ANALYTICAL INVESTIGATIONS CONCERNS REGARDING Ni AND Pb DISTRIBUTIONS AND MOBILITY IN RIVER SEDIMENTS AFFECTED BY MINING ACTIVITIES

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Abstract

The heavy metal pollution is among the most disseminated environmental contamination, at least in some regions of Romania, having a particularly adverse effect on surface water and sediments in affected areas.

This type of contamination could be directly linked to some industrial activities like smelting and mining.

The main task of this study is to assess the heavy metal outflow from the contaminated sediment to the aquatic environment, with its subsequent toxic effect on the living organisms in water.

In this paper we study the distribution and mobility of nickel and lead in sediment samples taken from a highly heavy metals polluted area, the principal anthropologic input being from existing and former mining activities.

The main objective of this study was to evaluate the ecological pollution degree by determining the mobility and distribution of nickel and lead in sediments of rivers polluted by industrial human activities.

In order to determine the mobile fraction of nickel and lead in sediment samples we used BCR extraction method that separates three fractions which differ in the mobility of existing metal chemical species and a method of leachable extraction fraction by cold extraction method using certified reference material.

Our results show that by applying BCR sequential extraction method on sediment, it is found that nickel due to its higher mobility than lead, induce a significant degree of pollution by its migration from sediment to surface water.

Keywords: sediment, mobility, sequential extraction, heavy metal, bioavailability

Introduction

The composition of the metals in the sediment is determined by natural processes (mineralogy, weathering and digenetic mechanisms) and by anthropogenic processes.

Today it is recognized that the effects of trace metals in the environment components, water and sediment, is determined more by the different existing physic-chemical species then by total metal concentration. Therefore, metals speciation is largely responsible for their bioavailability and toxicity [1].

Speciation consists in identifying and quantification of the different species or forms of phases in that chemical elements appear. The data on the existing different physic-chemical forms of an element are important for understanding its mobility and bioavailability.The investigation of distribution and speciation of heavy metals could provide significant data about pollution degree, and information about the pollution sources, about real impact of the heavy metals on the environment and about the their bioavailability. [2-7].

There are several techniques for achieving speciation. Of these, the sequential extraction allows determined the fraction of the metal that is available for plants or accessible for the environment. All sequential extraction schemes imply successive digestion of the sample with different reagents, every one extract representing a fraction of the metal from the total content. The extraction capacity of the reagent mixtures in a sequential extraction increases from the initial step, which uses soft reagents (like water, salt solutions or diluted acetic acid) to the last step in the scheme in which mixtures of strong mineral acids are used, capable to digest the metal fractions with the lowest mobility.

Extraction processes involve relatively simple chemical reactions, like ion exchange reactions, reduction of the hydrated oxides, oxidation reactions or digestion [8].

Although there have been proposed numerous suggestions both for one step extractions and for sequential extractions, none of them was accepted unanimously, to become a standardized procedure [9]. One reason for this is that no one single method could accurately estimate the availability of all metals existing in a sample. Another difficulty is the lack of appropriate reference materials, which limits the quality control.

Speciation of the metals contained in the solid phases could be analyzed either by one step extraction or by sequential extractions. Usually, the one step extraction is intended for studying the slightly soluble metal fraction (mobile fraction) in a sample i.e. the environmentally bioavailable fraction [10]. The sequential extractions are designed to study the partition of heavy metals in sediments, soils or wastes between different fractions, starting with the easily soluble ones up to the phases where the metal is most strongly bound [11].

The elements such as Ni, Pb, Cd, Cu, As, Zn could exist in environmental samples in different species: soluble fractions, fractions bound to the hydrated iron and manganese oxides, or fractions in which the elements are bound to organic matter. All these fractions can be modified by environmental factors among which there are: pH, temperature, redox potential, organic matter composition, etc.

The main objective of this paper is to evaluate the ecological pollution degree by determining the mobility and distribution of nickel and lead in sediments of rivers polluted by anthropic activities.

Methods and materials

For achieving the objectives, were taken sediment and surface water samples from 11 points established on a stretch of river, its influential and mine water from the basin of Certej river (a tributary of Mures river in Hunedoara county) - see Figure 1.

Both surface water and sediments shows an acidic pH ranges from 2.17 to 2.61 in surface water and pH range between 2.5 to 5.3 in sediments samples.

The sediment samples were taken at depth of 0-5 cm from several sites close to the mining activities; the samples were kept in polypropylene containers which were preserved at 4ºC during the transport to the lab till the moment of the analysis. At the same time, water samples were taken from the same locations as sediments. These water samples were kept in high density polyethylene bottles and preserved by addition of ultrapure nitric acid.

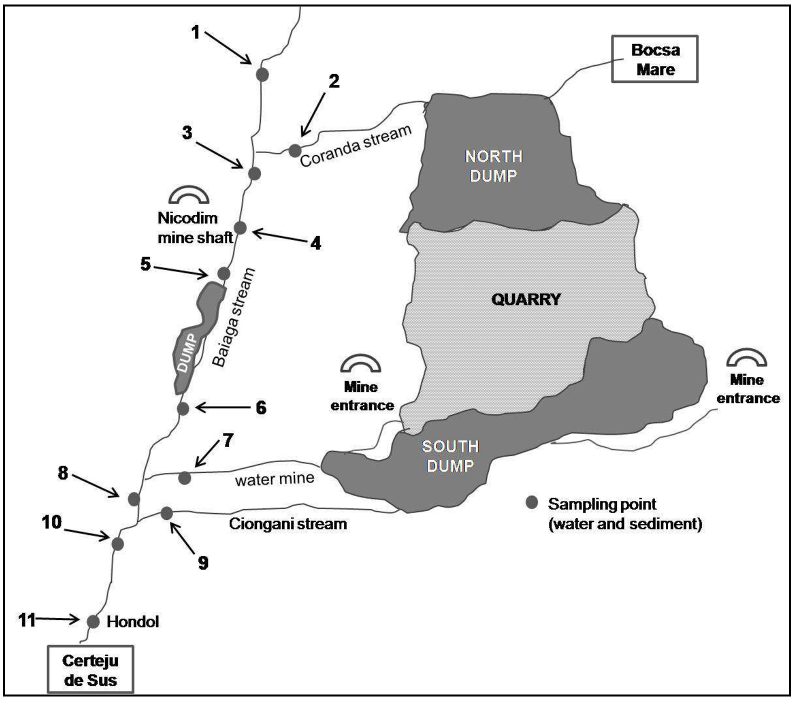

Figure 1.–*The locations from which the sediment and water samples have been taken*

For assessing the speciation and mobility of nickel and lead, in the 11 sediment samples two analysis methods have been used, namely BCR method (European **C**ommunity **B**ureau of **R**eference), validated by using as reference material MRC 701 (degree of reproducibility situated between 98.25% - 99.32% for Ni and 98.14% - 99.06% for Pb respectively) and a cold extraction method, by using the reference material being WQB-1 (degree of reproducibility situated of 97.85% and 95.76% for Ni and 98.02% - 99.28% for Pb). Reference material WQB-1 shows both the certified values for total concentrations of metals which totally destroys the sample matrix and in addition for some metals the bioavailable concentrations are certified [12-15].

BCR method

The BCR extraction scheme is widely applied now for the analysis of the sediments, soils, muddy soils and waste [13]. Some reference materials are already assigned to the BCR sequential extraction and the values of different element concentrations in these materials, in each extraction step, is certified.

Below is given the procedure used throughout the study. This method has three extraction steps separating three fractions:

1) Exchangeable fraction (slightly soluble fraction): in an iodometric flask, to the 0.5 g of sediment (sieved - 63 µm fraction) 20 mL acetic acid 0,11 mol·L^{-1} is added. The flask tightly closed are then put in an ultrasonic bath at 40 000 Hz and 25°C for 15-30 min. Then the samples were filtered and the insoluble residue is washed. This fraction includes metal species which are weakly adsorbed on sediments, those that are released by ion exchange and metal fractions liked with carbonates.

2) Reducible fraction - the fraction bound to Fe and Mn oxides*:* to the solid residue from the first step, 20 mL hydroxyl ammonium chloride 0.5 mol·L^{-}1 is added at pH =2, followed by ultrasonic treatment for 15-30 min. and the obtained residue being washed. This soluble fraction is named “reducible” because in this step the metals are released by reduction with hydroxyl ammonium chloride.

3) Fraction bound to organic matter*:* in the third step of BCR, to the residue from the second step 5 mL hydrogen peroxide is added and the suspended residue is left at room temperature for 1 hour; after that the sample tubes are tightly closed and heated at 85°C for one hour. The suspension is evaporated and brought to 1 mL. Another 5 mL of hydrogen peroxide is added and the heating with closed tubes is repeated. Finally the suspension is evaporated to almost dry on water bath. After cooling, 25 mL ammonia acetate 1 mol·L^{-1} (brought to *p*H = 2 with HNO_3) is added and the obtained suspension was subjected to sonication for 15-30 min. The supernatant after sonication represents fraction three, named “oxidable fraction” as the metals were released by oxidation.

Cold extraction method

It is a method of extraction of leachate fraction in different operation conditions beside the BCR method.

For estimating the bioavailable fractions the sediment is extracted with 5% HCl (sediment : HCl solution ratio being 1:20).

In our study 5g of sediment sample (63 µm fraction) was shaken at room temperature (cold extraction) for 12h in 5% HCl (sediment : HCl solution = 1:20). The suspension was filtered on a glass microfiber filter [Whatman 4.25 cm GF/C].

In our study the total metal content and the metal concentrations (Ni, Pb) for each extraction step applying the two methods have been determined by an ICP-MS (inductively coupled plasma with mass spectrometer), Aurora M90, Bruker instrument.

Results and Discussion

The obtained results for sequential extraction of nickel and lead (mg/kg dry wt) in sediment samples by applying the BCR extraction procedure are presented in Tables 1 and 2. Metal concentrations in 1-3 steps were added and through difference from total concentration was determined concentration of the two metals in the residual phase.

Table 1. *Nickel partition in sediment samples*

Location	Total content (mg/kg dry wt)	Ni content (mg/kg dry wt; %) from total concentration							
		Exchangeable fraction (slightly soluble)		The fraction bound to Fe and Mn oxides		Oxidizable-organic matter and sulfides		Residual fraction	
		mg/kg dry wt	% (from total)	mg/kg dry wt	% (from total)	mg/kg dry wt	% (from total)	mg/kg dry wt	% (din total)
P1	**19.54**	4.89	**25.03**	2.20	**11.26**	2.95	**15.09**	9.5	**48.62**
P2	**32.27**	8.05	**24.95**	3.40	**10.54**	4.31	**13.36**	16.51	**51.16**
P3	**16.71**	6.55	**39.20**	1.32	**7.90**	3.20	**19.15**	5.64	**33.75**
P4	**58.34**	14.79	**25.35**	7.75	**13.28**	5.79	**9.92**	30.01	**51.44**
P5	**18.21**	8.04	**44.15**	5.36	**29.43**	2.73	**14.99**	2.08	**11.42**
P6	**33.88**	19.25	**56.82**	8.22	**24.26**	4.91	**14.49**	1.5	**4.43**
P7	**16.53**	8.63	**52.21**	1.75	**10.59**	2.60	**15.73**	3.55	**21.48**
P8	**8.44**	2.60	**30.81**	0.99	**11.73**	3.25	**38.51**	1.60	**18.96**
P9	**43.85**	8.42	**19.20**	6.33	**14.44**	8.37	**19.09**	20.73	**47.27**
P10	**30.53**	9.32	**30.53**	8.97	**29.38**	7.58	**24.83**	4.66	**15.26**
P11	**30.95**	10.55	**34.09**	4.35	**14.05**	6.93	**22.39**	9.12	**29.47**

Table 2. *Lead partition in sediment samples*

Location	Total content (mg/kg dry wt)	Pb content (mg/kg dry wt; %) from total concentration							
		Exchangeable fraction (slightly soluble)		The fraction bound to Fe and Mn oxides		Oxidizable-organic matter and sulfides		Residual fraction	
		mg/kg dry wt	% (from total)	mg/kg dry wt	% (from total)	mg/kg dry wt	% (from total)	mg/kg dry wt	% (din total)
P1	**58.42**	1.52	**2.60**	1.96	**3.35**	2.31	**3.95**	52.63	**90.08**
P2	**129.1**	10.26	**7.95**	8.68	**6.72**	13.07	**10.12**	97.09	**75.21**
P3	**111.4**	10.04	**9.02**	6.13	**5.50**	3.22	**2.89**	92.01	**82.59**
P4	**264.7**	8.50	**3.21**	4.63	**1.74**	33.40	**12.61**	218.23	**82.44**
P5	**109.2**	3.72	**3.41**	9.69	**8.87**	3.90	**3.57**	91.89	**84.15**
P6	**254.1**	9.98	**3.93**	65.34	**25.71**	35.38	**13.92**	143.4	**56.43**
P7	**120.2**	3.36	**2.80**	5.03	**4.18**	4.50	**3.74**	107.31	**89.28**
P8	**266.1**	11.76	**4.42**	57.38	**21.56**	21.45	**8.06**	175.51	**65.96**
P9	**28.8**	4.77	**16.56**	2.51	**8.72**	1.26	**4.38**	20.26	**70.35**
P10	**64.9**	3.72	**5.73**	1.85	**2.85**	2.09	**3.22**	57.24	**88.20**
P11	**103.2**	4.51	**4.37**	4.48	**4.34**	2.16	**2.09**	92.05	**89.20**

From the results shown in Table 1, we found that in four sediment samples corresponding to P1 , P2 , P4 and P9 , the sum of fractions determined by the BCR method is approx. 50 % of the total nickel content from these sediments. From the same data, it follows that in sediment samples P5 , P6 , P8 and P10 the nickel content is mainly in the three fractions resulted with the BCR applied method and in a residual phase is below 19 %. For the other three samples, nickel is found in the residual phase ranging between 21.48 % and 33.75 %.

By analyzing the concentrations of nickel from mobile fractions of the 11 samples of sediments and comparing them with the sum concentrations of the other two fractions (fractions 2 and 3), the following conclusions can be drawn:

- for sediment samples P3, P6 and P7, the concentration of nickel is greater in the easy soluble fraction than the sum of the concentrations of the other two fractions. That means an increased potential of water pollution of water by migration of nickel from sediments into the surface water .

- for the other 5 sediments corresponding to the P1 , P2 , P4 , P5 and P11 points, the nickel concentration from easily soluble fraction is approximately equal to the sum of the concentrations of the other two fractions, aspect that also highlights an increased potential of pollution (by passing the mobile form of nickel from sediments into the surface water).

- only for three sediment samples corresponding to P8 , P9 and P10 , the concentration of nickel from the first fraction is much smaller (at least twice) than the sum of nickel concentrations in fractions 2, and 3 , which shows a low potential of pollution because nickel migrates from sediments into the surface water; in these sediments is revealed the existence of a large amount of nickel species in which Ni is bound in inorganic forms as Fe and Mn oxides and, in relatively equal proportion is bound to organic matter. In the other two cases mentioned above, the nickel mainly exists as: easily adsorbed compounds, bounded by ionic bonds or as carbonates forms.

Opposed to nickel, lead has a very different behavior in terms of solubility/mobility.

The results presented in Table 2 show that lead is mainly in residual phase.

For 7 sediment samples corresponding P1 , P3 , P4 , P5 , P7 , P10 and P11 the residual phase contains more than 82 % Pb concentrations and the sum of lead concentration in the 3 fractions detected by BCR method is below 18%.

For the other four sediments (P2 , P6 , P8 and P9), residual phase contains Pb immobilized in it between 56.43 % and 75.21 %.

Comparing the concentrations of lead in easy soluble fraction with sum of its concentrations in the other two fractions (2 and 3) we found that:

- for sediment samples P1 , P2 , P3 , P4 , P5 , P6 , P7 , P8 and P11 , the lead concentration is less than the sum of the concentrations of the other two fractions , inducing a low potential of pollution by its migrating from sediment into the surface water. In sediment samples P4 and P6, lead concentrations from easy soluble phase are 4.5 times (P4) to 10 times (P6) lower than the sum of the concentrations of the other two fractions (2 and 3) , highlighting that lead is mostly bound as compounds in the form of Fe and Mn oxides (P6) and as lead compounds bound to organic matter and sulfides (P4 , P6) .

- for other sediment samples (P9 and P10), the concentrations of lead from the first fraction (the easy soluble) are approximately equal to the sum of the concentrations of the other two fractions (2 and 3) , but represents only about 5 % from the total concentration of lead present in those sediments. This aspect indicates a low potential for pollution of the water ecosystem by migration of lead from sediment into the surface water.

From the results presented above (Tables 1 and 2) by BCR sequential extraction method the following conclusions can be drawn :

- concentration of mobile forms of nickel (easy soluble) in a majority amount constant almost all the way along investigated river and its tributaries, induces an **increased potential of pollution** by passing nickel from sediments into the surface water.

- in the case of lead , its majority presence in residual phase and in fractions 2 and 3 (lead bound as Fe and Mn oxides and lead compounds as organic matter and sulfides) indicates a **low potential of pollution** of surface water due to immobilization and its absorption in sediments and the trend to form poorly soluble complex salts.

The results on nickel and lead concentrations in 11 samples of surface water (mg/L) are shown in Table 3.

Table 3. *The Ni and Pb concentrations (mg/L) in surface water*

Location	**Total content of Ni in surface water (mg/L)**	**Total content of Pb in surface water (mg/L)**
P1	0.15	0.35
P2	1.19	5.5
P3	0.55	5.3
P4	4.42	11
P5	0.46	2.8
P6	0.47	4.5
P7	0.48	1.4
P8	0.87	5.1
P9	0.74	4.8
P10	0.59	4.4
P11	0.48	1.6

The variation of concentration of nickel and lead in surface waters taken and analyzed from the 11 samples (Table 3) shows influence of Coranda river, of water from Nicodim gallery, of mine water and river Ciongani on the water quality of Baiaga river.

For example, Ni content of 1.19 mg/L in river Coranda leads to the increase of the Ni content from Baiaga river from 0.15 mg/L upstream to 0.55 mg/L downstream.

Similar variations are highlighted also for other Baiaga tributaries. The measured values for Ni and Pb concentrations upstream and downstream of the confluence points with Baiaga river are dependent on both the content of two metals in influent and especially on their flow with reference to Baiaga river.

For example, water from Nicodim gallery has the highest concentration of both Ni and Pb and despite this fact, the increase the concentration of metals downstream with reference to upstream is small. The explanation is that the water flow from Nicodim gallery is very low compared to flow of Baiaga river.

The concentrations of those two metals (Ni and Pb) in the surface water are also influenced by their mobility determined in the sampling points. Since the mobility of the two metals as well as their concentrations in surface water were determined from the instantaneous samples, is difficult to emphasize the influence of their sediment mobility upon metal concentrations in the surface water .

Basically, due to the difference between high flow rate of surface water and slow rate of the sediment movement is impossible to pinpoint the balance between metals from sediment and their contents in surface water.

For the determination of nickel and lead mobile forms by cold extraction method were chosen for analysis three sediment samples from eleven samples (P5, P6 and P7) due to obtained the high concentrations in easy soluble fraction by BCR method.

The obtained results for total and mobile concentrations of Ni and Pb using the cold extraction method are presented in Tables 4 and 5.

Table 4. *Ni mobile content by cold extraction method*

Metals	P5	P6	P7
Ni total (mg/kg su)	18.21	33.88	16.53
Ni mobile (mg/kg su)	2.95	7.52	3.36
Ni mobile (%)	**16.19**	**22.21**	**20.32**

Table 5. *Pb mobile content by cold extraction method*

Metals	P5	P6	P7
Pb total (mg/kg su)	109.2	254.1	120.2
Pb mobile (mg/kg su)	22.28	53.18	18.92
Pb mobile (%)	**20.40**	**20.93**	**15.74**

The results presented in Tables 4 and 5 highlight for both (Ni and Pb), an evolution of their mobility, similar to that determined by the BCR method. Thus, for P6 sample the mobile form of nickel is higher than the one determined for P5 and P7 samples, evolution evidenced by the results shown in Table 1.

This finding is valid also for the mobility of lead in the same 3 points under discussion.

What should be noted is that due to different working conditions for the two methods, the values for mobility of lead by cold extraction method are higher than the mobility of nickel, while for the BCR method the evolution is reversed.

CONCLUSIONS

According to the results obtained by applying the BCR sequential extraction on analyzed sediments, it is found that nickel due to its higher mobility than lead, induces a significant degree of pollution by its migration from sediment into the surface water. The pollution degree influenced to a smaller extent by the concentration of lead on aquatic analyzed system (Baiaga river and its influential).

Because, conditions for obtaining mobile phase by BCR method are closer to natural conditions in the field, this method is more appropriate for the study of the pollution of surface water induced by metals' transition from sediment into water.

REFERENCES

[1] GREENWAY, G.M., SONG, Q.J., J. Environ. Monit., **4,** 2002, p. 300.

[2] BAEYENS, W., MONTENY, F., LEERMAAKERS, M., BOULLION, S., Anal. Bioanal. Chem., **376,** 2003, p. 890-901.

[3] ***VIGANÒ, L.*,** ARILLO, A., BUFFAGNI, A., CAMUSSO, M., CIANARELLA, R., ***Water Res.,*** *37*, 2003, p. *501*–518.

[4] CICERI, E., GIUSSANI, B., POZZI, A., DOSSI, C., RECCHIA, S., Talanta, **76**, 2008, p. 621-626.

[5] ARAIN, M.B., KAZI, T.G., JAMALI, M.K., SARFRAZ, R.A., Pedosphere, **19**(4), 2009, p. 476-485.

[6] LEERMAKERS, M., BAEYENS, W., DE GIETER, M., SMEDTS, B., MEERT, C., DE BISSCHOP, H.C., MORABITO, R., QUEVAUVILLER, PH., Trends in Analytical Chemistry, **25**(1), 2006.

[7] FAGBOTE, E. O., OLANIPEKUN, E.O., J. Appl. Sci. Environ. Manage, **14** (4), 2010 p. 47-51.

[8] GRUEBEL, K. A., DAVIS, J. A., LECKIE, J. O., Soil Science of America Journal, **52**, 1988, p. 390-397.

[9] FIEDLER, H.D., LOPEZ-SANCHEZ, J.F., RUBIO, R., RAURET, G., QUEVAUVILLER, PH., URE, A.M., MUNTAU, H. Analyst, **119**(6), 1994, p. 1109-1114.

[10] GUPTA, S. K., VOLLMER, M. K., KREBS, R. Science of the Total Environment, **178**, 1996, p. 11-20.

[11] BELZILE, N., LECOMTE, P., TESSIER, A,. Environmental Science and Technology, **23**(8), 1989, p. 1015-1020.

[12] QUEVAUVILLER, PH., RAURET, G., LÓPEZ-SÀNCHEZ, J. F., RUBIO, R., URE, A.M., MUNTAU, H., Science of the Total Environment, **205**, 1997, p. 223–234.

[13] RAURET, G., LÓPEZ-SÀNCHEZ, J. F., SAHIQUILLO, A., BARAHONA, E., LACHICA, M., URE, A. M., Journal of Environmental Monitoring, **2**, 2000, p. 228–233.

[14] AGEMIAN, H., CHAU, A.S.Y., Analyst **1207** (101), 1976, p.761-767.

[15] National Laboratory for Environmental Testing (NLET) - National Water Research Institute (NWRI) of Environment Canada in Burlington, Ontario.