Distribution of Trace Metals in Surface Water and Streambed Sediments in the Vicinity of an Abandoned Gold Mine from Hunedoara County, Romania

LIDIA KIM[1], GABRIELA GEANINA VASILE[1]*, BOGDAN STANESCU[1], CRISTINA DINU[1], CORINA ENE[2]

[1]National Research and Development Institute for Industrial Ecology ECOIND, 71-73 Drumul Podu Dambovitei Str., 060652, Bucharest, Romania,

[2] Petroleum-Gas University of Ploiesti, Faculty of Economic Sciences, 39 Bucharest Blvd.,100680, Ploiesti, Romania

The present study investigates the distribution of some toxic metals such as As, Cd, Cu, Cr, Co, Hg, Ni, Pb, Ti within sediments and surface water from Baiaga stream, situated near an abandoned mining site from Certeju de Jos, Hunedoara County, in the vicinity of two mining sterile dumps and Coranda Pit. The entire studied area indicates an acid pH, both in surface water and sediments. Mobile metallic concentrations were evaluated using first step of BCR 701 sequential extraction modified scheme. The total and mobile content of metals from sediments were determinate using inductively coupled plasma optical emission spectrometry. Calculated bioavailability index (I_{bio}) was used in order to correlate the presence of toxic metal in surface water. The experimental data shows important concentrations of metals (Cd, Co, Cu, Ni, Pb) in surface water correlated with relatively high bioavailability index, that include the surface water in fifth quality class (the worst) according to Romanian Order 161/2006. Low content of metals (As, Hg, Ti) in surface water despite the high concentrations presented in sediments represents the effect of lack of mobility (I_{bio} less than 0.1%). The bioavailability index represents a useful tool for sediment control in acidic mining sites.

Keywords: sediments, bioavailability index, mining site, metals distribution, surface water

Nowadays there is a growing worldwide concern about water contamination with metallic elements [1,2], given their environmental persistence and toxicity effects on living organisms, beside the fact that water quality evaluation itself may be a complicated practice.

Metals introduced by human activities into the aquatic environment accumulate in sediments and represents indicators of anthropogenic inputs, like mining and smelting activities, discharge of untreated or partially treated effluents with content of toxic metals. Heavy metals discharged into a river system by anthropogenic sources (such as industrial sites) during their transport are distributed between the aqueous phase and bed sediments [3-6], resulting in high ecological risks. Nevertheless, understanding pollutants sources in aquatic sediments is an important step for pollution control, alongside with ecological and toxicity risk assessments of the environmental pollution for different receptors, including humans [1, 2].

Unlike organic chemicals, the majority of metals cannot be easily metabolized into less toxic compounds, a characteristic of them being lack of biodegradability. Once introduced into aquatic environment, metals are redistributed throughout the water column, accumulated in sediments or consumed by biota [7]. Due to desorption and remobilization processes of metals, the sediments constitute a long – term source of contamination to the food chain. Metals residues in contaminated habitats have the ability to bioaccumulate in aquatic ecosystems [2, 8] - aquatic flora and fauna - which, in turn, may enter into human food chain and result in health problems [9].

Metals accumulation in sediments occurs through processes of precipitation of certain compounds, binding fine solid particles, association with organic molecules, co-precipitation with Fe or Mn oxides, or species bounded as carbonates - according to the physico-chemical conditions existing between the sediment and the associated water column [10, 11].

Usually, functional and out of service metalliferous mines are associated with high levels of heavy metals due to discharge and dispersion of mine wastes into soils and water systems; the contamination levels around these sites depends on geochemical characteristics and sediments mineralization [12]. In recent times, as a particular field, gold mining is considered a significant source of Hg contamination of the environment owing to activities such as mineral exploitation, ore transportation, smelting and refining, disposal of the tailings and waste waters around mines [13].

Heavy metals contamination affects some areas in Romania, such as Baia Mare, Rosia Montana, Certej, Oas Land where for long historical periods, were conducted mining and processing activities [14-16].

The aim of the study was to investigate the process of accumulation and distribution of some toxic metals (As, Cd, Cu, Cr, Co, Hg, Ni, Pb, Ti) in sediments and surface water from Certej River in the area situated between junctions with Bocsa Mare and Bocsa Mica Creeks. In the studied area are situated some processing facilities belonging to abandoned gold mines (underground or open mines) and a waste dump.

Experimental part

Study area

The area under study is located in a region with intensive mining activities, zone situated on the territory of Certeju de Jos village, in the drainage area of the Certej River. The mining activities of nonferrous ore developed in the region for several hundred years have been generated acid wastewaters with high concentration of heavy metals.

---

* email: gabriela.vasile@incdecoind.ro; Tel.: (+40)720048195

Table 1
DESCRIPTION OF SAMPLING POINTS FROM CERTEJ MINING SITE

Code	GPS	Description of the sampling points
P1	N45^{0}59.843'/ E023^{0}00.259'	Sampling point on Coranda Spring - upstream
P2	N45^{0}59.819'/ E023^{0}00.131'	Sampling point situated on Baiaga Spring, before crossing with Coranda Spring
P3	N45^{0}59.801'/ E023^{0}00.063'	Sampling point situated at the exit of Nicodim gallery (infiltration water, red-orange color)
P4	N45^{0}59.677'/ E022^{0}59.966'	Sampling point situated on Baiaga Spring, downstream of the confluence with water from gallery Nicodim
P6	N45^{0}59.418'/ E022^{0}59.740'	Sampling point situated on Baiaga Spring, upstream of the confluence with career water
P6	N45^{0}59.417'/ E022^{0}59.739'	Sampling point from career water, before confluence with Baiaga Spring (reduce flow)
P8	N45^{0}59.398'/ E022^{0}59.741'	Sampling point from Ciongani Spring before crossing with Baiaga Spring
P7	N45^{0}59.410'/ E022^{0}59.722'	Sampling point on Baiaga Spring situated upstream of the confluence with Ciongani Spring and downstream of the confluence with career water
P9	N45^{0}59.398'/ E022^{0}59.683'	Sampling point on Baiaga Spring, downstream of the confluence with Ciongani Spring
P10	N45^{0}59.207'/ E022^{0}59.065'	Sampling point from Baiaga Spring in Hondol village.

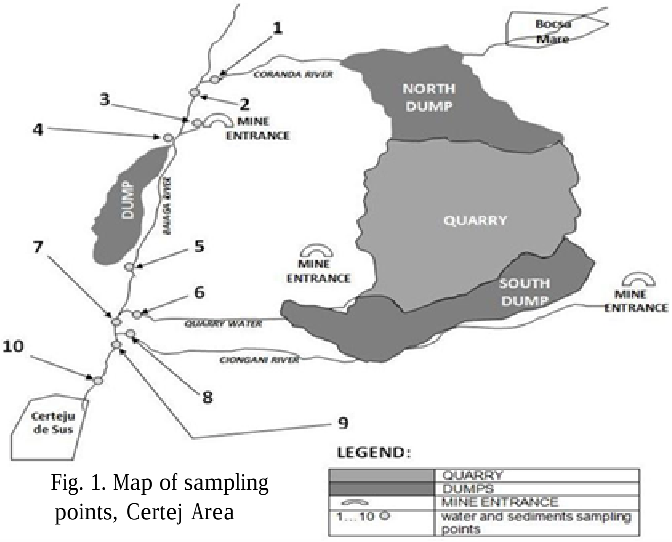

Fig. 1. Map of sampling points, Certej Area

The area was mapped using a GPS receiver with an accuracy of ± 5m. The schematic map of the studied area showing the sampling points is provided in figure 1, also the description of sampling points is presented in table 1.

Sample collection and preparation

Ten sediment and surface water samples in contact with sediments were collected from ten sampling points situated in Certej catchment area (Hunedoara County, Romania) in a sampling campaign performed in April 2014.

Water samples were collected and stored in polyethylene bottles. From each sampling location, 10 L of water were collected. The sediment samples were taken using a Van Veen Bottom Sampler and collected in glass bottles (SR ISO 5667/6, SR ISO 5667/12) [17, 18]. All samples were kept in cooling boxes at 4° C during transportation and the analyses were performed immediately after receiving the samples in the Pollution Control Department, *Water, Soil, Wastes Pollution Control Laboratory* from National Research and Development Institute for Industrial Ecology, Bucharest, Romania, in accreditation system according to (SR EN ISO 17025/2005) referential standard [19].

Analytical procedures

A part of sediment samples was dried on laboratory temperature, homogenized, crushed to fine particles and sieved in a Fritsch Analysette 3 Spartan Vibratory Sieve Shaker and the fraction less than 63 μm was collected for evaluation of the total content of metals. The other part of sediment samples, in order to maintain the same structure as in natural conditions, was sieved in wet condition using surface water from same sampling point and particle size less than 63 μm was collected. A subsample of each dry sediment sample (particle size less than 63 μm) was dissolved with a mixture of strong mineral acids (HCl: HNO3 = 1:3) in a Microwave Laboratory Ethos System, so that the total concentrations of metals were obtained.

In order to determinate de total content of metals in surface water, 150 mL of samples was digested with 5 mL of ultrapure nitric acid and concentrated to 25 mL (volumetric flask).

In a previous study [20], the optimal extraction method of metallic mobile fraction from analyzed sediments was established. Figure 2 presents the steps followed for the determination of metals in sediments, starting with the sieving step and ending with the detection step using inductively coupled plasma optical emission spectrometry technique.

The sediment dry weight was determined on a separate subsample and a correction to *dry matter* (quantity of metal per g dry sediment) was applied to all analytical results (total content).

In case of wet sediments, a dry matter correction was performed before the suspensions were prepared, in order to maintain same ratio between sediment and solution.

Analytical technique used for determination of As, Cd, Cu, Cr, Co, Hg, Ni, Pb, Ti, V, W from surface water and sediment samples (total and mobile fraction) was inductively coupled plasma optical emission spectrometry performed using an Perkin Elmer Optima 5300 DV ICP-EOS Spectrometer. All the chemicals were of analytical reagent grade (Merck quality). Matrix of the solution used for calibration curve matched with the extraction solutions.

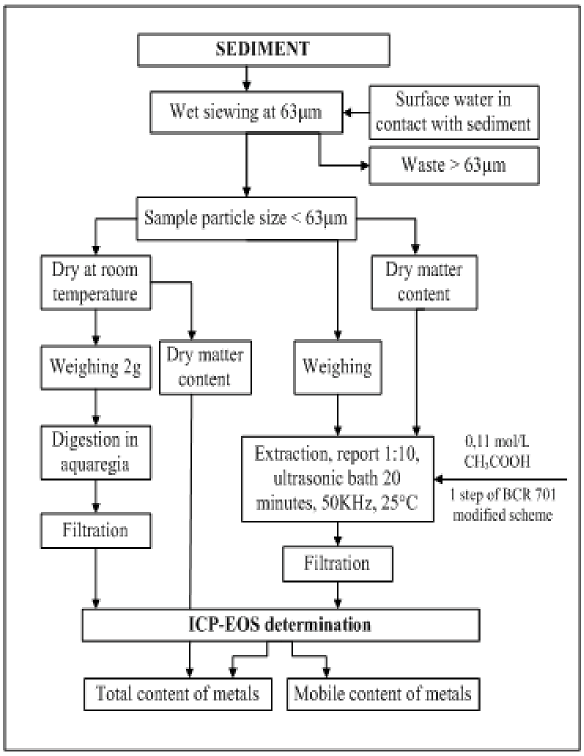

Fig. 2. Flow scheme for metals determination (total and mobile) in sediment sample

Results and discussions

Total concentrations of metallic elements in surface water

The experimental data obtained for surface water samples are presented in table 2. Bolded results represent concentrations situated over the maximum admissible for 5th class surface water quality [21]. Comparing the results with the limits imposed by the Romanian Order no. 161/ 2006 [21] for surface water quality, the *p*H values were within the acid range, around 3.7 *p*H unit, outside the set points. Within the entire area, the quality of surface water was situated in 5th class, represented the worst quality.

Coranda and Ciongani Springs represents receptors for percolated water from career and sterile mining waste dump. Career water collects mine water and washing water dumps and represents an important source of contamination of the springs. Pollution in surface water is strongly dependent by the water flow that is in contact with rocks / sediments and causes leaching of the metals. Depending on the amount of rainfall in the area, surface water can be loaded or diluted.

Total concentrations of metallic elements in sediment

The total content of analyzed metallic elements dissolved in aqua regia from sediment samples are presented in table 3.

Table 2

TOTAL CONTENT OF METALS IN SURFACE WATER SAMPLES (μg/L)

Metal	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10	MAV* (quality class)	
											IV	V
As	40.8	28.8	**1070**	45.3	19.1	<2**	<2	8.1	20	16	100	>100
Cd	**430**	**170**	**1206**	**200**	**188**	**446**	**155**	**284**	**197**	**179**	5	>5
Co	**388**	**159**	**553**	**172**	**167**	**451**	**153**	**283**	**191**	**172**	100	>100
Cr	54.4	21.1	96.8	22.8	19.7	29.9	8.7	23	15.9	14.1	250	>250
Cu	**2159**	**839**	**3319**	**913**	**858**	**1033**	**399**	**893**	**691**	**618**	100	>100
Hg	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1	>1
Ni	**1550**	**638**	**1930**	**680**	**654**	**1450**	**548**	**963**	**686**	**623**	100	>100
Pb	27.2	11.4	<1	11.1	11.2	15.8	13.4	13.4	12.2	11.9	50	>50
Ti	0.9	1.2	16	1.4	<0.5	<0.5	2.1	<0.5	<0.5	0.8	-	-
V	31.8	23.9	74.1	24.5	21.5	28.4	20	24.4	22.2	21.7	-	-
W	1.4	<1	1.5	<1	<1	<1	<1	<1	<1	<1	-	-

* Maximum admissible values according to Ref [18]

**Detection Limit of the analytical method

Table 3

TOTAL CONTENT OF METALS IN SEDIMENTS SAMPLES (mg/kg d.m.)

Metal	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	MAV*
As	**545**	**314**	**3497**	**1197**	**592**	**1172**	**938**	**691**	**1540**	**361**	**29**
Cd	**18.4**	**10.5**	**106**	**34.8**	**17.9**	**37.1**	**33.6**	**22.1**	**49.3**	**13.5**	**0.8**
Co	6.99	5.3	24.7	5.0	5.42	10.8	59.8	9.9	61.9	24	-
Cr	30.7	55.2	**162**	53.7	**132**	33	**274**	63.7	**156**	**141**	**100**
Cu	35.4	**68.7**	**151**	38.5	38.1	35.6	**298**	**76.1**	**379**	**160**	**40**
Hg	0.22	0.08	**0.32**	0.05	0.11	**0.49**	**0.70**	**0.31**	**1.21**	**0.74**	**0.3**
Ni	**54.7**	22.7	**67.6**	21.7	**310**	23.3	**386**	**39.3**	**235**	**166**	**35**
Pb	38.1	25.5	**258**	34.4	53.8	**426**	**441**	**190**	**467**	**183**	**85**
Ti	103	108	1163	26.9	115	129	1135	755	2197	488	-
V	41.3	32	255	36.9	38.8	46.2	251	48.2	375	97.1	-
W	0.43	0.61	10.3	1.12	0.59	1.09	0.72	2.63	2.81	0.68	-

* Maximum admissible values according to Ref [17]

As presented in table 3, all sediment samples show As and Cd contents over the maximum admissible limit imposed by in force legislation [20]. By far, the most polluted sediment sample is the one collected from the point S3, sampling point situated at the exit of Nicodim gallery, in which all metals monitored by law (As, Cd, Cr, Cu, Hg, Ni, Pb) reach values above maximum limits.

Based on current legislation, exceeding concentrations were observed for Cr (S3, S5, S7, S9, S10), Cu (all the samples without S1, S4 ÷ S6), Hg (S3, S6 ÷ S10), Ni (S1, S3, S5, S7 ÷ S10), Pb (S3, S6 ÷ S10). Regarding non-standardized elements, concentrations above hundreds of mg/kg d.m. and even thousands in the case of titanium, tens in the case of cobalt and vanadium, and units in the case of tungsten were observed.

Also, it was noted that most of the analyzed metallic elements accumulate in sediment collected from Baiaga Spring, as a result of repeated washing of polluted areas from abandoned gold mines and waste dump, as result of rain falls.

Mobile fractions of metallic elements in sediments - Index of Bioavailability (iBA), %

The ability of sediment to transfer metals to surrounding environment (e.g. plants) was estimated using the Bioavailability index, according to the following formula [22, 23]:

$$iBA_m (\%) = (C_{m(l)} \,.\, 100)/C_{m(total)} \qquad (1)$$

where:

$C_{m(l)}$ is the content of metal from exchangeable form, water soluble and weak acid soluble fraction (carbonates), table 2; $C_{m(total)}$ is the total concentration of metal in sediment sample.

The data reported in table 4 indicate that bioavailability index for Hg and W is zero and so, the impact of these elements in the environment is extremely low, correlated with the metals content in surface water samples (table 2).

Bioavailability indexes of Ti are either 0% or fall below 0.02% in S3 and S5 samples. In the case of vanadium, bioavailability indexes fall in the value range of 0.2 - 2.5%, its mobility being low. The results correlate both with the total amount extracted from the aqua regia, and the values recorded in surface water. The bioavailability index for Cr was situated in the range 0.04% to 1.65%. The Cr mobility towards surface water is low, as evidenced by the small concentrations of these elements in surface water.

Repartition of metallic elements in aquatic ecosystem components

In figures 3-5 are shown metals distribution maps in investigated points by reporting each metal concentrations to the average metal concentrations in all 10 sampling points, expressed as *high values*, *moderate values* and *values below average* compared to the average concentration. Both for surface water and the sediment, the most polluted area corresponds to the area associated to Nicodim gallery (S3) and the area of the mine water disposal, corresponding to S6 and S7 sampling points.

Bioavailability indexes for Cd and Ni are ranked between 2.80 - 13.9% (Cd) and between 1.45%and 36.7% (Ni). The transfer of these metals in surface water is high in S1, S2 and S10 sampling points for Cd and in S1, S2, S3, S4, and S6 for Ni. In other sampling points, high concentrations of sediment elements correlated with their mobility lead to the presence of these metals in surface water at concentrations exceeding 1000μg / L in S3 sampling point for Cd and 500 μg / L in S5, S7 S8, S9, S10 stations for Ni (table 2, fig. 3).

Metal	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
As	0	0	0.03	0.01	0	0	0.02	0	0	0
Cd	**13.9**	**10.6**	7.01	3.62	5.64	7.74	5.92	8.82	2.80	**11.3**
Co	**35.8**	**20.6**	**15.5**	**26.4**	**20.8**	**24.4**	4.9	**20.4**	2.3	8.4
Cr	1.56	1.65	0.62	1.36	0.40	0.97	0.04	0.57	0.08	0.11
Cu	**38.9**	**22.6**	**13.2**	**25.4**	**23.3**	**14.2**	5.44	**10.9**	3.48	**11.5**
Hg	0	0	0	0	0	0	0	0	0	0
Ni	**17.4**	**19.2**	**20.4**	**21.1**	1.45	**36.7**	2.2	1.8	2.9	3.4
Pb	1.94	6.63	0	4.01	4.67	0.05	0.20	0.36	0.42	0.97
Ti	0	0	0.02	0	0.01	0	0	0	0	0
V	2.5	1.6	0.5	1.6	1.2	2.4	0.4	2.03	0.2	0.9
W	0	0	0	0	0	0	0	0	0	0

Table 4
BIOAVAILABILITY INDEX (%) FOR 11 METALS IN SEDIMENTS SAMPLES

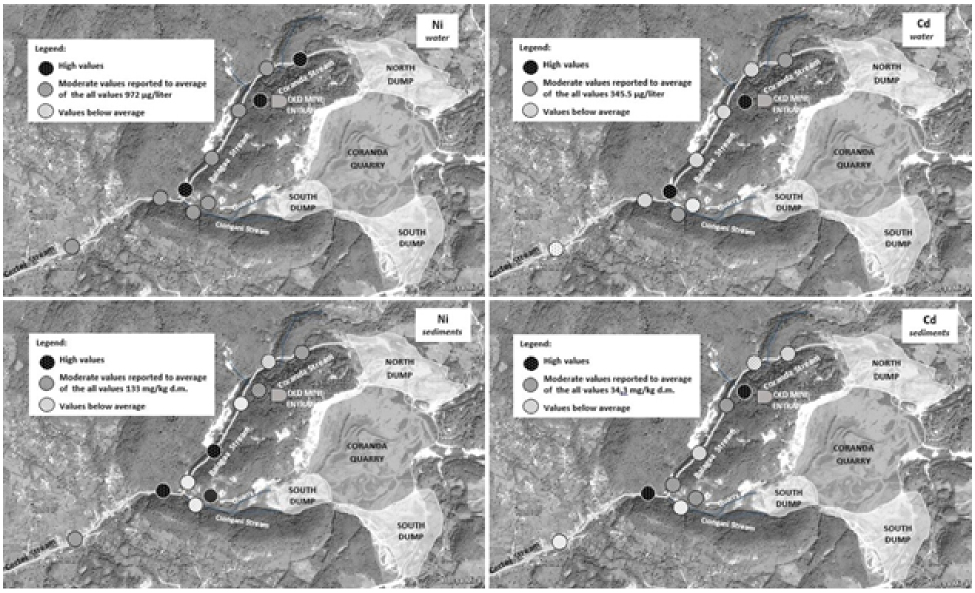

Fig. 3. Distribution of Nickel and Cadmium concentrations in surface water and sediments

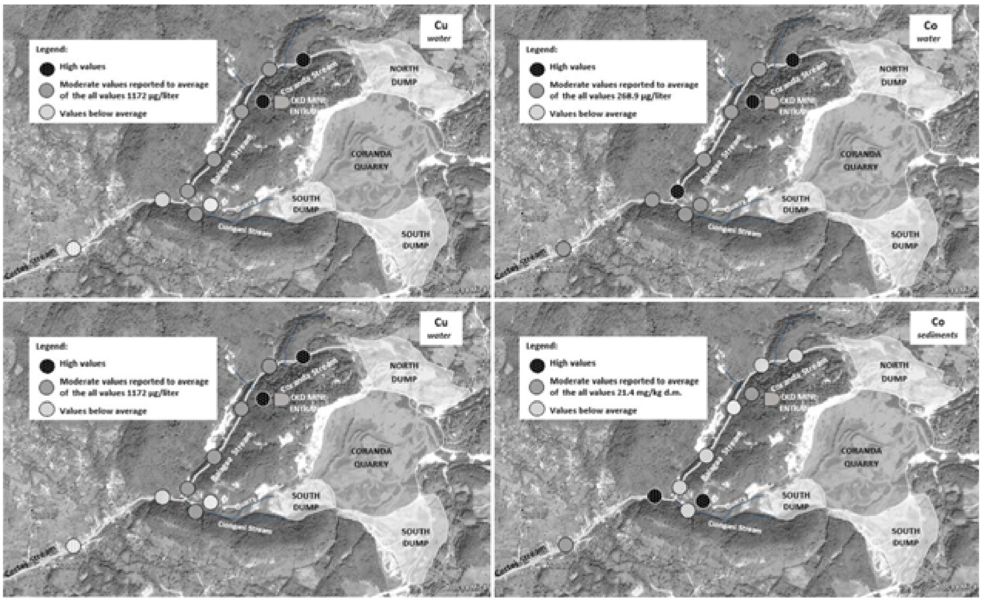

Fig. 4. Distribution of Copper and Cobalt concentrations in surface water and sediments

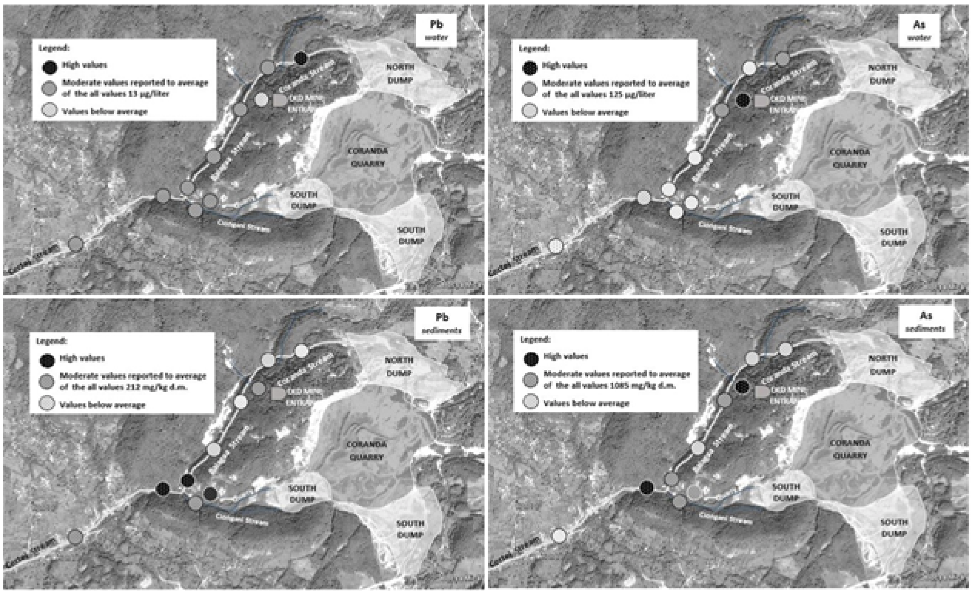

Fig. 5. Distribution of Lead and Arsenic concentrations in surface water and sediments

Metals Co and Cu are found in a bioavailable form in each investigated samples. In S1-S6 sampling points, bioavailability indexes exceed 14%, indicating a high transfer of these metals in the sediment surface water. Even if the Co content is not high within the sediment, its high percentage of availability allows this element to be found in concentrations between 150 ÷ 550 µg / L in surface water. Regarding the Cu content, surface water values (400 ÷ 3300 µg / L) is due both to total Cu content within the sediment and the fact that it is present in a bioavailable form (fig. 4).

Bioavailability indexes are situated in the range 0 % to 0.03% for As and between 0.05% and 6.63 for Pb. These low percentages of mobility are reflected in relatively low concentrations of these elements in surface water, even if the total metal content in the sediment is exceeded in some sampling points. The exception is the S3 sampling point, situated at the exit of Nicodim gallery (infiltration water, red-orange color), where the correlation between the low water flow, extremely high concentration of arsenic in the sediment and the bioavailability index of As lead to concentrations above 1 mg / L (fig.5).

Conclusions

The study zone represents a heavily polluted area due to mining activity carried out in the past, therefore the area continues to pollute both surface water and sediments (Coranda, Ciongani and Baiaga Springs). Some general characteristics of the area can be highlighted, such as: acid pH values, high contents of total metals (As, Cd) and mobile metals (Cd, Co, Cu, Ni).

The experimental data showed a significant pollution with As, Cd, Co, Cu, Ni in surface water, hence the quality of surface water was situated in 5th class, represented the worst quality.

Using bioavailability index in the chemical characterization of the studied area allowed the obtaining of important information on the metal potential to migrate from the sediment structure, entering into the water body. The experimental data have shown a strong connection between the bioavailability percentage of the metal and its content in surface water.

Acknowledgements

This study has been carried out within the framework of the NUCLEU Program (Environmental Research - Priority in Sustainable Industrial Development – MEDIND, PN 09 13-02-19).

References

1. WU, B., WANG, G., WU, J., FU, Q., LIU, C., PLoS ONE, **9**, no. 7, 2014.
2. HASAN, M.R., KHAN, M.Z.H., KHAN, M., AKTAR, S., RAHMAN, M., HOSSAIN, F., HASAN, A.S.M.M., Environ. Sci., **2**, no. 1, 2016, p.1.
3. HRONCOVÁ, E., LADOMERSKÝ, J., DIRNER, V., Carpathian J. Earth Environ. Sci., **9** no. 2, 2014, p. 199.

4. CESAR, R., EGLER, S., POLIVANOV, H., CASTILHOS, Z., RODRIGUES, A. P., Environ. Earth Sci., **64**, no. 1, 2011, p. 211.

5. TEODOROF, L., NASTASE, C., ANUTI, I., Rev. Chim. (Bucharest), **60**, no. 10, 2009, p. 1098.

6. IONESCU, P., RADU, V. M., GYORGY, D., IVANOV, A. A., DIACU, E., Rev. Chim. (Bucharest), **66**, no. 8, 2015, p. 1088.

7. FRÉMION, F., BORDAS, F., MOURIER, B., LENAIN, J. F., KESTENS, T., COURTIN-NOMADE, A., Sci. Total Environ., **547**, 2016, p. 282.

8. BUMBAC, C., LEONTE, E.P., DUMITRESCU, C., GHITA, I., STEFANESCU, M., J Environ Prot Ecol., **11** no. 3, 2010, p. 822

9. VAROL, M., ªEN, B., Catena, **92**, 2012, p. 1.

10. EQUEENUDDIN, S. M., TRIPATHY, S., SAHOO, P., PANIGRAHI, M., J. Geochem. Explor., **124**, 2013, p. 230.

11. VASILE, G., CRUCERU, L., PETRE, J., IANCU, V., Rev. Chim. (Bucharest), **56**, no. 8, 2005, p. 790.

12. NAVARRO, M.C., PEREZ-SIRVENT, C., MARTIUNEZ-SANCHEZ, M. J., VIDAL, J., TOVAR, P. J., BECH, J., J. Geochem. Explor., **96**, no. 2-3, 2008, p. 183.

13. ARMAH, F. A., OBIRI, S., YAWSON, D.O., PAPPOE, A.N.M., BISMARK, A., J. of Environ. Stat., **1**, no. 4, 2010, p.1.

14. VASILE, G.D., VLÃDESCU, L., Environ. Monit. Assess., **167**, no. 1-4, 2010, p. 349.

15. RESETAR-DEAC, A. M., DIACU, E., Rev. Chim. (Bucharest), **66**, no. 9, 2015, p. 1535.

16. VASILE, G. D., NICOLAU, M., VLADESCU, L., Environ. Monit. Assess., **160**, no. 1-4, 2010, p. 71.

17. ***SR ISO 5667-6. 2009. Water quality. Sampling. Part 6: Guidance of sampling rivers and streams. Romanian Standard Association, 24 p.

18. ***SR ISO 5667-12. 2001. Water quality. Sampling. Part 12: Guidance on sampling of bottom sediments. Romanian Standard Association, 44 p.

19. ***SR EN ISO 17025. 2005. General requirements for the competence of testing and calibration Laboratories, Romanian Standard Association, 36 p.

20. VASILE, G.G., KIM, L., GHEORGHE, S., STANESCU, B., International Multidisciplinary Scientific GeoConference: SGEM: Surveying Geology & mining Ecology Management, **1**, 2013, p. 299.

21. ***Order no 161/2006 for the approval of the Norm concerning the reference objectives for the surface water quality classification, The Ministry of Environment and Water, Official Monitor of Romania, Part 1, no. 511 bis.

22. RODRIGUES, M. L. K., FORMOSO, M. L. L., Water Air Soil Pollut, **169**, no. 1-4, 2006, p. 167.

23. CHAPMAN, P. M., WANG, F., JANSSEN, C., PERSOONE, G., ALLEN, H. E., Can J. Fish Aquat. Sci., **55**, no. 10, 1998, p. 2221.

Manuscript received: 15.12.2015