CONTRIBUTIONS TO RESTORATION OF WASTE DUMPS OF SULFUR FROM THE CĂLIMANI MOUNTAINS

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Abstract

The problem of ecological reconstruction of mining dumps, industrial, domestic or other sources is particularly difficult, due to the substrate with extreme properties for the installation of vegetation. Among these dumps with great difficulties of restoration are the waste dumps from sulfur quarry in the Călimani Mountains, mainly due to the high acidity of the substrate, the very high content of mobile aluminum and the lack of fertilizers for plant installation and growth. In the years 2009-2010, several experimental plots were placed at 1500 m altitude with improvement variants for correcting the acidity of the substrate and providing fertilizers for the sown grass species. After 10 years, the best variant with 90% land cover (30% Betula pendula, 27% Salixcaprea, 3% Picea abies, 24% sown grasses and 6% grasses from spontaneous flora) was the variant amended with 10t / ha CaO , chemically fertilized in 4 stages, every 2 years, with 100 kg / ha nitrogen, phosphorus and potassium. Through these methods of substrate improving, begin the processes of solification and final installation of the spontaneous vegetation around these sulfur dumps, extremely polluting.

Key words: sulfur mining dumps, substrate improvement,ecological reconstruction

INTRODUCTION

The problem of restoration of dumps of different origins (mine tailings, ore flotation, district heating of solid fuels, household waste and others) - product of economic activities and human existence, is a complex process through grassy and / or woody vegetation is installed on a surface with low natural fertility, more or less conductive to the growth and development of plants for fixation, solification, environmental protection, economic capitalization and landscape completeness (Marușca et al. 2000; Brejea 2008).

The dump is a distinct anthropogenic ecosystem in a first phase, with different degrees of subsequent integration in the zonal ecosystems and the types of surrounding landscape. (Harris et al. 1996; Oros 2002).

The installation of vegetation can take place on its own in a long period of time or through the immediate intervention of those who made the dump.

Certainly, it is the obligation of the economic factors that have produced these serious imbalances in the environment to act firmly to limit and eliminate the pollution. Among the methods of ecological reconstruction, most of the time, forestation is used, which is also the final goal in the areas where the forest can be installed (Căpitanu et al. 1999; Dumitru et al. 1999; Mocanu et al. 2007).

Until forestation, there are some situations and not a few when dumps with powdery materials require a fast grassing stage, to stop wind deflation and rain erosion. Therefore, it is necessary to pay special attention and often more to the grass that is applicable on dumps in all situations and only after a number of years of pedogenesis should intervene with forestation if it's necessary.

Thus on the dumps grassing can be a universal "panacea" and more economical than forestation, which is done only in some situations and these at very high costs.

Dumps from different sources are real sources of pollution for water, air, soil and landscape.

To remedy the situation, before forestation as a final method of consolidation, it is considered that rapid grassing is in a first phase, the best method to prevent particularly active erosion on the slopes and the flat top (cover) of the dump (Marușca, Dincă 2001; Marușca et al. 2009).

A very special problem is the renaturation of the dumps inside some areas protected by law, as is the case of those resulting from the exploitation of sulfur in the Călimani Mountains. (Cenușă-Leberciuc 2018).

In protected areas, the introduction of plant species from outside or even new varieties of existing species in these areas is strictly prohibited. Gathering seeds from the spontaneous flora as a solution for weeding is a utopia, as it would not be enough for 1-2% of the bare vegetation area in Călimani, in addition to very high labor costs.

Also, in these areas it is forbidden to use synthetic or chemical fertilizers such as those containing nitrogen, phosphorus and potassium, the main fertilizers necessary for the installation, growth and development of grassy or woody plants.

Without fertilizing elements derived from organic or chemical fertilizers, the vegetation cannot be installed on an inert substrate, almost completely devoid of natural fertility, such as the waste dumps from Călimani.

The provision of organic fertilizers in households, in this case is illusory. First of all, they cannot be bought and secondly, the distance to where they must be transported (40 - 50 km) and the quantities used per hectare, which are very large (30 - 50 tons / hectare).

The question is what do we do in this extreme situation, wait decades to recover on its own or intervene forcefully to reduce and stop, as much as possible by grassing, the catastrophic erosion of these dumps with pollution of water downstream for tens of kilometers with the disappearance of aquatic life, due to its acidity and very high content of elements and chemicals harmful to life.

These open wounds of the land that currently are devoid of protective vegetation are much more polluting and unbalanced for the environment and biodiversity in general than the use for grassing varieties of perennial grasses and legumes from species that are widespread in the area and using of calcareous amendments and chemical fertilizers with a time-limited effect, which would make it possible to install vegetation with an anti-erosion and pedogenesis role as a viable support for the species in the spontaneous flora that will eventually settle on their own over time.

Furthermore, more "noble" or pretentious sown species supported by short-lived chemical fertilizers will be gradually replaced by spontaneous species from surroundings better adapted to these extreme conditions, so for medium and long term, biodiversity will not suffer too much.

MATERIAL AND METHOD

The dumps from Călimani National Park, from the point of view of renaturation are quite similar to those from Bozânta and Meda Ponds near Baia Mare, in terms of physical and chemical characteristics of the substrate, especially the very acid reaction, the lower content of fertilizers and toxic effect of excess content in mobile aluminum (Oros 2002).

In 2009, in August, samples were taken from the dumps from Călimani, which were then analyzed from an agrochemical point of view at OSPA Braşov.

Agrochemical analyzes were performed according to the following methods:

- pH in water: potentiometric in water suspension in soil-solution ratio 1:2.5;
- hydrolytic acidity (Ah): extraction in sodium acetate solution at pH 8.3;
- sum of exchange bases (SB): extraction with HCl solution 0.05 N. Kappen - Schofield - Chiriță method;
- organic carbon (Humus): wet oxidation and titrimetrically dosing, Walkley - Black method with the Gogoasa modification;
- mobile phosphorus (P_{AL}) and mobile potassium ((K_{AL}): extraction in acetate - ammonium lactate, Egner - Riehm Domingo method;

- exchangeable aluminum (Al^{3+}): extract in solutions of unstamped neutral salts (KCl) Sokolov method.

The materials disturbed inside the Puturosu dump had a very pronounced acidity of 2,7 – 2,9 pH in H_2O and a very low content of humus, P, K and other elements which makes it impossible to install the vegetation on its own, without calcium amendment and fertilization.

Materials settled after 15 - 20 years of deep leaching of acid fractions, the pH index increases about 1 unit, reaching from 2,7 – 2,9 to 3,8 – 3,9, thus favoring the installation of several pioneers species in the form of isolated bushes, the most widespread is *Deschampsia flexuosa* followed by *Deschampsia caespitosa* and in some spruce seedlings (*Picea abies)* and after a few years of installation disappear one by one as the roots penetrate deep into the substrate, which in time it is enriched in mobile aluminum that reaches 11-20 me / 100 g of soil, very toxic for plants (Maruşca, Haș 2015).

Considering the urgent needs to take measures of ecological reconstruction by grassing with the support and agreement of the builder, a German company, ICD Pajiști Braşov initiated a simple experiment of calcium amendment and grassing in 7 different locations: 5 on Puturosu dump (3 near the former headquarters and 2 at the station) and 2 on the Pinu dump after the company's requests.

The variants were:

A. Untreated variant- Control

B. Chemical fertilization 625 kg / ha NPK complex (16-16-16) without amendment;

C. Applied 5 t / ha lime powder (CaO) +chemical fertilization NPK idem B;

D. Applied 10 t / ha lime powder + chemical fertilization NPK idem B and C;

The size of a plot is 50 sqm (10x5 m) and a plot of 6,25 sqm (2.5x2.5 m). Calcium amendment and chemical fertilization were carried out in autumn 2009. Sowing was done in two phases: at the end of September 2009 and at the beginning of May 2010, immediately after the snow melted and the weather warmed up.

The complex mixture that was applied consisted of 50% grasses. (*Festuca rubra, Phleum pratense, Dactylis glomerata, Festuca pratensis and Poa pratensis*) 25% perennial legumes (*Lotus corniculatus, Trifolium pratense* and *Trifolium repens*) and 25% straw cereals (rye and oats).

Because of very low trophicity of the substrate, the fertilization with NPK complex chemical fertilizers was repeated in the spring of 2011, 2013 and 2015 in the same dose of 625 kg / ha at variants B, C and D, thus ensuring 100 kg / ha of the main fertilizer elements.

After the last NPK chemical fertilization (16x16x16) in 2015 on variants B, C and D, no other improvement measures were applied.

In August 2020, 10 years after the calcium amendment, four-stage NPK fertilization and sowing, soil and vegetation studies were continued on two experimental plots on the Puturosu dump under the demolished former sulfur station.

RESULTS AND DISCUSSION

In the autumn of 2011, 2 years after the application of the calcium and chemical fertilization amendments, soil samples were taken again with the agrochemical probe on two depths 0-10 and 10-20 cm (Table 1).

On average on the 5 plots in variant A (control) and B (without amendment) the pH is very low by 3,9 at a depth of 0-10 cm and 2,9 – 3,0 at a depth of 10-20 cm. After applying the amendments, the pH improves, having an index of 4,5 – 5,6 on the depth of 0-10 cm and 4,3 – 4,9 at 10-20 cm.

Table1

The average agrochemical composition of the mining dump substrate from Călimani, 2011

Variant	Adc. (cm)	pH	V_{Ah} (%)	Humus (%)	IN	P_{AL} (ppm)	K_{AL} (ppm)
A – Control	0-10	3,9	12,4	1,19	0,13	11,5	98
	10-20	2,9	10,4	0,56	0,05	6,0	54
B-100kg/ha NPK	0-10	3,9	12,2	1,40	0,17	23,8	120
	10-20	3,0	9,5	0,35	0,03	15,5	46
C-5t/ha CaO+NPK	0-10	4,5	52,6	1,05	0,48	21,0	105
	10-20	4,3	46,4	0,63	0,33	15,0	46
D-10t/ha CaO+NPK	0-10	5,6	80,7	0,98	0,68	22,0	132
	10-20	4,9	69,5	0,28	0,47	15,0	58
Relativ content (%) **B - A**	0-10	100	98	118	131	207	134
	10-20	103	91	63	60	258	85
C - B	0-10	115	431	75	282	88	88
	10-20	143	488	180	110	98	100
D - C	0-10	124	153	93	142	105	126
	10-20	114	150	44	142	100	126

Through the chemical fertilization of NPK in the 2 rounds (2009 and 2011), the trophic regime was greatly improved, and together with the improvement of acidity and the increase of the bases saturation after the calcium amendment succeeded in installing the sown grasses (Table 2).

Thus, on the A variant without intervention, no blade of grass was installed, as well as around the plots.

In variant B only with NPK fertilization, the cover with grassy vegetation was on average 21% and in general, lower in autumn and better in spring.

In the amended variants C and D the situation is much better, the vegetation covering the land in average 40% at autumn sowing and 52% for spring sowing in 2010.

Table 2

Successfully sowing perennial herbs on the mining dumps from Călimani depending on application season (% coverage 2011)

Variant	Season	Repetition					Average
		1	2	3	4	5	
A - control	Autumn	-	-	-	-	-	-
	Spring	-	-	-	-	-	-
	Dif.	-	-	-	-	-	-
B - NPK	Autumn	-	-	5	10	25	8
	Spring	2	5	20	30	50	21
	Dif.	+2	+5	+15	+20	+25	+13
C-5t/ha CaO+NPK	Autumn	20	25	40	60	40	37
	Spring	40	60	65	70	50	57
	Dif.	+20	+35	+25	+10	+10	+20
D-10t/ha CaO+NPK	Autumn	25	40	50	70	50	47
	Spring	35	70	70	80	70	65
	Dif.	+10	+30	+20	+10	+20	+18
AVERAGE **B, C, D**	Autumn	15	22	32	47	38	31
	Spring	26	45	52	60	56	48
	Dif.	+11	+23	+20	+13	+18	+17

The influence of trophic factors (fertilization and amendment) on the success of sowing is maximum in variant D, where was applied 10 t / ha CaO + 2x100 N + 100 P_2O_5+ 100 K_2O kg / ha and absent in variant A (control) (Table 3).

Table 3

The influence of treatment of the mining tailings substrate on the success of the sowing of perennial herbs in the second year of vegetation, 2011

Specification	Variant			
	A	**B**	**C**	**D**
Vegetation covering(%)	0	15	47	56
Influence NPK + CaO	100	150	470	560
Influence 5t CaO + NPK		100	313	373
Influence 10t CaO + NPK			100	119

Between 5 t / ha (variant C) and 10 t / ha CaO, the difference of plus 19% of coverage is not too big at first sight, but it was assumed that the effect will be longer until the fallow thickening and consolidation.

Another finding is related by the success of legumes, which are completely absent in variants A and B (Table 4).

Table 4

The average structure of the grass carpet formed
from sown perennial grasses and legumes (% coverage 2011)

Variant	Graminee * (%)	Legumes ** (%)
A. -control	0	0
B. 100 kg/ha NPK	15	0
C. 5 t/ha CaO + NPK	27	20
D. 10 t/ha CaO + NPK	35	21
Relative difference (%)		
C - B	+ 12	+ 20
D - B	+ 20	+ 21
D - C	+ 8	+ 1

*) Grasses in the order of dominance:*Festuca rubra, Phleum pratense, Dactylis glomerata, Festuca pratensis* and *Poa pratensis*
**) Legumes: *Lotus corniculatus, Trifolium pratense* and *Trifolium repens*

Perennial legumes (guinea fowl, red and white clover) fixing atmospheric nitrogen are present in a proportion of 20 - 21% coverage in variants C and D, which joins the grasses covering 27 - 35% of the land in the 2nd year of vegetation . After 10 years from setup of the experimental plots, the agrochemical characteristics of the soil suffered major changes (Table 5).

Table 5

Physical and chemical values of the substrate from the mining dump from Călimani, after 10 years from the calcium amendment and 4 stages of chemical fertilization
(depth 0-10 cm)

	UM	Variant				Relative values to A		
		A	**B**	**C**	**D**	**B**	**C**	**D**
Skeleton 2-25 mm	%	55,6	55,7	58,6	60,3	100	105	108
Roots	%	0	0	0,2	1,7	x	x	x
Soil < 2 mm	%	44,4	44,3	41,2	38,0	100	93	86
pH in H_2O	ind.	3,5	3,55	3,95	5,25	101	113	150
Humus	%	0,92	1,04	1,21	2,20	119	132	239
Nitrogen index (IN)	%	0,19	0,21	0,30	1,78	111	158	937
Mobile phosphorum (P_{AL})	ppm	4,0	6,5	4,8	7,8	163	120	195
Mobile potasium (K_{AL})	ppm	50	53	110	105	106	220	210
Sum of changeable bases (SB)	me/100g sol	2,3	2,7	3,5	16,3	117	152	709
Hydrolitic acidity (Ah)	me/100g	11,2	10,2	8,5	3,8	91	76	34
Cation exchange capacity (T)	me/100g	12,0	12,9	13,5	20,1	108	113	168
Degree of base saturation (V)	%	17,0	20,9	29,2	81,1	123	172	477
Exchangeable aluminium (Al^{3+})	me/100g	4,598	3,895	2,703	0,089	85	59	2

First of all, the reaction of the soil (pH) at a depth of 0-10 cm in August 2020 compared to 2011 is generally lower by 0,4 units (3,9-3,5) in the control variant A with 0,3 (3,9-3,6) in variant B with 0,5 (4,5-4,0) in variant C and 0,3 units (5,6-5,3) in variant D, the best.

Another limiting agrochemical factor for plant growth, mobile aluminum has decreased significantly from 11-12 me / 100 g soil in 2009 to more than half (4,6 me) in 2020 in the control variant A without improvement treatment of substrate. Following the calcium amendment and fertilization, the highly toxic aluminum for plants decreases by 15% in variant B, 41% in variant C and 98% in variant D where 10 t / ha of lime powder (CaO) were applied.

Progressively from variants B, C and D depending on the intensity of the improvement factors, the agrochemical characteristics of the soil are more favorable for plant growth although the skeleton content (2-25 mm) is 56-60% of the weight of the soil samples.

The weight of the roots of the existing plants in the soil at a depth of 0-10 cm after 10 years from sowing, was missing in variants A, B, with 0,2% of the total soil sample in variant C and 1,7% in variant D, which means that the fallow process is very slow.

From the species sown in autumn 2009 and spring 2010, in 2020, only *Festuca rubra* (9%), *Lotus corniculatus* (4%), *Poa pratensis* (3%), *Trifolium repens* (3%), *Dactylis glomerata* (2%) survived on average on the amended variants C and D (Table 6).

In the rest appeared grassy species from the spontaneous flora, especially *Deschampsia flexuosa* and *Polytrichum juniperinum*, but in a large content appeared woody species.

In variants A and B are presented *Betula pendula, Picea abies* and *Vaccinium myrtillus* in early stages.

In variant C and D where it was amended, *Salix caprea* is additionally installed with a coverage of 15-27% together with *Betula pendula* (18-30%) and *Picea abies* (2-3%) much better developed than in the variants A and B. Regarding the number of seedlings of birch (120-260) and spruce (40-65) trees spontaneously installed in variants C and D per 100 sqm, it can be noticed that they are sufficient for a future self-forestation of the land.

The height of the birch reaches 1-1,5 m and of the spruce 20-50 cm, lower in variant A and B and higher in variants C and D.

Table 6

Degree of installation of sown grasses and spontaneous vegetation after 10 years from improvement of the substrate in Călimani Mountains, 1500 m altitude
(% participation)

Specification	Variant			
	A Control	**B** NPK	**C** 5t/haCaO+NPK	**D** 10t/haCaO+NPK
Coverage	**2**	**10**	**65**	**90**
Sown species	(-)	(-)	(16)	(24)
Dactylis glomerata	-	-	+	3
Festuca rubra	-	-	7	10
Poa pratensis	-	-	2	4
Trifolium repens	-	-	2	4
Lotus corniculatus	-	-	5	3
Spontaneous grassy species	(1)	(9)	(12)	(6)
Deschampsia flexuosa	1	9	5	2
Chamerion angustifolium	-	-	-	+
Moss (*Polytrichum*)	-	-	7	4
Spontaneous woody species	(1)	(1)	(37)	(60)
Betula pendula	+	+	18	30
Picea abies	+	1	2	3
Salix caprea	-	+	15	27
Vaccinium myrtillus	1	+	2	-
No. tree saplings to 100 sqm				
Betula pendula	10	10	120	260
Picea abies	10	15	40	65

In the coming years, as these trees species grow, we will draw the necessary conclusions about their survival in this hostile stationary environment.

The coverage of grassy and woody vegetation of 65% in variant C and 90% in variant D show the special importance of correcting the acidity of the substrate through calcium amendment.

CONCLUSIONS

1. The substrate of the tailings dumps from the sulfur quarry in the Călimani Mountains is extremely acid, with a toxic content of mobile aluminum and very poor in fertilizer elements where for three decades of spontaneous flora no anti-erosion protective vegetation has been installed;

2. Applying 5-10 t / ha of calcium oxide (CaO), NPK chemical fertilizers (16x16x16) in doses of 625 kg / ha every 2 years and sowing perennial grasses, a protective grassy carpet is made that favors the installation of grassy and woody vegetation from the surroundings;

3. After 5-6 years from weeding on amended and fertilized land *Salix caprea, Betula pendula and Picea abies* begin to occupy more and more land, being a guarantee of the renaturation of these dumps compared to areas without intervention and vegetation, where rain and wind erosion processes with the pollution they produce are very active.

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