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Article

ECOLOGICAL RESTORATION STUDIES OF SOME BIOLOGICAL INERT, HAZARDOUS WASTE

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ABSTRACT

In this study, the results of research on ecological restoration of a deposit of 150ha of fly ash and boiler slag are presented. The nutrients for plant growth were done with organic fertilizer, slaughterhouse sludge. Stimulation of vegetation was done with an agent based on brown algae extract. The study was conducted over two successive years. Plant growth was performed in fertilization variants with optimum amount of10t/ha slaughterhouse sludge with growth stimulus. The stimulus advantages have been the increase of seed amount of up to 37% and reduction of plant toxic metal content *i.e.* for Pb with 62.1%.

Keywords: fly ash, boiler slag sludge, slaughterhouse, ecological restoration.

1. INTRODUCTION

Waste disposal on uncovered deposits is a usual way to remove it from anthropogenic activities areas. Waste deposits are located in the vicinity of sources: *i.e.* fly ash and boiler slag deposits from power. The studied lignite fly ash and boiler slag deposit is a plain deposit that occupies an area of 150 ha. It has a height of 500m and a capacity of over 4.8 million cubic meters. It is located at a distance of 1.5-4 km from inhabited areas. To protect the environment numerous arrangements were conducted: a well compacted clay base layer of 3.5-6.5 m to limit water percolation, perimeter dams of the storage area for limiting the scattering of particles by erosion, systems for drainage, collection and storage of water. The deposit contains three compartments that fill up successively. The deposit has operating permit under the laws of Romania. With all the arrangements made, the deposit is an area

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with potential danger to dissipate through deflation lightweight materials in the neighbouring agricultural areas, to gravely alter the ecosystem, and strongly alter the landscape etc.

Fly ash and boiler slag deposits in Romania contain mostly aluminium, silicon, calcium, iron, magnesium, sodium, phosphorus and sulphur, and do not retain water in the upper layers [1, 2]. They are biologically inert. Carbon content is due to partially burned coal and is 0-15% range [3]. Nitrogen content is extremely small, and dependent on the type of coal burned [4]; its concentration in charcoal is between 0.3-3% and decreases by combustion to 0.01-0.1%. The maximum range of the nitrogen content of slag and ash may be due to partially burned coal, or can be of atmospheric origin [5, 6]. Ashes are inert, lacking any life form. The proliferation of microorganisms is hampered by unfavourable conditions of humidity, temperature, nutrition, in the upper layers. From the older layers of fly ash and boiler slag microorganisms were isolated but they are present only in the spore form [6]. When the deposit is not administered, then the field can develop weed species that tolerate the hostile environment but by their spreading can affect negatively the neighbouring crops. Moreover, selected plant species can be planted directly. But this is a risk, because the chemical and physical characteristics of the soil can seriously affect plant growth.

Therefore, organic amendments are added to support plant growth. Partially dehydrated municipal sludge, different composts, chicken manure, green compost and others can be used. These materials are mixed with 5-10 cm surface layer of ash to form a layer of fertile, artificial soil. Many researchers show that these used organic substances promote an ecosystem in the formed layer and support microbial communities necessary for the formation of plant growth conditions. The positive effect of organic amendments is endorsed by a number of researchers [6, 7]. The role of these materials in the recovery of damaged areas is demonstrated in many countries [8-10] both for grassland plants and specific shrubs. Vegetation strategy relates generally to the improvement of the physical, chemical and biological characteristics of the destroyed land for vegetation: low nutrient content, inappropriate texture, minimized capacity of water retention, high content of heavy metals etc. Selection of plant species is an important factor because they must tolerate pedoclimatic regime of the deserted area. From the experience of many researchers, the most tolerant plant species are those from the Gramineae and Leguminosae families. [11, 12]

In this study, the results obtained regarding: 1. The recycling of nutrients embedded in biodegradable organic sludge, slaughterhouse sludge; 2. Environmental protection against the dispersion of pollutants, the restoration of damaged ecosystems and landscape near the city; 3. Obtaining seeds and biomass with reusable possibilities, are presented.

2. METHODS

The experimental study was done in the experimental bloc with three variants: va s1, va s 2, va s 3. The experiments were carried in pots. The pots were fitted with inert fly ash and boiler slag of thermal plants and fertilized with slaughterhouse sludge in quantity of 5.0, 10.0, respectively 25.0 $t \cdot ha^{-1}$ and bacterial stimulus *Bio complex 900*, provided Ekogea Slovenia. Control variant – pot, va s2, was fitted with boiler slag and fertilized with 5 $t \cdot ha^{-1}$ sludge without algae addition. Each variant is done in three replicates. The quantity of metals from the boiler slag used in this study is presented in Table 1.

Table 1. The content of heavy metals from the fly ash and boiler slag used.

pH	*Heavy metals from the fly ash and boiler slag used [mg·kg^{-1} D.M.]							
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
7.11± 0.2	2.7 ±0.9	75.0 ±4.6	62.1 ±.2	2060.0 ±53.3	238.4 ±5.8	85.1 ±2.9	35.2 ±0.8	169.2 ±6.2

* Values are means of 12 samples

The slaughterhouse sludge characteristics used in this study is presented in Table 2.

Table 2. The slaughterhouse sludge characteristics

The slaughterhouse sludge characteristics				
pH	Humidity[%]	Organics [%]	Total nitrogen [%]	Total phosphorus[mg·kg^{-1} D.M.]
7.1	71.86	90.77	2.314	1126±55

Determination of soil metals (to unfertilized/fertilized fly ash and boiler slag), i.e. Cd, Cu, Cr, Ni, Pb, Zn was done according to SR ISO 11047-99. The principle of the method consist in aqua regia metals extraction according to ISO 11466-99. Iron determination in soil samples was made in accordance with ISO 11466- 99 SR. Soil extract analysis was done by atomic absorption photometry in accordance with SR 13315-96/C91:2008. It was used an Atomic Absorption Spectrophotometer, GBC Avanta AAS, GBC Scientific Equipment Ltd. Company. Total nitrogen determination was performed according to ASTM D 5373-08, SR ISO 10694-98 and STAS 398-92. Phosphorus determination was performed according STAS 12205-84.

During sowing, the topsoil - fly ash and boiler slag - was watered with a mixture of brown algae extract and water (ratio 1:50). The experiment was carried out in pots with 6.5 kg of soil. In the pots, 20 g/pot of seeds from the *Lolium perenne* plant species were planted. The species tolerates pedoclimatic conditions specific to the western part of Romania. Plants were seeded in the spring. Pots were placed in the open and watered periodically. In the first year of culture, plant samples were harvested between July and October, every two weeks. In the second year of culture, plant samples were harvested in May-July, every 2 weeks. During August – September, cultures were not harvested to allow their fructification. Seed biomass harvesting was performed at the end of September. Metal analysis was done for the aerial parts and seeds of the plants obtained in the 2nd year of culture. Heavy metals of tissues of mature plant was determined and compared with Romanian standard. Plant tissues were thoroughly washed 3x 25ml with de-ionized water, at room temperature, to remove any soil particles attached to plant surfaces. Plant sampling was performed in agreement with the standardized methodology (the methodology described in STAS 9597/1-74, and the sample analysis was done in accordance with STAS 9597/17-86): 5g plant tissues were dried to constant weight at 105 °C. Plant samples with precise weight are then brought to 550°C; to the residual materials 3.5ml of concentrated hydrochloric acid (d =1.189 kg·L^{-1}) are added, samples are maintained 30 minutes on the dry sand bath. Then, 1.5ml hydrochloric acid (d =1.189kg·L^{-1}) : de-ionized water, 1:1 solution was added. After very slowly filtering on a paper filter (filtration smooth type 640de Mackerel-Nagel Germany), the samples were taken to calibrated flasks (25mL) with hydrochloric acid (d=1.189kg·L^{-1}) : de-ionized water, 1:1 solution. Heavy metals content from plant tissues extracts analysis was determined using an

Atomic Absorption Spectrophotometer, GBC Avanta AAS, GBC Scientific Equipment Ltd. Company. The detection limit of the device for Cd is 0.0431mg/L, for Cr - 0.0386mg/L, for Cu - 0.0349mg/L, for Fe - 0.0408mg/L, for Mn - 0.0421mg/L, for Zn is - 0.0358mg/L, for Pb - 0.0393mg/L for Ni - 0.0446 mg/L.

3. RESULTS AND DISCUSSIONS

The plants sprouted at 2-3 weeks after sowing. Vegetation coverage at 30 days after seeding was 80-90%. After this period, the plants sprung on the experimental variant fertilized with slaughterhouse sludge in the absence of the stimulus dried in a proportion of 55%. The remaining plants showed signs of suffering (yellowing and drying of basal leaves). In the second year of culture, the green cover grown on the experimental variant fertilized with slaughterhouse sludge in the absence of the stimulus was restored.

3.1. Results

Table 3 shows the amounts of biomass harvested periodically from the aerial parts of the *Lolium sp.* plants. In the first year of culture, the amount of harvested green mass was similar in all variants fertilized with slaughterhouse sludge in the presence/absence of growth stimulus. It is noted that in the second year the amount of harvested biomass was 40.9-57.2% higher than in first year of culture. This increase demonstrates the gradual adaptation of plants to the conditions imposed by this experiment. The amount of biomass harvested in the first year of culture was influenced by the amount of fertilizer used. The optimal amount of fertilizer for obtaining a high yield of biomass was 10t/ha. The addition of growth stimulus in the first phenological phases of development resulted in an increase to 10% vs. crop biomass resulting from the variant fertilized in the absence of the stimulus.

Table 3. The amount of biomass harvested from the aerial parts of plants from *Lolium sp*.

No	Variant	Harvest [g /pot]		Harvest increase, second year vs. first year. [%]	Total harvest [g /pot]
		first year of culture	the 2nd year of culture		
1	va s1	170.0±2.5	392.0±32.7	56.6	462.0±39
2	va s2	181.0±2.9	423.0±35.9	57.2	604.0±40
3	va s3	180.2±2.8	305.0±29.7	40.9	485.2±35
4	va 2	177.0±2.8	369.0±31.5	52.0	546.0±29

Table 4 shows the seeds quantities harvested from the experimental variants. It is seen from Table 2 that the use of optimal dose of fertilizing agent in combination with growth factors previously determined, of 10t/ha, increased the amount of seeds by 37% vs. the quantity of seeds harvested from the same fertilized variant in the absence of the stimulus. This stimulating agent positively influenced the quantity of seeds obtained in the 2nd year of culture.

Table 4. The quantities of seeds from fly ash and boiler slag cultivated with *Lolium perenne*

No.	Harvest	Amount of seeds from [t·ha^{-1}]			
		without stimulus	with stimulus		
		va 2	vas 1	vas 2	vas 3
1	Seed Second year	1.35± 0.05	1.4± 0.04	2.13± 0.07	3.60± 0.09

Table 5 shows metal quantities that have accumulated in the green biomass harvested in the second year of culture, in the aerial parts.

Table 5. Metal quantities accumulated in the green biomass harvested in the second year of culture, in the aerial part

Variants	Metal content [mg·kg^{-1} D.M.]							
	Cd min - max	Cr min - max	Cu min - max	Fe min-max	Mn min-max	Ni min - max	Pb min - max	Zn min - max
va s1	0.35-0.54	1.68-1.77	1,40-1.57	30.6-36.3	22.2-33.7	1.35-1.55	6.34-7.14	11.7-15.7
va s2	0.37-0.64	1.78-1.90	1.67-1.70	39.5-44.5-	34.0-38.8	1.45-1.67	5.09-5.20	18.0-23.7
va s3	0.39-0.57	1.90-2.07	1.85-1.95	46,0-48.2	30.0-36.8	1.37-1.71	5.00-6.77	17.4-19.0
va 2	0.45-0.67	1.92-2.13	2.70-2.96	70,0-82.9	59.9-67.2	1.54-1.83	11.9-13,2	22.3-25.8
Maximum Romanian limit for organic matter with 12% humidity [13]	1.0	*	*	*	*	*	100	*

* Without analyzing

3.2. Discussion

It is seen from the tables that the aerial part of the plants harvested from fertilized variants in the presence of the stimulus, have accumulated small amounts of toxic metals, such as: Cd, Cu, Cr, Ni, Zn, Mn and Fe. Instead, plants accumulate large amounts of lead, 5.0-7.14 g • kg^{-1} D.M. It is observed from the table that plants grown on variants fertilized and treated with stimulus have accumulated lower amounts of metals than plants grown on control, fertilized in the absence of the stimulus. Thus, the accumulation of Pb decreases by 45.9-62.1% vs. the bioaccumulation in plants grown on variants fertilized in the absence of the stimulus. With all this Pb content reduction in plant crops in the second year of culture, plants will be used as compost add so that by mixing they will decrease the content of this metal to the limits allowed by compost law. Seeds harvested from the herbaceous plants culture resulted in the second year can however be used for next sowings. It is necessary that all crops resulting from the slag and ash fertilized with slaughterhouse sludge in the presence/absence of a plant growth stimulus to be closely monitored. Plant crops can be used in animal feeding only if the bioaccumulation of metals does not endanger their health.

4. CONCLUSIONS

The strategy of ecological vegetation/restoration of fly ash and boiler slag, biologically inert, non-hazardous deposits with slaughterhouse sludge regards the improvement of the physical, chemical and biological properties of fly ash and boiler slag deposits in order to facilitate plant growth. Selected plants of the *Lolium perenne* species are an essential factor in restoring the landscape as they quickly form a stable and sustainable vegetation cover. Use as a fertilizing agent of the slaughterhouse sludge provided the basic compounds of C, N, P, for a lasting development.

The addition of organic Many thanks are due to Prof. Nicolae Dragomir at Banat University Agricultural Sciences and Veterinary of Medicine, from Timisoara, Romania and SC. EKO GEA EAST SR. Romania. The research was given by the Ministry of Education Research, Youth and Sports which provide financial support for Nuclear program ON 09-13.based on marine brown algae in combination with fertilizing agent resulted in resistant crops under extreme hydro climatic conditions specific to the warm season in western Romania. The use of growth stimulus mixed with slaughterhouse sludge at optimal doses has determined also the increase of the seed quantities by up to 37% vs. in the absence thereof. In addition, the use of growth promoters to used fertilizers led to significant reductions of bioaccumulation of toxic metals in the case of Pb, reaching up to 62.1%. Residual bioaccumulation of lead in grass crops imposes the need to manage them under monitored regime but seeds harvested from inert land, treated with organic fertilizer may be used in future seeding.

It is necessary that all crops resulting from the fly ash and boiler slag deposits, fertilized with slaughterhouse sludge in this/absence of plant growth stimulus, to be closely monitored. Plant crops can be used in animal feeding only if the bioaccumulation of metals does not endanger their health.

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