

GEOCHEMICAL CHARACTERIZATION OF SOME OLD MINE WASTE DUMPS FROM BAIJA MARE AREA AND THEIR INFLUENCE ON THE NATURAL VEGETATION

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Abstract. The mineralogical composition of the mine waste dumps influence the chemical composition of the products resulted from the specific weathering reactions of the metallic and gangue minerals. The geochemistry characteristics of the mine waste dump influence natural installation of the plants species. The chemical analysis of the material and of the natural vegetation from the mine waste dumps emphasizes the high concentrations of: Pb, Cu, Zn, and Mn. The plants which adapted to the particular conditions of the different zones in the studied mining sites can be used as vegetable material for the mining waste rehabilitation. The study of the flora from the old mine waste dumps offers information about the chemistry of the substratum which favoured the installation of the vegetation and about the plants species associations.

Keywords: old mine dumps, heavy metals, essential nutrients, adapted natural plant species, dump rehabilitation.

1. INTRODUCTION

The chemical composition and the interactions with hydrological, chemical and biological factors of the mineral aggregates from the mine waste dumps, represented by rock fragments and sulphides, determine a high concentration in: Pb, Cu, Zn, and Mn. The rehabilitation of the surfaces covered by mine waste products by covering them with vegetation is the optimum method, but in a longer period than the rehabilitation techniques, (Setyawan et al. 2002). Installing the vegetation in a natural way on the old mine waste offers the opportunity to study the local chemical conditions in the dump and their influence on the vegetation, (Alvarez, H., et al 1974, Sitášová, E. 2003). The study of natural vegetation recovery on waste dump has successfully been used in the old coalmine waste, (Cheng, J. 2005).

For this purpose, we studied the mine waste dumps, where the storage activity has stopped from decades.

The analysis of the metal content of the material from the mine waste dumps and of the naturally installed vegetation, revealed the adaptation of some species of

plants to the particular conditions of high concentration in heavy metals. The plants which adapted the best to the particular conditions from the mine waste dumps can be used as material for the installation of the vegetation in a short time. The study of the flora from the old mine waste dumps gives information on the chemistry of the substratum that favoured the installation of the species of plants.

2. GENERAL PRESENTATION OF THE OLD MINE WASTE DUMPS

The study sites are situated in the western part (Nistru zone) and in the central part (Red Valley) of the Baia Mare area, (Fig.1). The metallogenetic district Baia Mare represents the NW part of the Neogene Volcanic Chain inside the Carpathian Mountains. This district is the most productive and includes gold and base-metal ore deposits.

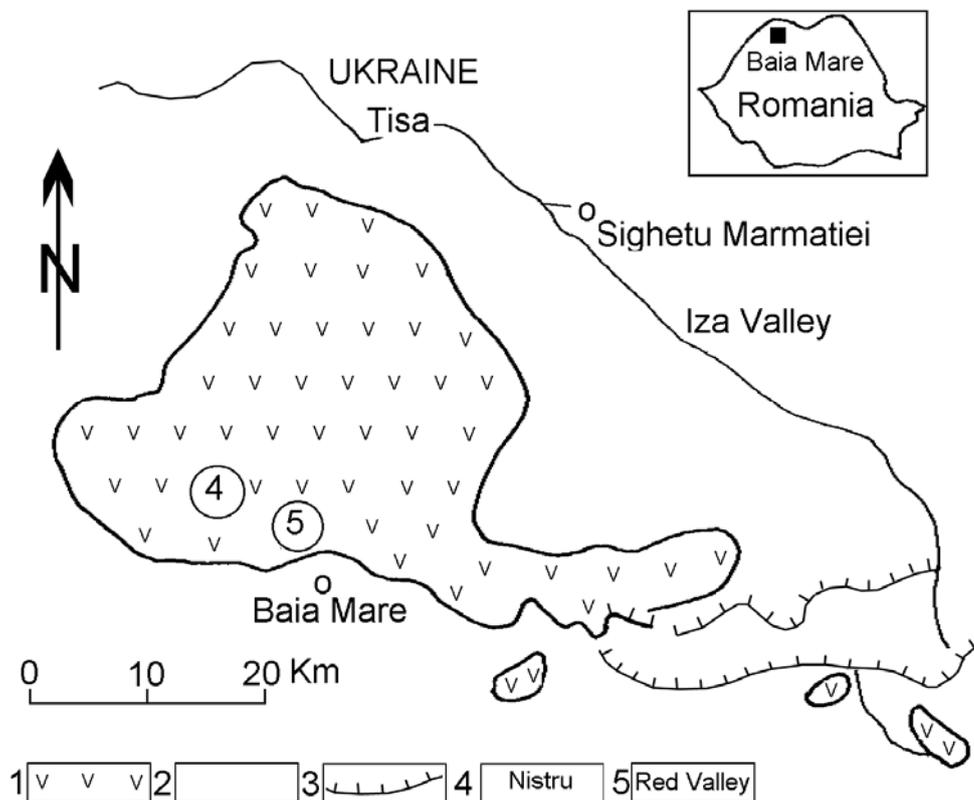


Fig. 1. Localization of the studied mine waste dumps in the Baia Mare area: 1-volcanic rocks, 2-sedimentary rocks, 3-nappe, 4-Nistru zone, 5- Red Valley zone.

2.1. The mine waste dump from the Nistru zone

In the Nistru zone there have been studied two mine waste dumps from the Nistru Valley: the Partially Rehabilitated dump of the base-metal veins and the "Old

mine dump" of the cupriferous vein (Nepomuc vein).

The Partially rehabilitated dump from the Nistru Valley is situated at approximately 500 m from the Nistru village. The material from the mine waste dumps consisted in a mixture of weathered ore-deposits and rocks with various particle sizes, from clay to large fragments, results from the exploitation activity of the base-metals ore mine, representing the NE part of the Nistru area. The rehabilitation works consisted in the installation of some stick fences together with the planting of *Betula verrucosa*. At the surface, the material of the mine dump is inhomogeneous as composition and size particles due to the washing of the fine material deposited in the depth zones. At the surface zones of the mine dump, the concentration in metals is lower due to the increased migration induced by the flowing waters.

"The Old Mine Dump" of the Nepomuc vein is situated at the distance of approximately 2.3 km up from the Nistru village, close to the zone where the Nepomuc vein outcrops. The mine dump storage activity stopped 80 years ago. The material of the Old Mine Dump from the Nistru Valley consists in pyroxene andesites fragments, sedimentary and volcano-sedimentary rocks. Together with these, there could also be found cupriferous mineral fragments represented by vein quartz impregnated with sulphides: pyrite and chalcopyrite, subordinated sphalerite and galena, completely substituted by the iron hydroxides. The leant of these rock and mineral fragments is represented by the clay material. The mine waste dump material is also structureless.

On the mine dump there can be observed the effects of the natural installation of the vegetation and also an evolution of the spontaneous installation of the flora on the entire mine dump surface.

2.2. The mine waste dump from the Red Valley (400 m altitude)

The Red Valley zone belongs to the central part of the southern slope of the Gutai Mountains, being situated at approximately 2 km north-east from Baia Mare (Fig.1). The blank storage activity stopped here in 1988. The deposited material consists of volcanic rock fragments (quartz andesites, pyroxene andesites), pyroclastic rocks, sedimentary rocks and also abundant mineral fragments characteristic to the gold mineralization. These are represented by vein quartz associated with calcite and sporadically with barite. The metallic minerals can be found in small quantities and are represented by: pyrite, chalcopyrite, galena and marcasite. Most of them are transformed in secondary compounds.

Generally, in this zone there can be observed the effects of the natural installation of the vegetation, especially on the horizontal platform of the mine dump and in the marginal zones of this platform.

3. CHEMICAL FEATURES OF THE MATERIAL DEPOSITED IN THE STUDIED MINE WASTE DUMPS

The chemical analyses carried out on the samples from the studied mine waste dumps emphasized the content in heavy metals of the material deposited.

The chemical analyses established very different contents for the studied heavy metals. In order to evaluate the chemical features of the material from the mine waste

dumps, samples were taken from every dump at 0.05 m depth and at 0.3 m depth. The results are shown in tables 1 and 2. The concentrations in the heavy metals are very different in the material of the mine waste dumps. By analyzing the contents in heavy metals, comparatively for the two zones, the Nistru zone and the Red Valley zone, very important differences have been observed for all the metals. The Nistru zone has higher contents than the Red Valley. For each of the zones the content in metals increases with the depth.

Table 1. Chemical composition of the material from the mine waste dumps from Nistru zone

Sample	Depth	Heavy metals (ppm)			
		Pb	Cu	Zn	Mn
NO1-	0.05m	379.41	19.67	22.35	-
NO2-	0.05m	278.57	60.34	205.11	1233.33
NO1-	0.3m	589.20	74.39	303.51	210.00
NO2-	0.3m	600.14	233.21	502.30	1664.29
NPR3-	0.05m	91.17	96.72	42.35	409.83
NPR 4-	0.05m	115.12	58.23	186.21	1253.11
NPR 3-	0.3m	198.40	150.40	203.58	729.00
NPR 4-	0.3m	315.27	90.25	417.03	2591.67

NO-Nistru –Old Mine dump; NPR- Partially Rehabilitated Nistru-Mine dump

Table 2. Chemical composition of the material from the mine waste dump from Red Valley zone

Sample	Depth	Heavy metals (ppm)			
		Pb	Cu	Zn	Mn
VR1	0.05m	-	26.23	14.11	131.14
VR2	0.05m	10.54	27.86	41.17	508.19
VR1	0.3m	180.30	65.35	150.20	362.50
VR2	0.3m	300.58	81.13	170.14	1231.50

VR-Red Valley mine waste dump.

The contents in phosphorus and potassium have been established by analyses carried out on the samples taken from the surface of the mine waste dumps. The acidity of these samples was also measured. The results are shown in table 3.

The chemical analyses of the nourishing elements phosphorus and potassium, P-AL (phosphorus acetate lactate) and K-AL (potassium acetate lactate), carried out on the superior part of the mine waste dumps, revealed extremely low contents in phosphorus. The value of the phosphorus concentration in the material is indicative of a weak insurance state with phosphorus. The contents in potassium obtained for the studied mine dumps are indicative of a good insurance state with potassium.



Fig. 2. *Betula verrucosa*



Fig. 3. *Vaccinium myrtillus*



Fig. 4. *Calluna vulgaris*



Fig. 5. *Populus tremula*

We consider that the supplies in potassium of the dump material are due to the lithologic material, especially to the secondary mineral compounds sericite, illite, formed from the primary minerals contained in the volcano andesite rocks. The presence of the potassium played an important role in the growth of the plants after installation.

Table 3. The pH and the content in P and K in the mine waste dumps material

Sample	pH	P (ppm)	K (ppm)
VR1	3,30	1	140
VR2	6,55	1	140
NO1	4,60	0	180
NPR3	4,20	1	160

4. PRESENTATION OF THE SPECIES OF PLANTS FROM THE STUDIED MINE WASTE DUMPS

4.1. Old mine waste dump - Nepomuc vein - Nistru.

Generally, on these mines waste dumps there can be observed the spontaneous plant formation with special characteristics concerning both the presented species domination and its specific nature. Thus, one can distinguish a young *Betula verrucosa* tree, (Fig. 2) with an uneven distribution of the plants: in some regions they are associated in clusters and in others as separate individuals.

The *Vaccinium myrtillus*, (Fig. 3) and the *Calluna vulgaris*, (Fig. 4) are installed on the horizontal side of the dump as excessively developed grassy species. The *Vaccinium myrtillus* plentifully develops on the basal side of the dump. The size for some birch tree specimens surpasses 5 m, being accompanied by younger individuals less than 1.5 m height, this showing that this species is well installed. The *Betula verrucosa* is the species successfully used in the rehabilitation of the lands deteriorated by the mine waste products from the Nistru perimeter (NPR- Partially Rehabilitated Nistru-Mine dump).

4.2. The Red Valley Mine waste dump (400 m altitude)

Represents an example for some species of plants as regards the installation, growth of a heavy metal rich substrate with a low content in nutritious compounds and on a surface consisting in rock and mineral fragments included in a fine and well compactly material. On the horizontal surface of the mine dump there can be identified many species of trees such as: *Betula verrucosa*, *Populus tremula*, (Fig. 5), *Salix caprea*, (Fig. 6), the acacia, the durmast and the pine. Their installation can be followed from the marginal zone of the dump to its central part.

Among these trees there are also some grassy species with an uneven development (raspberry bush, *Tussilago farfara*, (Fig. 7). The tree species appear in the mixture, especially *Betula verrucosa*, *Populus tremula*, *Salix caprea*. These species have close heights indicating that they were installed from the beginning, their growth being very fast in the first years of vegetation. The most frequent is the *Betula verrucosa*, followed by the *Populus tremula* and the *Salix caprea*. The dimensions of the bushes surpass 3 m in height. The durmast and the pine are very rare, having small dimensions.



Fig. 6. *Salix caprea*



Fig. 7. *Tussilago farfara*

4.3. The heavy metals content of the natural vegetation from the mine waste dumps

The chemical analyses carried out on the plant species naturally developed on the studied mine dumps, showed some important contents in heavy metals, (Tables 4 and 5). The analyses were carried out on the plant ashes as regards the trees and on dry plants for the grassy species.

The content of heavy metal in plants was determined by Atomic Absorption Spectrometry (AAS) Carl Zeiss Jena with multi-elements cathode lamp and absorption in the acetylene flame. The detection limits for Cu, Zn, Cd is 0.05ppm and for Pb is

0.1ppm.

Table nr. 4. The content in heavy metals of the natural tree species from the mine waste

Plant name	Pb g/t green mass	Pb g/t ash	Cu g/t green mass	Cu g/t ash	Zn g/t green mass	Zn g/t ash
Populus tremula VR	596.6	15512	2.7	70.2	11.8	306.8
Salix caprea VR	719.5	16909	4.5	105.75	9.3	218.55
Betula verrucosa VR	580.1	17405	3.2	96.2	8.7	261
Acacia VR	330.1	11752	2.8	99.68	9.2	327.52
Betula verrucosa NO	68.1	2523	12.5	462.5	21.4	791.8
Betula verrucosa NPR	60.2	8251	14.2	1945.4	22.3	3055.1

Table nr. 5. The content in heavy metals of the natural grassy species from the mine waste

Plant name	Pb g/t green mass	Pb g/t dry mass	Cu g/t green mass	Cu g/t dry mass	Zn g/t green mass	Zn g/t dry mass	Mn g/t green mass	Mn g/t dry mass
Tussilago farfara VR	8,01	22,5	4,46	12,29	13,15	36,17	65,57	180,32
Callum vulgaris NO	9,08	16,17	3,67	6,55	16,52	29,41	151,96	270,49
Vaccinium myrtillus NO	-	-	3,67	6,55	14,04	25	414,4	737,7

The relatively high concentrations in heavy metals from the old mine waste dumps material induced their accumulation in the plants body. Thus, on the two old mine dumps (Nistru and Red Valley) one can distinguish some indicator plants which develop especially on the heavy metals rich material such as *Betula verrucosa* tree and acacia and species with local development such as *Populus tremula* and *Salix caprea* on the Red Valley and *Vaccinium myrtillus* and *Calluna vulgaris* at Nistru.

5. CONCLUSIONS

On the old mine waste dumps there can be observed a natural installation of some vegetable species and their development, specific to the local chemical conditions: the low content in essential nutrients, the high level in heavy metals and the acid pH. On the two old mine dumps the vegetation has installed very slowly.

As regards the heavy metals content the chemical features of the material from the two old mine dumps are not favourable to the development of the vegetation. The essential nutrients, nitrogen and phosphorus, necessary to the growth of the plants are either absent or in small quantities. Instead, the potassium content obtained for the studied mine dumps indicates a good insurance state with potassium. Thus, by

analyzing the samples from the two old mine dumps, there can be observed the existence of a material, favourable to the installation of the soil. The long time action on the mine dump material of the physical-chemical factors determined its advanced grinding degree. The grassy vegetation, represented by the *Vaccinium myrtillus* and the *Calluna vulgaris*, at least on the Nistru Old Mine dump, induces the moisturizing of the substratum, this favouring the intensification of the bacterial activity in the mine dump.

The bacterial activity influences the degree of solubility and the release of the chemical elements and also the dispersion during their migration in the mine dump material. The precipitation, the deposition and the concentration of the chemical elements is realized through some geochemical barriers. These barriers are due to many factors, among them the biological factors. The adaptability of the plants species, studied in the conditions characteristic to the mine waste dumps material, can be used for the selection of the most resistant species in order to accomplish the ecological actions of these sites. It is also necessary to concentrate the substratum with organic or mineral fertilizing elements. Given the different manner, the heavy metals are concentrated by some species, their growth degree and the way the naturally installed species associate. For the ecological purpose, it is recommended to use them as mixture, as follows: *Populus tremula*, *Betula verrucosa*, *Salix caprea*, *acacia*, *Calluna vulgaris*, and *Vaccinium myrtillus*.

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