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STERILE DEPOSITS IMPACT ON ENVIRONMENT QUALITY IN THE MOLDOVA NOUA REGION

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Abstract. The accelerated industrialisation enforced by the communist regime strongly affected the region of Banat mountains, an area with strong traditions in mining activities and concentrated important resources. A strong mining industry was established, with mining centres at Moldova Noua (complex ores), Cozla, Baia Noua (coal), Iliseva (radioactive ores), etc. The present article is trying to quantify the effects on environment quality of the sterile deposits from the Moldova Noua region, resulted from the complex ores plant from Moldova Noua and mining activities developed in Baia Noua. The analytical methods to be used in the present study are inductively coupled plasma – optical emission spectrometry for heavy metals analysis and gas chromatography – mass spectrometry for PAHs.

Keywords: sterile deposits, soil contamination, heavy metals.

AIMS AND BACKGROUND

Soil contamination by waste deposits is one of the most severe aspects of environmental pollution in Romania, independently of the origin sources (domestic or industrial activities) or type of disposal (organised landfill or hazardous deposits)[1,2]. This fact is the consequence of the poor state of the existing waste deposits in Romania and of the significant costs involved by the establishing of a new landfill according to the international regulations.

An area with tradition in mining activities, Iron Gates Natural Park also has significant problems related to habitats destruction and malfunctions in ecosystems equilibrium due to human activities. The region of the Iron Gates reservoir lock was declared a protected area – Natural Park through Ministry of Water, Forests and Environmental Protection Order 84/1998, due to its floristic and zoological importance. The declaring of this protected area was purely theoreti-

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cal, no restrictions on the economic activities were being enforced and no rehabilitations of the damaged areas being performed[3,4].

Baia Noua coal sterile deposit (BN) is located in the northern limit of Baia Noua village and has a reduced surface (about 0.5 ha). The activities performed by the Moldova Noua plant (MN) for copper ores primary processing include crushing, beating and wet flotation. The deposit is located close to the Danube shore and has a surface of about 250 ha, which includes a settling pond (Lunca Dunarii, about 60 ha). Due to poor isolation of it, contaminations of Danube river sediments were reported by Matache et al.[5]

EXPERIMENTAL

In order to properly quantify the pollution effects on soil quality, the team opted for an exploratory sampling that according to literature seemed to be the most adequate. The sampling plan was designed according to the presumed causes of disturbances, considering the disturbances nature and the natural division of the landscape[6,7].

Two sampling depths were used for each vertical: at 5 cm and at 35 cm for the MN deposit. For the deposit from BN, only three sampling sites were chosen due to its small surface and only the sample from 5 cm. For the MN deposit, together with five sampling sites, leachate samples were also collected and samples from the plants used for sterile dust immobilisation. For both deposits, sterile composition was also studied.

SAMPLING SITES DESCRIPTION

BN. All sampling points are located at deposit basement, in north, west and east, the access road to the deposit being in the southern part. Sample No *1* was taken from a mechanically disturbed soil, in which the soil horizons were mixed with sterile from the deposit. Samples Nos *2* and *3* showed no signs of sterile mixing.

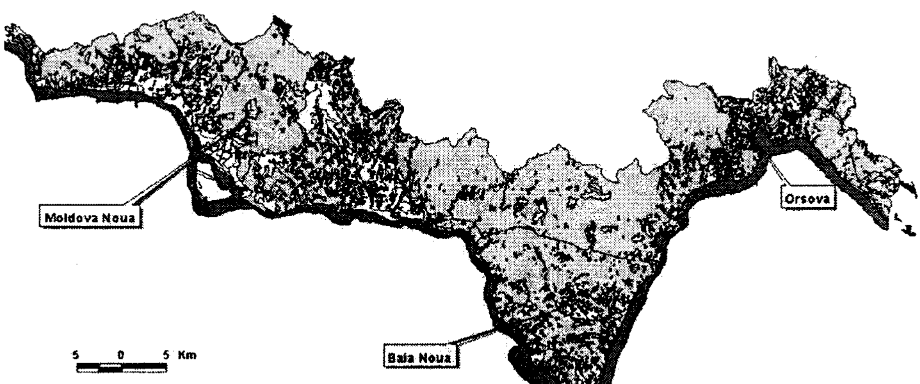

Fig. 1. Iron Gates Natural Park

MN. Sampling points Nos *1* and *2* are characterised by red colour of the upper part of the soil horizon, lack of vegetation and reduced humidity. It was impossible to say whether the sampling was performed from a contaminated soil or from a sterile stratum. Sampling points Nos *3-5* showed well-developed weed vegetation and a high humidity for a dark-brown soil colour. Leachate and water samples were collected as follows: *1* – Bosneagu river; *2* – Lunca Dunarii pond; *3* – primary settling pond; *4* – leachate from the pipes system; *5* – leachate accumulated on the ground, close to industrial facilities; *6* – leachate accumulated on the ground in the northern part of the deposit.

SAMPLES PROCESSING

Soil samples were digested in an open system with concentrated acids (hydrochloric, hydrofluoric, perchloric, nitric), then, filtered on Whatman No 54 paper, the residue suffers an alkaline melting with borax and sodium carbonate. The analytes are determined in both filtrates and the total was calculated by adding the two values. This digestion method was successfully used in several studies of environmental assessment[8-11]. Concentration of microelements was quantified using inductively coupled plasma – optical emission spectrometry (ICP-OES). Instrumentation and operating conditions for the ICP-OES spectrometer are listed in Table 1a. The detection limit of the method was 1 μg/kg. PAHs are extracted with methylene dichloride from the soil samples at pH = 3. For analysis is used a gas chromatograph HP 5890 coupled with a mass spectrometer with quadrupol HP 5972, series II. The parameters are displayed in Table 1b.

Table 1a. Operating conditions for the ICP-OES instrument

Plasma generator	
Cooling gas flow-rate	12 ml/min
Auxiliary gas flow-rate	0.8 l/min
Gas flow-rate	1 l/min
Coil radio frequency	27.12 MHz
Spectrometer	
Air polychromator	210-480 nm
Air polychromator	210-590 nm
Vacuum polychromator	165-210 nm
Air monochromator	210-480 nm
Height observation	12 mm

Table 1b. Operating conditions for the GC-MS instrument

Column type	HP1, 5% phenyl-methyl-siloxan
Length	30 m
Diameter	0.25 mm
Depth	0.25 μm
Carrier gas	He
He flow-rate	2 ml/min

RESULTS AND DISCUSSION

BN coal sterile deposit. The analyses performed in order to determine sterile composition emphasised high concentrations of aluminium, chromium and nickel that might contaminate the soils surrounding the sterile deposit (Table 2). Anyway, sample *1* (anthroposoil resulted in the mixture of forest soil and sterile washed from the deposit) clearly emphasises the input of the sterile to nickel concentration in the sample. Thus, for chromium, copper, nickel and zinc, concentrations in sample *1* are similar with those determined in the sterile samples and much higher than in samples *2* and *3* (Fig. 2). From the four elements, only nickel exceeds the limit admitted by the Romanian legislation (Table 3).

Table 2. Composition of the sterile from BN deposit

Trace element	Concentration (ppm)
Aluminium	1390
Cadmium	0.3167
Chromium	28.0167
Copper	8.4667
Molybdenum	2
Nickel	35.9
Lead	7.55
Antimony	0.76
Tin	1.2667
Zinc	10.93

Table 3. The Romanian regulation standard for trace elements in soils

Element	Normal value	Element	Normal value
Aluminium	–	nickel	20
Cadmium	1	lead	20
Chromium	30	antimony	–
Copper	20	tin	20
Molybdenum	2	zinc	100

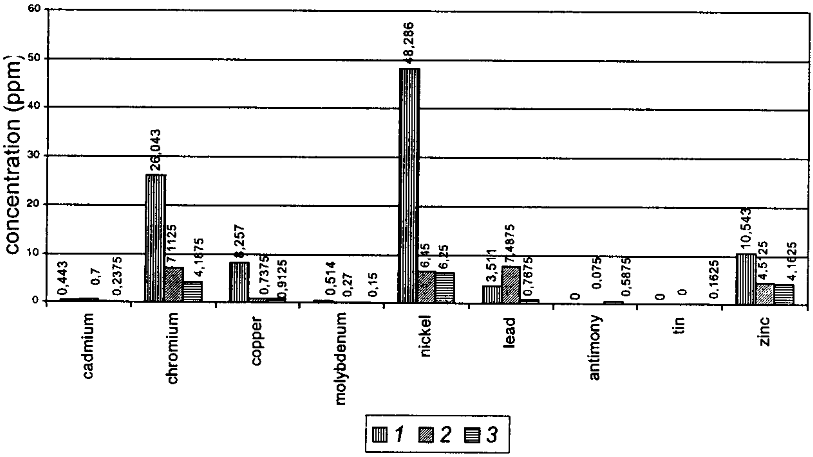

Fig. 2. Trace elements concentration in soil samples from BN

Total PAH concentration in all sterile samples was lower than the accepted limit (0.5 ppm).

High amounts of trace elements were determined in a water sample from the waste waters evacuated from the mine. Its low pH (around 5.4) enhanced the dissolution of important amounts of trace elements in the waste waters and indirectly in the Tisovita creek. No problems were generated by the PAHs concentration in water sample, despite their presence (Table 4).

Table 4. Trace elements concentration in waste waters released from the BN mine. Comparison with the Romanian and USEPA standards for surface waters

Trace element	Standard values (ppm)		Concentration in water samples (mg/l)
	EPA	STAS[a] 1342/91	
Aluminium	0.05	–	2.077
Antimony	–	–	0.0014
Cadmium	–	0.003	BDL[b]
Chromium	0.112	0.5	BDL
Copper	0.28	0.05	BDL
Iron	4.6	0.3	7.18
Molybdenum	5.4	0.05	0.0133
Manganese	3.23	0.1	0.581
Nickel	0[c]	0.1	0.2081
Lead	0.14	0.05	BDL
Zinc	1.18	0.03	0.0155
PAHs (total)	2.0×10^{-4}	2.0×10^{-4}	10^{-5}

[a] STAS – Romanian Standard; [b] below the detection limit; [c] EPA standard considers that no nickel should be found in surface waters.

MN sterile deposit. For water and leachate accumulated on the soil, some of the elements concentration was higher than the maximum admitted concentrations (CMA) from the Romanian standard for surface waters as it follows: aluminium and iron (samples *1–6*); cadmium, chromium and nickel (sample *5*); copper and zinc (samples *1* and *5*); lead (samples *1*, *3* and *5*). It is possible to notice that all mentioned elements exceed the CMA in sample 5, with huge values for iron and copper (1281 ppm and 69.8 ppm). Considering that calcopyrite ($CuFeS_2$) is the raw material processed in the plant, it is almost a certitude what the leachate source is. In what regards the metals concentration in soil samples, the analysis revealed the following aspects:

– normal values registered for cadmium, chromium, nickel, lead, tin, antimony and zinc;

– concentrations exceeding normal values were registered for copper – sampling site 1 (5 and 35 cm), site 2 (35 cm), site 3 (5 cm), site 4 (5 and 35 cm), site 5 (5 and 35 cm) and molybdenum – sites 2 and 3 (5 cm); concentrations exceeding

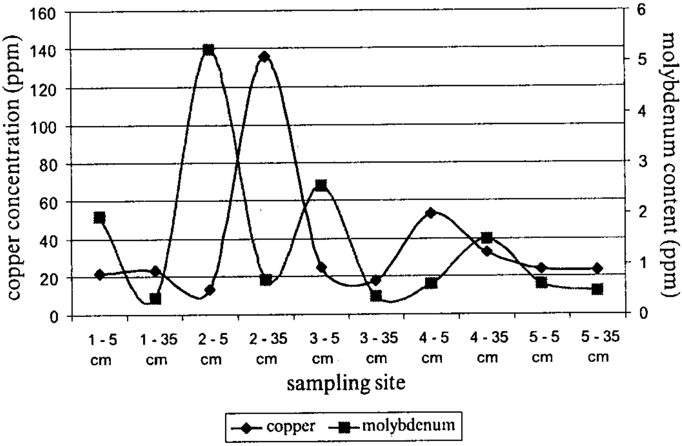

Fig. 3. Copper and molybdenum content profiles

alert rank were registered for copper – site 2 (35 cm) and molybdenum – site 2 (5 cm) (Fig. 3).

Molybdenum, as molybdenite, appears frequently associated to minerals such as pyrite or calcopyrite[12]. It is possible to notice that in sampling site 2, copper and molybdenum concentrations are anti-correlated (at 5 cm, high concentration of molybdenum, but a concentration of cooper significant lower than in the other samples, but especially the one from 35 cm, where the concentration of molybdenum decreases drastically). The correlation is respected in a lower percent for the last samples.

CONCLUSIONS

Soils contamination appears frequently in areas located close to sterile deposits. In both considered case studies, at least one of the indicators is exceeding the normal values of concentration in soils (nickel in coal sterile deposit from Baia Noua, copper and molybdenum for the deposit in Moldova Noua). The use of phytoremediation techniques can be a solution for limiting sterile deposits effects on surroundings, but conditioned by the full performing of it (seeding, plants growth, harvesting, harvest combustion, microelements recovering from ash). Trace elements inputs from the sterile deposits are affecting also Bosneag river and on long term the Danube river ecosystems (through sediments contamination, their dissolution when water chemistry changes determining trace metals releasing into the water), due to a poor isolation and its improper localisation.

The sterile deposits require a continuous careful monitoring in order to emphasise any accidental release of toxic compounds into the environment components (e.g. groundwater contamination, aquatic ecosystems perturbation, etc.).

REFERENCES

1. R. LACATUSU, I. RISNOVEANU, B. KOVACSOVICS, M. LUNGU: Stiinta Solului, 34 (2000) (in Romanian).
2. M. MATACHE, L. ROZYLOWICZ, M. ROPOTA: Wastes Deposits and Their Impact on Environment Quality. Case study: Sfantu Gheorghe city, Covasna county. In: Proc. of 5th Symp. on Envir. Contam. in Central and Eastern Europe, Prague, September 12–14, 2000, published by the Institute for International Cooperative Environmental Research, Florida, USA.
3. MAPPM – Ministry for Waters, Forests and Environmental Protection, 1998, No 84/30.01.1998.
4. CCMESI – Centre for Environmental Research and Impact Studies. Biota and Non-biota Resources Assessment in the Iron Gates Natural Park, 2002, www.portiledefier.ro.
5. M. MATACHE, C. PATROESCU, I. V. PATROESCU-KLOTZ: Revue de Chimie, **53**, September (2002).
6. J. CREPIN, R. L. JOHNSON: Soil Sampling for Environmental Assessment in Soil Sampling and Methods of Analysis (Ed. R. M. Carter). LEWIS Publishers, Boca Raton, 1993, p. 823.
7. J. C. DAVIS: Statistics and Data Analysis in Geology. 3rd ed., John Wiley, 2002, p. 638.
8. C. PATROESCU, I. V. KLOTZ, A. I. STOICA, M. MATACHE: Environmental Quality of the Danube River between Baziah and Iron Gates. EUROANALYSIS X, Basel, Switzerland, 1998.
9. M. ROPOTA, G. MACOVESCU, C. PATROESCU: Revue de Chimie, **8**, 572 (2000).
10. M. ROPOTA, M. MATACHE, P. CAPOTA, C. PATROESCU, M. BOSCAIU: Analytical Study on the Heavy Metals Concentration in Biological Samples from the Danube River Ecosystem. In: First International Conf. on Analytical Chemistry, Brasov, 2000.
11. F. S. ZHANG, S. YAMASAKI, K. KIMURA: Rare Earth Element Content in Various Waste Ashes and the Potential Risk to Japanese Soils. Envir. Int., **27**, 393 (2001).
12. minerals.galleries.com.

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