M., Ianitchi D., Popa D., 2008, Romanian Biotechnological Letters, 13(4), pp. 3859.

7. Sarkany-Kiss A., Ponta M., Fodor A., Telcean I.,1997, Bioaccumulation of certain heavy metals by fish populations in the Criş/Koros rivers. In: The Criş/Körös Rivers Valleys. Tiscia- Monograph series., Szolnok-Szeged-Tg Mureş, pp. 327.

8. Petrovici M., Pacioglu O., 2010, Heavy metal concentration in two Speacies of Fish from the Crişul Negru River, Romania, AACL Bioflux, 3(1), pp.51-60.

9. Adriano D. C., 2001, Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals, 2nd edition, Springer-Verlag, New York, Berlin, Heidelberg.

10. Vaněk A., Borůvka L., Drábek O., Mihaljevič M., Komárek M., 2005, Mobility of lead, zinc and cadmium in alluvial soils heavily polluted by smelting industry. Plant soil environ., 51, (7), pp. 316–321.