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ADVERSE EFFECTS CAUSED BY PYRITES AND STERILE DUMP FROM CENTRAL POND AREA ON ENVIRONMENTAL FACTORS QUALITY – GROUNDWATER AND SURFACE WATER

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Abstract. The paper presents results of the study on the emission sources based on the analyses of environment characteristics (underground and surface water) in emplacement and estimation of the potential effects on the environment. For assessment of the current situation of groundwater and surface water quality was developed a sampling program and some quality indicators (physicochemicals, biological and microbiological) were determined: for underground water – 7 control wells in Central pond neighbourhood and 1 in pyrites dumps (near Central pond); for surface water – 4 sections placed on the Racos and Sasar rivers upstream and downstream of pyrite dump near Central pond. For all samplings, the indicator values of sulphate, iron, manganese, cadmium are higher than the intervention threshold, and indicate a significant pollution. The pH values in all wells has acid character. For phytoplankton: the density of phytoplankton on the Sasar river (after confluence with the Racos river) is lower downstream of pyrite waste dump than the downstream the Racos section. Zooplankton is more sensitive to toxic action of heavy metals than phytoplankton, and it is absent in all control sections.

Keywords: biotic and non-biotic components, anthropic influence, aquatic ecosystems, waste dump, groundwater.

AIMS AND BACKGROUND

Pyrites dumps and Central pond in materials content – pyrite and sterile – represent pollution sources on environmental emplacement proximity.

The main effect that the dump generated on environment as long as it existed is the soil pollution by occupation of the land under the dump (the dump is realised without impermeablilisation of the land) and in neighbourhood cause of the

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sterile transpotation from pond by precipitation through rain wash and breath of wind in droughts periods.

The dump material participate in chemical reactions influenced by natural factors and this generates negative effects on soil, underground and surface waters.

Pyrite dumps represent major pollution sources for soil, first, because a large quantity of sterile and pyrites is stored straight on soil (this is taking up important surfaces) and second, cause of the emission in air and rain wash in rainy periods[1,2].

Taking over the materials from dumps and Central pond represent an alternative to make the depollution of the emplacements by eliminating the sources.

EXPERIMENTAL

POLLUTION SOURCES

The Central pond is localised in the east of the Baia Mare town and it was used as sterile deposit for almost 14 years. The sterile resulted from the 'Flotatia Centrala' plant since 1976 the Central pond is conserved.

The surface of the pond on embankment level is almost 50 ha and the sterile quantity from the pond is over 8 million tons. The present height level of the sterile depot is almost 290 mdMN (MN = Black sea).

Looking of the deposited materials and the age of the depots from the area, the present depots emplacement represent pollution sources of environment – surface water and underground water. For those two environment components the causes of pollution are as follows:

- The flow's water on waste dumps and pond embankments;
- The exfiltrations through depots slope;
- The infiltrations of drainage waters;
- The precipitation of waters drainage in surface water through sewer;
- The dispersion of fine particles – from the depots – in droughts periods, and laying down on the soil in neighbourhood; the low deep of groundwater in emplacement may cause the source of pollution for soil to became a source of pollution for underground water.

As an indirect source of pollution is the infiltrations in lands of depots emplacement – infiltration which washed and dissolved the chemical substances from deposited materials.

SURFACE WATER QUALITY

The Racos river, affluent of the Sasar river, is localised in the north of the Central pond.

For establishing the quality of the surface water and sediments of the Sasar and Racos rivers some physicochemical and biological parameters of the water samplings in September 2003, in the following control points were analysed:

– SAR – the Sasar river upstream of pyrites waste dump (water and sediment);

– SAH – the Sasar river downstream of pyrites waste dump (water and sediment);

– R – the Racos river upstream of pyrites waste dump (water and sediment);

– RAH – the Racos river downstream of pyrites waste dump (water without sediment because in that section the river has a controlled flow);

The analysed indicators of the samples were as follows:

For surface water:

– physicochemical indicators: pH, temperature, dissolved oxygen, sulphur, sulphate, cyanides, iron, copper, arsenic, lead, manganese, zinc, cadmium, nickel;

– bacteriological indicators: total coliform bacteria, faecal coliform bacteria;

– biological indicators: numerical density and biomass for phytoplankton and zooplankton.

For sediment:

– physicochemicals indicators: cyanides, iron, copper, arsenic, lead, manganese, zinc, cadmium, nickel;

– bacteriological indicators: total coliform bacteria, faecal coliform bacteria;

– biological indicators: numerical density and biomass for benthonic macroinvertebrates.

RESULTS AND DISCUSSION

Quality classes meanings are as follows:

• Ist class. The admissible limiting values reflect the natural reference conditions or the basic concentration. In case of hazardous substances (synthetics), the detection limit of the method of analysis is adopted. In the case of the natural origin substances, heavy metals including, the reference conditions refer to the natural basis which is established in the hydrographic basin. The reference sections correspond to those locations on which the pollutant influence is under 10%.

• IInd class. This class limits are corresponding to target-values (reference objectives) and reflect the aquatic ecosystem protection quality condition. For other toxic compounds, the target values will be established on the basis of the risk assessment.

• IIIrd-IVth classes. The limits corresponding to these classes are from two to five times more than those of the reference objective and reflect the pollutants contribution.

The analyses of the non-biotic components (physicochemical indicators – Table 1) and biotic components (bacteriological and biological indicators – Table 2) for the surface water in the aquatic ecosystems of the Sasar and Racos rivers allow to draw the following main conclusions (Table 3):

- The Sasar river upstream waste dump is between classes II and III – looking of the analysed indicators, except sulphate – class I, cadmium (class IV) and iron (class V), downstream of waste dump – Sasar is impure – the concentrations of sulphate, iron, lead, zinc, cadmium is over class V of quality;
- The Racos river quality is between classes II and III looking of the analysed indicators: nickel, copper, arsenic, lead, dissolved oxygen, the concentrations of sulphates, total iron, zinc, cadmium are over class V of quality. Those are significant differences for the river water quality upstream and downstream waste dump;
- The Racos river's contribution on the Sasar river pollution is evident in sulphate, zinc and cadmium concentration. The lead concentration is in class III of quality, similar with lead concentration upstream waste dump;

Table 1. Physicochemicals characteristics of surface water samplings from the Sasar and Racos rivers

Indicator	Measuring unit	Sampling				Measurements incertitude (mg/l)
		SAR	R	RAH	SAH	
pH		6.87	4.20	4.55	6.73	0.02
Temperature	^{o}C	17.12	13.80	15.10	13.70	–
Dissolved oxygen	mgO_2/l	4.76	6.33	4.64	4.66	0.02
Sulphate (SO_4^{2-})	mg/l	78.09	2857.46	1833.64	442.77	±10
Sulphur (S^{2-})	mg/l	<0.02*	< 0.02*	< 0.02*	< 0.02*	±0.006
Cyanide easy liberated	mg/l	<0.001*	< 0.001*	<0.001*	<0.001*	±0.001
Total cyanide	mg/l	0.0236	0.0236	0.017	0.017	±0.001
Total iron	mg/l	1.35	97.45	7.76	2.55	±0.08
Arsenic	mg/l	<0.001*	< 0.001*	<0.001*	<0.001*	±0.0008
Lead	mg/l	<0.01*	< 0.01*	<0.01*	0.13	±0.06
Zinc	mg/l	0.11	4.85	1.94	1.23	±0.02
Manganese	mg/l	0.29	54.51	12.26	2.83	±0.01
Cadmium	mg/l	<0.005*	0.011	0.011	0.006	±0.01
Copper	mg/l	0.039	0.14	0.17	0.19	±0.05
Nickel	mg/l	<0.005*	0.087	<0.005*	<0.005*	±0.05

* Under detection limit (UDL).

Table 2. Bacteriological and biological characteristics of surface water samplings from the Sasar and Racos rivers

Indicator	Measuring unit	Sampling			
		SAR	R	RAH	SAH
Bacteriological indicators					
Total coliformes bacteria	nr/100 cm^3	33×104	20	330	13×104
Faecals coliformes bacteria	nr/100 cm^3	14×103	absent	110	8×103
Biological indicators					
Phytoplankton					
Numerical density	nr/dm^3	106×103	44×103	38×103	22×103
Biomass	mg/dm^3	0.076	0.03	0.013	0.0098
Zooplankton					
Numerical density	nr/dm^3	absent	absent	absent	absent
Biomass	mg/dm^3	absent	absent	absent	absent

Table 3. Admissible limit values on quality classes according to 1146/2003 Normative for surface water

Indicators	Measuring unit	Admissible limit value on quality classes according to 1146/2003 Normative				
		I	II	III	IV	V
Physicochemical indicators						
pH		6.5-8.5				
Temperature	°C	no norms				
Dissolved oxygen	mgO_2/l	7	6	5	4	< 4
Sulphate (SO_4^{2-})	mg/l	80	150	250	300	> 300
Sulphur (S^{2-})	mg/l	no norms				
Cyanide easy liberated	mg/l	no norms				
Total cyanide	mg/l	no norms				
Total iron	mg/l	fond*	0.1	0.3	1.0	> 1.0
Arsenic	µg/l	fond	5	10	25	> 25
Lead	µg/l	fond	5	10	25	> 25
Zinc	µg/l	fond	100	200	500	> 500
Manganese	µg/l					
Cadmium	µg/l	fond	1	2	5	> 5
Copper	µg/l	fond	20	40	100	> 100
Nickel	µg/l	fond	50	100	250	> 250
Bacteriological indicators						
Total coliformes	nr/100 cm^3	500	10000	–	–	–
Faecals coliformes	nr/100 cm^3	100	2000	–	–	–
Biological indicators (phyto-, zooplankton)	–	no norms				

* Reflects the natural reference conditions of the basic concentration.

• For phytoplankton – the numerical density is variable in the Racos river – upstream and downstream waste dump in similar limits – 44-38 × 10 000/cm^3. Sasar – downstream waste dump, after confluence with Racos has a frequency of phytoplankton of 22×10 000/ cm^3, smaller than downstream Racos (cause of high concentration of iron, lead, zinc, cadmium – over class V of quality);

• Zooplankton – more sensitive to the toxic action of heavy metals – is absent in all control sections;

• The bacteriological indicators: total coliformes and faecal coliformes – show class I of quality.

NON-BIOTIC AND BIOTIC COMPONENTS FOR SEDIMENT

For sediment samples – the physicochemical indicators (copper, lead, zinc, cadmium, arsenic) – only copper and arsenic content is over the limits (cadmium in the Sasar river and arsenic – in the Sasar and Racos rivers), for the last indicators the values are within the admissible limits (Tables 4 and 5).

Table 4. Chemical, bacteriological and biological characteristics for sediment samplings from the Sasar and Racos rivers

Indicators	Mesuring unit	Samplings				Measurements incertitude (mg/l)
		SAR	R	RAH	SAH	
Chemical indicators						
Cyanide easy liberated	mg/kg	0.201	0.15	–	0.16	± 0.001
Complex cyanides	mg/kg	0.201	0.42	–	0.16	± 0.001
Total iron	mg/kg	34626.81	30231.24	–	40103.58	± 0.08
Lead	mg/kg	1174.4	615	–	1972.7	± 5
Zinc	mg/kg	4662.4	836.5	–	5839	± 5
Manganese	mg/kg	1575.3	797.5	–	2364	± 5
Cadmium	mg/kg	13.06	2.03	–	11.9	± 0.5
Copper	mg/kg	1098	382.3	–	1615	± 5
Nickel	mg/kg	21.04	<1	–	24.24	± 5
Bacteriological indicators						
Total coliforms	nr/100g	3048	absent	–	111	–
Faecals coliformes	nr/100g	1651	absent	–	37	–
Biological indicators benthonic macroinvertebrates						
Numerical density	nr/dm^3	1496	30	–	504	–
Biomass	mg/dm^3	1.44	0.09	–	0.34	–

Table 5. Admissible limit values for sediment according to 1146/2003 Normative

Indicator	M.U.	Limit concentration
Physicochemical indicators		
Cyanide easy liberated	mg/kg	no norms
Complex cyanides	mg/kg	no norms
Total iron	mg/kg	no norms
Lead	mg/kg	90
Zinc	mg/kg	300
Manganese	mg/kg	no norms
Cadmium	mg/kg	3.5
Copper	mg/kg	200
Nickel	mg/kg	no norms
Bacteriological indicators		
Total coliformes	nr/100g	no norms
Faecals coliformes	nr/100g	no norms
Biological indicators (Benthonic macroinvertebrates)		no norms

The benthonic macroinvertebrates from the Racos and Sasar rivers sediments are present as a dominant group – *chirominides* – specific for polluted water, but this group is not affected.

UNDERGROUNDWATER QUALITY

The quality of the underground water and the evolution in time was investigated in September 2003 and February 2004. The investigation consisted in determination of the principal value of quality indicators for groundwater samples.

The samples were from 7 control drillings (FC1-FC7) – near the Central pond and 1 control drilling (FC8) – near waste dump – in pond's neighbourhood.

The parameters analysed were: pH, SO_4^{2-}, S^{2-}, iron, arsenic, zinc, manganese and lead.

The physicochemicals characteristics for the control drillings FC1-FC8 are demonstrated in Table 6.

The comparison of the results with the norms (CMA) leads to the following conclusions:

– for all the samples analysed, the values of the indicators – sulphate, iron, manganese and cadmium are higher than the intervention threshold, thus indicating a significant pollution;

– for the samples from the control drillings FC5, FC6, FC7, FC8 the values of lead and copper content are higher than intervention threshold, thus suggesting a significant pollution;

– the pH values are in almost all drillings very high.

Table 6. Some physicochemical indicators for the control drillings FC1-FC8

Indicator	MU	Sample								
		FC1	FC2	FC3	FC4	FC5	FC6	FC7	FC8	CMA
pH		6	5.5-6.2	6-7	6-6.5	4.0-4.5	6.5-7.2	7-7.9	6.5-7.55	6.5-7.4
SO_4^{2-}	mg/l	1388-1397.45	345-364.58	345.6-2012	1642.7-2530	1432.02-2257	798-1272.35	1476.46-3768	1603-5170	200
S^{2-}	mg/l	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0
Fe	mg/l	2.4-25	22-25	2-50	30-72	5-14	50-175	5-100	20-30	0.1
As	mg/l	< 0.001	< 0.001	< 0.001-0.0013	0.003-0.012	< 0.001	< 0.001-0.002	0.001	<0.001-0.007	0.05
Pb	mg/l	< 0.01-0.02	< 0.01	< 0.01	0.02-0.009	0.2-0.22	0.04-0.21	0.18-0.46	< 0.01-0.22	0.05
Zn	mg/l	<0.001-0.06	0.015-0.29	0.037-0.12	0.36-1.2	1.5-4	0.007-0.34	0.8-3	0.01-0.39	5
Mn	mg/l	1.75-2.4	4.85-5.48	1.19-10.3	26.2-38.09	16.57-20	10.62-23	1.35-13	8.07-11	0.05
Cd	mg/l	0.002-0.019	0.005-0.017	0.008-0.02	0.009-0.013	0.02-0.021	0.01-0.014	0.013-0.04	<0.001-0.016	0.005
Cu	mg/l	0.021-0.032	0.019-0.025	0.025-0.03	0.035-0.044	0.312-0.47	0.05-0.188	0.2-0.535	0.0047-0.09	0.05

CONCLUSIONS

The groundwater and surface water in almost all the samples are highly polluted with heavy metals. The flora and fauna are affected, too. The density is lower cause of effects of pollution. The process has a very important impact both on the environment and human health.

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