SPATIAL AND TIME VARIATION INFLUENCE OF SOME HEAVY METAL ION SPECIES CONTENTS ON THE EVOLUTION OF ECOLOGICAL RISK

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Abstract

Environmental authorities are more and more involved in planning of the evaluation strategies for the ecological risks implied by sediments contamination. Nevertheless, the estimation of the long term effects of the sediments contamination is still difficult and implies a high degree of uncertainty. Sediments represent an important pollution source for the aquatic environment, because are the final accumulation medium for a multitude of organic or inorganic contaminants.
This paper presents the investigations carried out on the quality of surface water and sediments collected from Abrud hydrographic basin affected by long lasting activity extraction of minerals. Investigations carried out have as purpose to establish the water quality Abrud river upstream and downstream of the pollution sources including Foiesu river (right tributary of Abrud) and also the changes induced upon them along investigated time period.
It was also evaluated the partition of some metals (Cu, Cd) within all fractions defined by sequential extraction operations using the BCR (Community Bureau of Reference). Metal distribution in those fractions offers information on their bio-availability, which in turn allows aquatic environmental risk assessment.
It is found that the risks induced by the two analyzed metals are changing according to the conditions of surface water flow, sediment composition punctual and weather conditions.
It highlights for both heavy metals the positive evolution of environmental risk over time.

Keywords: sediment, ecological risk, sequential extraction, metals mobility

INTRODUCTION

Heavy metal pollution captures more attention to the whole world because of the dramatic increase of its presence in air, water and soil. This type of pollution in aquatic environment is a long term and irreversible process.

Pollution may have natural origin, contamination being due to the dissolution of minerals and rocks in an aqueous medium, or anthropogenic origin especially the mining industry, which produced in time large amounts of wastes with high metal content [1].

Environmental contamination due to historical mining activities has been observed in many regions, the most common effects are acidification and metal contamination of surface water, sediment, soil and groundwater [2]. Production of acidic mine waters is due to exposure of pyrite (FeS_2) and other sulphide minerals to air or water. So takes place sulphide oxidation and that produces a high acid concentration due to sulphates, iron and other metals, because between pH and heavy metals concentrations there is a strong negative correlation [3]. The production of acid mine water is a quick and self-supportive process that continues as long as pyrite, air and water are available. Similarly are occurring reactions which are releasing large amounts of other metals such as Mn, Cu, Zn, Cd, etc. even long after the mining activity was stopped [4, 5].

Given the importance of ecological and environmental significance of river systems, much research has been focused on heavy metals pollution and their mobility in soil, suspended particulate matter (SPM) and sediments in watershed systems in recent decades [6,7]. Retention of metals on to solid phases is an important issue in the study of heavy metals pollution. Most metals retention study and sorption data have been obtained using batch equilibrium techniques and adsorption isotherms models. Adsorption isotherms provide useful information about metals adsorption. However, the adsorption mechanism and the interaction of metals with chemical compounds in solid media cannot be described by isotherm models. To overcome this limitation and gain better information and the mechanism of sorption, research has been performed to evaluate the risk of metal release from metal-loaded solids; it is useful to combine investigations on metals sorption with sequential extraction procedures [8, 9].

Sequential extraction procedures are based on the principle that heavy metals are in different chemical fractions and can be extracted from geochemical phases using appropriate extracting reagents. Sequential extraction procedure in three steps proposed by BCR (Community Bureau of Reference) [3] was developed in order to standardize different extraction schemes described in the literature. It was widely accepted and applied by different authors on different types of solid samples: river sediment, marine, soil, sludge, particles in suspension.

In the last 20 years, the potential risk of metal release from sediment into the aquatic environment has been a topic of focus. A code for assessment of the risk of sediment pollution in aquatic environment was first presented by Perin in 1985 [10]. The risk assessment code (RAC) resulted from the sequential extraction method and different strengths of metal bonds [7]. The potential release risk of metals from sediments in this method (RAC) is evaluated based on metals fractionation and the percent of metal bound in different chemical bonds within the sedimentary phase. Metals within weak bonds are readily released than those within strong ones. Therefore, it is

supposed that the higher metal fraction in exchangeable and carbonate bonds is related to higher remobilization and release risk.

This paper presents the investigations carried out on the quality of surface water and sediment collected from Abrud hydrographic basin affected by long lasting activity extraction of minerals and evolution of ecological risk based on the results of fraction study.

Study area

The study was conducted in Abrud basin (Abrud river, creek Foiesu a tributary of the Abrud river, Aries river) – Rosia Montana - located in the Romania. Rosia Montana is an area where gold has been mined since the Roman Empire. Modern mining involves environmental remediation affected by mining, while previous exploits have left abandoned in a heavily degraded environmental states. The main source of pollution in the environment is acidic water. Exposure of rocks containing sulphur to the action of oxygen and water result in a weak solution of sulphuric acid which dissolves heavy metals from the rock and together with them eventually reach underground or surface waters without any treatment, leading to water pollution.

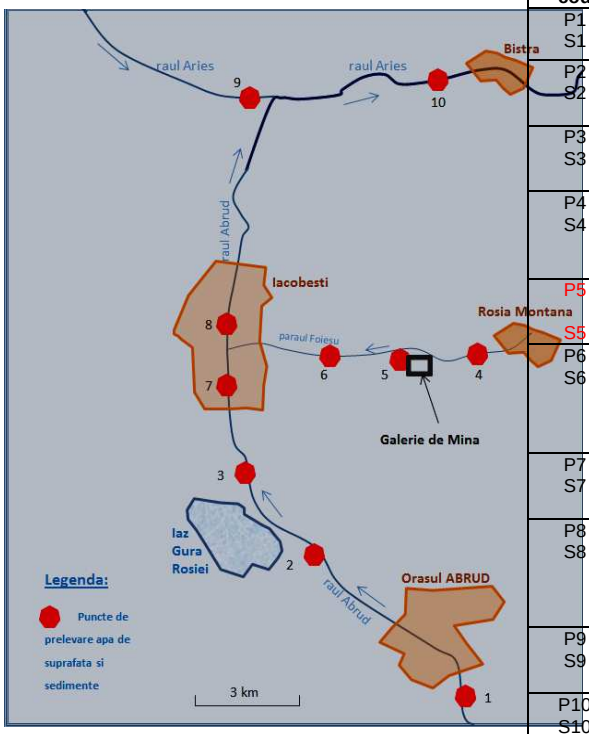
From old mining galleries (of approximately 140 km) Foiesu (Red river) river every second takes 20 litres of acidic water and hence pollution propagates down the river a few miles in to Abrud and afterwards in to Aries river. Because acidic waters, few miles downstream on the river Foiesu and Abrud, flora and fauna are almost completely missing.

EXPERIMENTAL PART

Material and methods

Sampling points were established on the polluted sectors of water bodies in Rosia Montana area, taking into account major sources of pollution (water from mine wastes dumps) and being positioned upstream and downstream of them.

Sampling was carried out in October 2012. Samples from 10 control sections have been taken for surface water and sediments. Location of sampling points and GPS coordinates are shown in Fig. 1.



Sample cod	Sample tip	Sampling point	Coordonates (GPS)
P1 S1	Suface water, Sediment	Abrud river – before entry Abrud	N46 15.326 E23 05.810
P2 S2	Surface water, Sediment	Abrud river – upstream Iaz Gura Rosiei	N46 17.562 E23 03.503
P3 S3	Surface water, Sediment	Abrud river - downstream Iaz Gura Rosiei	N46 18.238 E23 03.266
P4 S4	Surface water, Sediment	Creek Foiesu – Before confluence with discharge water from mine	N46 18.213 E23 06.200
P5 S5	water from mine waste dumps sediment	mine water discharge channel from Mine	N46 18.296 E23 06.007
P6 S6	Surface water, Sediment	Creek Foiesu – downstream confluence with discharge water from mine	N46 18.308 E23 05.678
P7 S7	Surface water, Sediment	Abrud river – Before confluence with creek Foiesu	N46 18.502 E23 03.172
P8 S8	Surface water, Sediment	Abrud river – after confluence with creek Foiesu before the confluence with the river Aries	N46 18.760 E23 03.522
P9 S9	Surface water, Sediment	Aries river – before the confluence with the river Abrud	N46 21.595 E23 04.476
P10 S10	Surface water, Sediment	Aries river after the confluence with the river Abrud	N46 21.779 E23 04.904

Fig. 1. *Location of sampling points and GPS coordinates*

Surface water sampling was done according to SR ISO 5667-6/2000 - Guidance on sampling of rivers and streams and also SR ISO 5667-12/2000 - Guidance on sampling of bottom sediments for sampling sediments.

Samples of surface water and the sediment were tested as follows:

- quality indicators for surface waters were determined: pH, COD, filterable residue, sulphates, ammonium, nitrites, nitrates, chlorides, phosphates, calcium, magnesium, iron, manganese, copper, cadmium, zinc, arsenic;

- quality indicators for sediment were determined: pH, sulphates, iron, manganese, copper, cadmium, zinc, arsenic.

Applicable test methods are standardized and are presented in Table. 1

Table 1

Quality indicators	Analytical equipment	Method of analysis
Arsenic	ICP-MS	SR EN ISO 17294-2005
Ammonium	Spectrophotometric	SR ISO 7150/1-01
Nitrates	Spectrophotometric	SR ISO 7890/3:2000
Nitrites	Spectrophotometric	SR EN 26777:2002/ C91:2006
Cadmium	ICP-MS	SR EN ISO 17294-2005
Calcium	ICP-MS	SR EN ISO 17294-2005
COD	volumetric	SR ISO 6060-96
Chlorides	volumetric	SR ISO 9297-01
Cooper	ICP-MS	SR EN ISO 17294-2005
Iron total	ICP-MS	SR EN ISO 17294-2005
Phosphate	spectrophotometric	SR EN ISO 6878:05
Manganese	ICP-MS	SR EN ISO 17294-2005
Magnesium	ICP-MS	SR EN ISO 17294-2005
pH	electrochimic	SR EN ISO 10523:2009
Filterable residue	gravimetric	STAS 9187-84
Sulphates	gravimetric	STAS 8601-70
Zinc	ICP-MS	SR EN ISO 17294-2005

The results were compared with provisions of MMGA Order no 161/2006 approving the Normative on classification of surface water quality for establishing ecological status of water and quality standards for sediments metals.

Sequential extraction procedure

Sequential extraction offers detailed information regarding origin, method of dispersion, biological and physical-chemical availability, mobility and transport.

The following extraction agents were used: acetic acid 0,11 mol·L^{-1} *p*H 2.8; chloride hydroxylamine 0.5 mol·L^{-1} *p*H 2; ammonium acetate 1 mol·L^{-1} *p*H 2, identifying three fractions:

1) Exchangeable fraction: metals which are adsorbed, obtained by ion exchange processes and related metal carbonates. 2) Bound fraction of Fe and Mn oxides: called "reducible fraction" because metals are released when this fraction is reduced. 3) Bound fraction of organic matter: Called "fraction oxide" because the metals in this fraction are released by oxidation.

Reference material used is certified BCR - 701, is lake sediment produced by Standards, Measurements and Testing Programme - European Commission.

Risk assessment code (RAC)

RAC was used in this study to evaluate the risk of metal release from sediments. This index is independent of background concentration and is applied to assess the metal bioavailability. Table 1 presents the criteria to assess the risk of sediment pollution according to RAC. The percentages of metal partitioning in exchangeable and carbonate fraction provide the RAC criteria. Less than 1% participation of total metals in exchangeable and carbonate fraction is considered safe for the environment, while very high risk has to be considered when metal release in these fractions exceeds 50% of the total metal contents.

Table 1 Criteria for risk assessment code – RAC

RAC - risk assessment code	Percentage of metal partitioning in exchangeable and carbonate fraction (%)
No risk	<1
Low risk	1-10
Medium risk	10-30
High risk	30-50
Very high risk	>50

Result and discussion

- SURFACE WATER

The results of analytical determinations carried out on samples of surface water in the campaign - October 2012 are presented in table 2:

Table 2

No crt	Quality indicators	UM	P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
1	pH	unit pH	6,5	6,13	6,43	5,7	3,1	3,14	6,4	6,4	7,55	7,45
2	COD	mgO_2/l	1,52	1,14	6,84	8,74	3,04	1,9	1,9	11,4	8	14,8
3	Filterable residue	mg/l	464	592	744	756	6720	3960	1312	1340	932	1166
4	Sulphates	mg/l	286,4	302,4	319,7	157	4345,9	2675,2	855,5	856,7	23	66,3
5	$(N\text{-}NH_4^+)$	mgN/l	0,166	0,164	0,16	3,49	0,331	0,847	1,94	1,78	0,187	0,233
6	$(N\text{-}NO_3^-)$	mgN/l	0,39	2,89	2,9	1,98	0,27	0,81	0,58	1,05	0,22	0,61
7	$(N\text{-}NO_2^-)$	mgN/l	0,054	0,051	0,045	0,013	0,051	0,039	0,023	0,032	0,039	0,041
8	Chlorides	mg/l	6,39	20,76	22,36	22,36	33,96	25,56	22,36	24,56	10,96	12,78
9	Phosphate	mgP/l	0,205	0,213	0,215	0,212	0,213	0,22	0,212	0,228	0,213	0,215
10	Calcium	mg/l	110	107,4	120,9	113,5	263,1	155,3	139	148,2	19,3	37,88
11	Magnesium	mg/l	18,72	17,16	17,84	17,88	112,6	34,44	21,88	28,64	2,9	6,28
12	Iron total	mg/l	10,2	4,83	5,32	6,68	269,52	41,19	6,28	9,14	0,72	1,12
13	Manganese	mg/l	0,72	0,48	1,16	13,28	222,76	91,32	1,45	12,12	0,04	0,18
14	Cooper	mg/l	0,46	0,14	0,26	0,18	3, 39	1,4	0,28	0,48	0,005	0,014
15	Cadmium	mg/l	0,006	0,004	0,007	0,042	0,34	0,098	0,008	0,032	0,003	0,003
16	Zinc	mg/l	0,56	0,24	0,32	0,56	34,48	11,12	0,52	2,68	0,004	0,07
17	Arsenic	mg/l	-	-	-	-	0,23	0,049	-	0,022	-	-

Ecological status under Order MMGA no. 161/2006	I	II	III	IV	V
	Very good	Good	Moderate	Low	Very low

Given the positioning of the control points and the obtained results the following conclusions can be drawn:

- Because of Gura Rosia pond there is an influence on the water quality of Abrud river resulting in the high metal concentration in P8 sampling point;
- water Mine intake influences on creek quality Foiesu, implicitly river Abrud; this contribution is significant in terms of all analyzed indicators;
- After confluence Abrud with Aries (P10); a positive dilution is reported found, leading to the following results consorting for the water classification: class I – very good for 7 indicators in Class II - good, for two indicators in Class III - moderate for 3 indicators and Class IV - low for another 3 indicators; it should be noted that the influence of quality classes of Abrud river for different quality indicators that are worse than the receiver, does not negatively influence the previously quality indicators of Abrud river that most of them are of good and very good quality;
- Presence of metals in high concentrations in most sections control analyzed confirms of anthropogenic pollution the area with heavy metals.

SEDIMENTS The results of analytical determinations made under this phase in sediment samples are presented in Table 3:

Tabel 3

Quality indicator	**UM**	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**S7**	**S8**	**S9**	**S10**
pH	unit pH	6,45	5,95	6,16	4,95	3,45	3,55	3,1	3,93	7,16	6,78
Sulphates	mg/kg su	566,18	322,58	131,13	969	10471	920,78	2645	3508,6	560,13	74
Iron total	mg/kg su	21535	15550	17285	19121	44637	37913	28964	20613	21954	14540
Manganese	mg/kg su	211,8	87,57	124,7	129,3	423,8	177,38	668,6	127,4	131,5	82,35
Copper	mg/kg su	87,44	8,76	8,98	5,05	30,51	3,61	28,43	3,63	56,77	3,39
Cadmium	mg/kg su	1,09	1,55	0,99	0,73	0,95	0,78	1,31	0,97	0,14	0,58
Zinc	mg/kg su	103,83	25,24	34,43	34,12	61,98	7,74	55,15	42,46	312,3	58,13
Arsenic	mg/kg su	-	-	-	-	1219	609	-	622	-	-

The quality of sediments taken from the same sections as surface water samples relates to quality standards required under the Ministerial Order nr.161/2006 for metals in sediment fraction <63 μm. Among the metals investigated only for arsenic, copper, cadmium and zinc are limits quality standards are exceeded in samples S1 and S9 (for copper) in samples S1, S2, S3, S5, S7, S8 (cadmium) and the 3 samples S5, S6, S8 (for arsenic).

Sequential extraction

In this paper we extracted only Fraction 1 of conventional BCR procedure on the 10 sediments samples taken. Concentrations of Cu and Cd were determined in extracted fraction 1 (representing mobile forms) and results are presented in Table 4.

Fraction 1 = [M mobil] / [M total] x 100

Tabel 4 - Fraction 1 Cu and Cd

sample	Cu total (mg/kg su)	Cu mobil (mg/kg su)	**Fraction 1 (Cu) (%)**	Cd total (mg/kg su)	Cd mobil (mg/kg su)	**Fraction 1 (Cd) (%)**
S1	87,44	9,02	***10,3***	1,09	0,47	***43,1***
S2	8,76	1,49	***17,0***	1,55	0,52	***33,5***
S3	8,98	1,06	***11,8***	0,99	0,34	***34,3***
S4	5,05	0,59	***11,7***	0,73	0,19	***26,0***
S5	30,51	16,51	***54,1***	0,95	0,41	***43,2***
S6	3,61	1,08	***29,9***	0,78	0,12	***15,4***
S7	28,43	5,95	***20,9***	1,31	0,6	***45,8***
S8	3,63	0,29	***8,0***	0,97	0,33	***34,0***
S9	56,77	14,62	***25,8***	0,14	<0,02	**-**
S10	3,39	0,32	***9,4***	0,58	0,09	***15,5***

These results indicate a higher mobility of Cd compared to that of Cu.

As shown in table 1, the results obtained and processed contained in table 4 lead to the following conclusions:

- Cu is highlighted a:
  - **Very high risk in S5 sample**
  - **Medium risk in S1, S2, S3, S4, S6, S7, S9 samples**
  - **Low risk in S8, S10 samples**
- Cd is highlighted a:
  - **High risk in S1, S2, S3, S5, S7, S8 sample**
  - **Medium risk in S4, S6, S10 samples**

Environmental risk is dependent on the mobility of the two studied metals and river flow rate in sampling points.

In S8, after confluence river Abrud with creek Foiesu (that taks mine water) finds that in terms of the risk is low for Cu and in terms of Cd risk is high. These issues demonstrate that sediment in this set containing compounds mainly of Cu and mobil compounds of Cd. A similar situation is also seen in section S10.

Spatial ecological risk evolutions, are determinated by computation of risk taking in to account specific momentarly and spatial samples.

Another the spatial environmental risk was recorded and made into another campaign in May 2010. The obtained data revealed the following:

- Cu is highlighted a:
  - **Very high risk in S5 sample;**
  - **High risk in S2, S3, S4, S7 and S8 samples;**
  - **Medium risk in S1, S6, S9 and S10 samples;**
- Cd is highlighted a:
  - **Very high risk in S2 and S1 samples;**
  - **High risk in S1, S3, S7, S8 and S10 samples;**

Comparing ecological risk levels in the investigates areas of sampling points from two feels campaigns leads to the following conclusions:

- **for Cu:**
  - maintaining very high risk in S5 point and medium risk in S1, S6 and S9 sampling points;
  - decreased from high risk (2010 Campaign) to medium risk in S2, S3, S4 and S7 sampling points;
- **for Cd:**
  - maintaining high risk in S1, S3, S7 and S8 sampling points;
  - decreased from very high risk to high risk in S2 point, from high risk to medium risk in S10 point and from very high risk to medium risk in S4 point;

Time variation in environmental risk in 10 sampling points highlights a comparable evolution of the two metals:

- in 40% of cases, for Cu and Cd the risk was the same;
- for 60% of cases Cu and for 30% of cases Cd the two metals induce a decrease in the level risk.

CONCLUSIOINS

It is found that the risks induced by the two analyzed metals are changing according to the conditions of surface water flow, sediment composition punctual and weather conditions.

It highlights for both heavy metals the positive evolution of environmental risk over time.

Reproducibility of results relating to environmental risk measured by sequential extraction method demonstrates its validity and validates its use in environmental risk assessment studies.

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